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MERCURY DISTRIBUTION BETWEEN PARTICULATE AND DISSOLVED STATES IN WETLANDS IN CALIFORNIA, USA

MASTER THESIS

ELKE SÜß

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Declaration of Authorship

I certify that the work presented here is, to the best of my knowledge and belief, original and the result of my own investigations. Special assistance and information I received as well as utilized published information are properly and duly acknowledged.

Freiberg, 31st of August 2006

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Signature

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List of Abbreviations

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2BSWCA-HPoA	hydrophobic acid fraction from water of water conservation area 2BS in the Everglades
ASTM	former American Society for Testing and Materials, today ASTM international
avg.	average
CA	California
CALFED Bay-Delta Programm	California Federal Bay-Delta Programm
CBDA	California Bay-Delta Authority
CF06-0006-HPoA	hydrophobic acid fraction from Sacramento River water
CFW	sediment sample from Bear River Arm of Camp Far West reservoir (lake sediment)
CO	Colorado
COM	colloidal organic matter
conc.	concentration
CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectroscopy
DI water	deionized water
DOC	dissolved organic carbon
DOM	dissolved organic matter
e.g.	exempli gratia, 'for example'
E11-04	Standard Specification for Wire Cloth and Sieves for Testing (Committee E20 on Particle and Spray Characterization)
EDTA	ethylenediamine tetra acetic acid
EPA	U. S. Environmental Protection Agency
et al.	et alii, 'and others'
EXAFS	X-ray absorption fine structure spectroscopy
F1-FA	fulvic acid fraction from water of sampling site F1 in the Everglades
F1-HPoA	hydrophobic acid fraction from water of sampling site F1 in the Everglades
FA	fulvic acid

FT	filter test
GC	gas chromatography
HA	humic acid
HDPE	high-density polyethylene
Hg	mercury
Hg(0)	Hg^0, elemental mercury
Hg(II)	total dissolved mercury, Hg^{2+}
HH	hydroxylamine hydrochloride
HPi	hydrophilic fraction of DOC
HPLC	high performance liquid chromatography
HPoA	hydrophobic acid
HPoN	hydrophobic neutral fraction
i.e.	id est, 'that is'
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma – mass spectrometry
LC	liquid chromatography
MCL107A	sample of serpentine soil from UC-Davis McLaughlin Reserve (serpentine soil)
MCL131B	soil sample from floodplain soil (fluvent) at UC-Davis McLaughlin Reserve
MCL134B1	wetland sediment sample from UC-Davis McLaughlin Reserve (serpentine soil)
MCL137	soil sample from tailing material at UC-Davis McLaughlin Reserve site (tailing)
MDL	minimum detection limit
MeHg	methylmercury
MercAcid	mercaptoacetic acid
n	number, amount
n.m.	not measured
NIST	National Institute of Standards and Technology
no.	number
NOM	natural organic matter
p.	page

PE	polyethylene
POM	particulate organic matter
R	reductant
R^2, R-square	coefficient of determination, portion of variance of variable y
RB	reagent blank
RCF	relative centrifugal force
RPD	relative percent difference
rpm	rotations per minutes
SaliAcid	salicylic acid
SD	standard deviation
SOM	soil organic mater
Starr	sediment sample from sluice board of Starr tunnel (sluice sediment)
SUVA	specific ultraviolet absorbance [$L*mgC^{-1}*m^{-1}$]
Suw-HA	humic acid fraction from Suwannee River water
THg	total mercury [µg/G]
TN	total nitrogen [ppm, mg/L]
TOC	total organic carbon [%]
TPiA	transphilic organic acid fraction of DOC
TPiN	transphilic organic neutral fraction of DOC
UDL	upper detection limit
UPW	ultrapure water
USA	United States of America
USGS	United Staates Geological Survey
UVA	ultraviolet absorbance [cm^{-1}]
WCA	water conservation area
WL-HPoA	hydrophobic acid fraction from Williams Lake water
XAD-4	styrene-divinylbenzene resin, average pore diameter 5 nm
XAD-8	acrylic ester resin, average pore diameter 25 nm
XANES	X-ray absorption near-edge structure spectroscopy
XAS	X-Ray absorption spectroscopy
XRD	X-ray diffractometry

List of Symbols and Units

%	percent
%R	recovery
η	viscosity [Pa*s = kg*s/m*s2]
ρ_L	liquid density [g/cm3]
ρ_p	particle density [g/cm3]
°	degrees
°C	degrees Celsius
µeq	micro equivalent
µg	microgram [10^{-6} g]
µL	microlitre
µm	micrometer
µM	micromolar [10^{-6} mol/L]
Al-I	aliphatic carbon (NMR region: 0-62 ppm)
Al-II	aliphatic carbon (NMR region: 62-90 ppm)
Al-III	acetal (NMR region: 90-110 ppm)
Ar	aromatic carbon (NMR region: 110-160 ppm)
B	leaching experiment without pH and ionic strength adjustment
BE	leaching experiment with experimental conditions of pH 6.4 ± 0.1 and I = 0.1 M
C-I	carboxylic carbon (NMR region: 160-190 ppm)
C-II	ketone (NMR region: 190-230 ppm)
cm	centimeter [10^{-2} m]
d	particle diameter [m]
Da	Dalton [1 Da= $1.66*10^{-27}$ kg]
g	earth acceleration [m/s^2]
g	gram
h	hour(s)
I	ionic strength; leaching experiment with variable ionic strength
IC	leaching experiment for detection by ion chromatography
ICDOM	leaching experiment with additional DOM for detection by ion chromatography
K	kinetics experiment

KDOM	kinetics experiment with additional DOM
L	litre
M	matrix experiment
M	molar, mol per litre [mol//L]
MDOM	matrix experiment with additional DOM
meq	milliequivalent
min	minutes
mL	milliliter [10^{-3} L]
mM	millimolar [10^{-3} mol/L]
mol wt	molecular weight [g/mol or Da]
mol	mole
ng	nanogram [10^{-9} g]
pH	negative logarithm of hydrogen ion activity; leaching experiment with variable pH
ppm	parts per million
s	path length [cm, m]
t	resulting centrifugation time [min, h]
ν	sink velocity [m/s]

List of Chemical formulas

$2\text{-}HOC_6H_4COOH$	salicylic acid (O-hydroxybenzoic acid)
BDETH2	benzene-1,3-diamidoethanethiol
BrCl	bromium chloride
$C_{10}H_{14}O_6Na_2N_2*2H_2O$	ethylenediamine tetra acetic acid, disodium salt
$C_3H_3O_2SNa$	thiogylcolic acid sodium salt (mercaptoacetic acid, sodium salt)
Ca	calcium
$Ca(NO_3)_2*4H2O$	calcium nitrate, tetrahydrate
Cl	chloride
Cl^-	chloride
H_3PO_4	phosphoric acid
HCl	hydrochloric acid
Hg	mercury
Hg(0)	Hg^0, elemental mercury
Hg(II)	dissolved mercury, Hg^{2+}
$HgCl_2$	mercuric chloride
$HgSO_4$	mercurous sulfate
HH	hydroxylamine hydrochloride
HNO_3	nitric acid
KBr	potassium bromide
$KBrO_3$	potassium bromate
KOH	potassium hydroxide
Na_2HPO_4	sodium phosphate, dibasic, anhydrous
NaCl	sodium chloride
$NaClO_4$	sodium perchlorate
$NaH_2PO_4*2H_2O$	sodium phosphate, monobasic, dihydrate
NaOH	sodium hydroxide
$NH_2OH*HCl$	hydroxylamine hydrochloride
NO_3^-	nitrate
$SnCl_2*2H_2O$	stannous chloride
SO_4^{2-}	sulfate
ZnO	zinc oxide

Abstract

Mercury released from soil and sediment contaminated by historic gold mining is a major environmental concern in the San Francisco Bay area. To better understand the release mechanisms, six soil and sediment samples from the Coastal Range and the Sierra Nevadas with total mercury concentrations between 1 and 36 µg/g were subject to batch experiments under varying conditions. The effects on mobility of mercury due to pH, ionic strength, dissolved organic matter (in different concentrations and of varying chemical qualities), simple organic ligands (mercaptoacetic acid, salicylic acid, EDTA), and inorganic ions (chloride, calcium) were investigated.

Cinnabar was identified as the major mercury source in most of the soils and sediments by sequential extraction. Leaching experiments confirm that the water soluble mercury fraction is small (9 to 350 ng/L) and thus non-critical in terms of drinking water standards. However, its dissolution can further lead to increased methylation and biomagnification of neurotoxic methylmercury in the food web. A general increase in mercury release was observed with increasing pH, attributed to dissolution of soil organic matter, and with decreasing ionic strength, attributed to colloid stabilization. Higher DOC concentrations and higher reactivity of dissolved organic carbon caused a non-linear increase in dissolved mercury. The effects of adding different organic matter isolates seem to be a synergetic effect of various chemical properties of these isolates. Among the organic ligands, mercaptoacetic acid caused major mercury release, attributed to the strong complexation potential of its thiol group. Polyvalent cations strongly inhibit mercury release, because of their surface complexation of the minerals, whereas anionic inorganic ligands such as chloride form mercury complexes, favoring mercury dissolution.

The results from the investigations confirm the general notion that among all ligands found in natural systems, dissolved organic matter is the most important in influencing dissolution, mobility, and bioavailability of mercury under natural conditions.

1. Objectives and Deliverables

The present Masters thesis is part of a larger study initiated by the CALFED (California Federal) Bay-Delta Program to study environmental and health effects of mercury contamination in the Sacramento–San Joaquin Delta and the San Francisco Bay area. The final goal is the preparation of a regional mercury management plan to reduce mercury in fish and wildlife and to diminish the impact of mercury on human and environmental health.

The special objectives of this study were to determine effects on the release of mercury from soil, sediment, and tailing material in an aqueous solution under various experimental conditions. A series of batch experiments was used to determine the effects of varying pH, ionic strength, and the influence of dissolved organic matter (DOM) on the dissolution of mercury. In detail, the following investigations were conducted:

- X-ray diffractometry (XRD) analyses to determine the mineral composition of the soil material
- Kinetic experiments to establish the equilibration time for mercury dissolution from the soils in the presence and absence of DOM
- Control experiments and background eluates to examine the influence of laboratory equipment and chemical buffer substances used in the experiments on the mercury determination
- Matrix experiments to determine matrix influences from the leaching solution, with and without additional DOM, on the analysis of mercury with cold vapour atomic fluorescence spectroscopy (CVAFS)
- Batch experiments to determine the effects of the following experimental conditions on the release of mercury from soil material:
  - Variations of pH-value (pH 3, 4, 6, 8, 10, and 12)
  - Variations of ionic strength (0.1 mol/L, 0.01 mol/L, and 0.001 mol/L)
  - Addition of natural water from the Sacramento River
  - Addition of dissolved organic matter (DOM) (1 mg/L, 5 mg/L and 10 mg/L)
  - Addition of 10 mg/L DOM material of different origin, quality, and organic matter fraction

- Addition of the organic ligand ethylenediamine tetraacetic acid (EDTA, 20.8 µmol/L) and organic acids mercaptoacetic acid (69.4 µmol/L) and salicylic acid (29.7 µol/L)
- Addition of chloride (0.01 mol/L) and calcium ($2.5*10^{-4}$ mol/L) in presence and absence of DOM (10 mg/L)
- Colloid experiments: Leaching experiments with and without additional DOM, mercaptoacetic acid, EDTA, and calcium plus DOM, followed by centrifugation to separate and quantify dissolved mercury in the fraction <0.02 µm from colloidal mercury (0.02 µm – 0.45 µm)

The samples from all leaching experiments and from the control experiments were analyzed for reactive mercury by CVAFS, as well as for dissolved organic carbon (DOC) and ultraviolet absorbance (UVA), which then allowed for the calculation of the specific ultraviolet absorbance (SUVA, a measure of the aromaticity and reactivity of organic matter). Further analyses were done by ion chromatography (IC) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on part of the samples to determine the major anion and cation concentrations in the eluates. Fluorescence analysis was also performed to get an idea of the origin of the organic material.

The main deliverables of this Masters thesis are an improved knowledge of mercury release from historic mining sites with contaminated soil and sediments, as well as a better understanding of factors controlling the release of mercury from these sites. The specific issue is to establish the role of dissolved organic matter in the dissolution of mercury from these soils.

2. Introduction

Mercury is know to be a widespread and highly toxic pollutant, which originates from both natural sources (such as volcanic eruptions, mineral resources, and volatilization from the oceans) and anthropogenic sources (such as the combustion of fossil fuels, from fungicides, and from amalgamation during gold mining (EPA 2006a; GRAY et al. 2003; KRABBENHOFT and RICKERT 1996). Estimations from former studies imply that about one third of the mercury in the global cycle occurs from natural sources and the remaining two thirds from anthropogenic emissions (MASON et al. 1994). Mercury is of major concern in countless recent and previous studies, because of its poisonous affect to human and environmental health.

Overview about recent literature with detailed information about mercury

This section provides a brief overview of the recent literature regarding sources, distribution, toxicity, and analytical measurements of mercury in the environment. The focus here is in providing a list of recent papers important to the work described in this thesis. More mercury and DOM related literature can be found in the EndNote database (Appendix E – Literature database) attached on CD.

Resources to learn more about the overall view of mercury - An overall view of mercury sources, exposure pathways, and impacts on human and environmental health can be found in a recent report from the US Environmental Protection Agency (EPA 2006a). Additional resources include websites from the EPA and the US Geological Survey (USGS) (EPA 2006b; USGS 2006), whereby the latter comprises mostly US mercury studies founded from the USGS and the US Department of Interior (GRAY et al. 2003). There are also books with fundamental information about mercury pollution from a global view, e.g. EBINGHAUS et al. (1999), LACERDA and SALOMONS (1998), and PIRRONE and MAHAFFEY (2005).

Biogeochemical cycle of mercury and contamination sources - The biogeochemical cycle of mercury, especially with respect to anthropogenic influences is described in MASON et al. (1994) and SZYNKOWSKA et al. (2003), whereby the latter also gives information about mercury determination, locations with extreme concentrations, and human health affects of mercury. A literature review with detailed information about mercury contamination in aquatic systems is given by WANG et al. (2004), in which erosion, air deposition, mining, and agricultural activities are implicated as important mercury sources. Mercury emission sources, e.g. goal combustion, are discussed in EPRI (2004) and YUDOVICH and KETRIS (2005a; 2005b). HYLANDER and MEILI (2005) provide a global summary of mercury production and pollution during the last 500 years.

An interesting study by SCHUSTER et al. (2002) presents results of atmospheric mercury deposition and its sources measured in a 270-year old glacier ice-core from Wyoming.
To minimize harmful effects of mercury to human and environmental health, various studies were performed to figure out remediation techniques to remove mercury from water and contaminated sites. WANG et al. (2004) and HINTON and VEIGA (2001) give an overview of possible decontamination procedures, including capping of contaminated sites, dredging, soil leaching, vapour extraction, and natural processes used to decrease the contamination. ATWOOD and ZAMAN (2006) describe methods using the strong mercury-complexing ligand benzene-1,3-diamidoethanethiol (BDETH2) to remove mercury from water. Also, phytoremediation is a possibility for mercury removal (MEAGHER et al. 2000), but not if the mercury occurs as a strongly bound form (e.g. cinnabar) at the contaminated sites (KAPLAN et al. 2002).

Mercury speciation and natural organic matter – There are a number of biogeochemical factors and reactions which influence the speciation of mercury and its mobility, e.g. biotic and abiotic redox reactions, the presence and concentration of various inorganic ligands, pH, and clay and organic matter content (GRIGAL (2003) and GABRIEL and WILLIAMSON (2004)). Detailed information about the interaction of mercury with natural organic matter (NOM) can be found in RAVICHANDRAN's review (RAVICHANDRAN 2004), as well as in the recent studies of YAO et al. (2006), KHWAJA et al. (2006), and WAPLES et al (2005). Fundamental aspects of natural organic matter occurrence, chemistry, and isolation can be found in AIKEN et al. (1985b) and TAN and TAN (2003).

Analytical procedures to determine mercury speciation - To determine mercury in environmental samples, of which detecting the different species of mercury is important, several methods exist, e.g. CVAFS (TELLIARD and GOMEZ-TAYLOR 2002), cold vapour atomic absorption spectrometry (CVAAS) (MORITA et al. 1998), X-Ray absorption spectroscopy (XAS) - X-ray absorption fine structure spectroscopy (EXAFS) and X-ray absorption near-edge structure spectroscopy (XANES) (QUIAN 2001), chromatographic methods, and nuclear magnetic resonance techniques, especially for studies with model substances (BEBOUT AND BERRY 2006). The technical report from MORITA et al. (1998) provides detailed information about several mercury determination techniques in environmental samples. An overview of several spectroscopic methods to determine mercury in natural samples are given in the doctoral thesis of QUIAN (2001) as well as in the report of LEERMAKERS et al. (2005), who describe sampling and speciation methods and the use of techniques such as gas and liquid chromatography (GC, LC), CVAFS and ICP-MS in mercury analysis. Detailed information

about high performance liquid chromatography for detecting mercury is described in BOSZKE (2005) and the use of X-Ray absorption spectroscopy (XAS) is described by ANDREWS (2006).

Mercury toxicity - Numerous papers exist concerning mercury toxicity and the effects for human and environmental health, e.g. FLOREA and BUESSELBERG (2006), ZAHIR et al. (2005), and TCHOUNWOU et al. (2003), as well as a range of books, e.g. TSUGUYOSHI et al. (1991). WIENER et al. (2003b) highlight the ecotoxicological impacts of mercury.

Mercury in California - Because of the historic gold and mercury mining, mercury contamination is of major concern in California. Several studies examined contamination sources and sites, as well as mercury loads in waters, influence factors and environmental impacts of mercury in the California Bay area (ALPERS and HUNERLACH 2000; CALFED 2005; CBDA 2005; CHOE and GILL 2003; CHOE et al. 2003; DOMAGALSKI et al. 2004; FLEGAL et al. 2005; RYTUBA 2000; WIENER et al. 2003a). A regional fate and transport model of mercury in the San Francisco Bay was investigated by MACLEOD et al. (2005). Detailed information about former and recent studies and publications also can be found at the CALFED website (see CALFED 2003).

Mercury toxicity

The extent of mercury toxicity has been tragically known since the disaster in Minamata, Japan, where more than 100 people died and thousands suffered from Minamata disease (methylmercury poisoning), as a result of consuming contaminated fish (KUDO and MIYAHARA 1991). Among mercury species, the organic form, methylmercury (MeHg), causes the greatest human health concerns, because it is bioavailable and biomagnifies in the food web (ALPERS and HUNERLACH 2000; EPA 1997b; WIENER et al. 2003a). MeHg accumulates to a greater extent than other mercury forms in the fatty tissue of animals and in muscle tissue, especially in fish (EPA 2006a; MOREL et al. 1998). Biomagnification leads to an increase of methylmercury concentration with each step in the food chain by a factor around 10 (ALPERS and HUNERLACH 2000). Thus methylmercury, just a few percent of the total mercury in the water column, comprises the vast majority of the accumulated mercury in fish and humans. In humans – which are exposed to methylmercury primarily by the consumption of fish and shellfish– MeHg is neurotoxic and can cause damages on kidneys and the immune system (EPA 1997a; EPA 2006a; FLOREA and BUESSELBERG 2006; TCHOUNWOU et al. 2003). Also fish-eating animals and their predators are exposed to the risks of methylmercury – for example mortality, and decrease of reproduction and growth rates (EPA 2006a).

Mercury speciation

The speciation and complexation of mercury determines its fate and transport in the environment (WANG et al. 2004; WIENER et al. 2003b). In the environment mercury undergoes various reactions and transformations, as shown in Figure 1. The most important species of mercury in the environment are: elemental mercury, Hg(0) (Hg^0), divalent mercury, Hg(II) (Hg^{2+}), and methylmercury, MeHg (CH_3Hg^+).

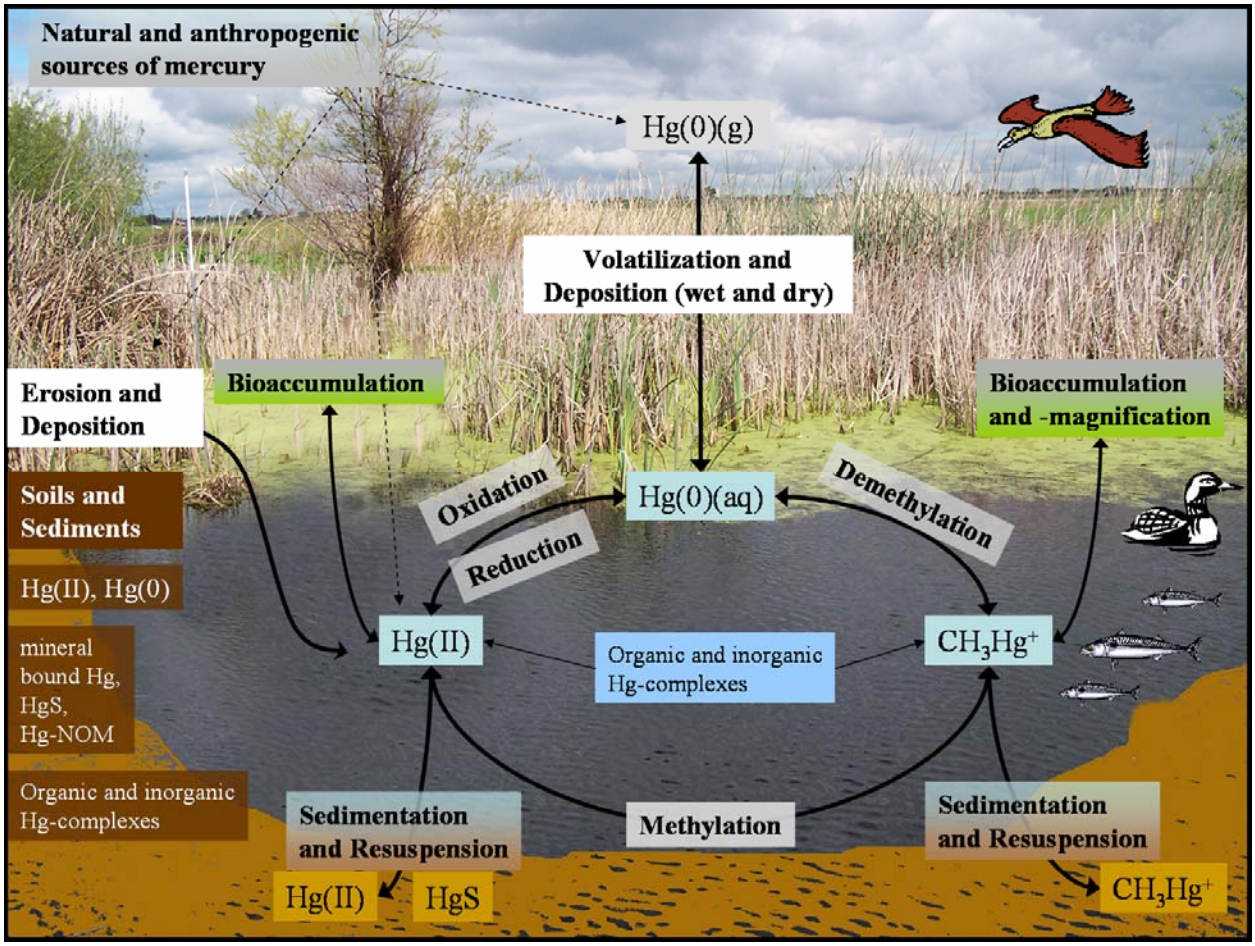


Figure 1. Mercury cycle
Figure modified from MASON et al. (1994), GRAY (2003), and WIENER et al. (2003b)), showing the major mercury species (Hg(II), Hg(0) and MeHg as CH3Hg+) and the main transformation processes and reactions (oxidation, reduction, demethylation and methylation).

Hg(0) can comprise up to 30 % of total dissolved mercury in ocean water (MASON et al. 1994). This species is relatively unreactive, and it is readily exchanged with the atmosphere (Figure 1) because of its volatile character and low aqueous solubility (MASON et al. 1994; MOREL et al. 1998). Hg(0) is slowly oxidized to Hg(II) in the air, which results in a residence time of about one year in the atmosphere (MOREL et al. 1998). In water mercury undergoes both oxidation and reduction reactions (Figure 1). In aquatic systems Hg(II) mostly occurs as complexes with

chloride, hydroxide, sulfide, and DOM (MOREL et al. 1998). Hg(II) is a very reactive species, which can adsorb to clay and oxides in soils (SCHUSTER 1991; YIN et al. 1996) as well to soil organic matter (SOM) (QUIAN 2001; SCHUSTER 1991; YIN et al. 1996). Obviously the SOM bound mercury comprises the majority of water soluble mercury in soils (WILKEN 1992).By sulfate reducing bacteria Hg(II) can be methylated (MOREL et al. 1998).

Numerous studies have shown that the biogeochemistry of mercury is influenced by numerous processes and environmental conditions for example: pH (DREXEL 2000; GABRIEL and WILLIAMSON 2004; MOREL et al. 1998), redox potential (MASON et al. 1994)), ionic strength (DUARTE et al. 1991; NOCITO-GOBEL and TOBIASON 1996; SLOWEY et al. 2005; WANG et al. 1991), presence of reducing bacteria,(MASON et al. 1994), photoreduction processes (MOREL et al. 1998; O'DRISCOLL et al. 2006), presence of inorganic ligands such as chloride (DREXEL 2000; MOREL et al. 1998; RAVICHANDRAN et al. 1998; YIN et al. 1996) and the presence of polyvalent cations such as calcium (RAVICHANDRAN et al. 1998). Particularly important for the complexation of mercury is dissolved organic matter. DOM is known to strongly bind mercury, and dominates the complexation of mercury in many environments (MEILI 1991). DOM is an important factor controlling the solubility of mercury and its watershed exports from contaminated sites (MIERLE and INGRAM 1991).

Organic matter and its interaction with Hg(II)

Dissolved organic matter plays an important role affecting the behavior of metals in the environment, influencing bioavailability, toxicity, and transport (AIKEN and COTSARIS 1995; RAVICHANDRAN 2004). In soils, organic matter occurs from biological and microbial degradation of organic materials, e.g. leaves and dead organic matter (AIKEN and COTSARIS 1995). By grouping regarding its solubility organic matter can be divided into the following fractions (AIKEN et al. 1985a):

- Humine – not soluble in water,
- Humic acid – soluble under more alkaline conditions, greater pH 2,
- Fulvic acid – soluble over the complete natural occurring pH range.

The fulvic acids are of lower molecular weight, with a higher oxygen and lower carbon content comparing to humic acids (STEVENSON 1985). Fulvic acids can be more reactive due to a higher content of acidic functional groups and that most of the oxygen is linked as functional groups, like COOH, OH, and C=O, whereas in humic acids, oxygen is a structural element of the nucleus, e.g. as ester or ether (STEVENSON 1985). Total acidity for fulvic acids are in a range of

890 to 1420 meq/100 g, and for humic acids from 485 to 870 meq/100 g. In soils a wide spectrum of humic substances exists, because of interactions between humic substances and building of subgroups. According to STEVENSON (1985) soil organic matter occurs as a major part as insoluble macromolecular complexes, bound together by polyvalent cations, and as clay-humus complexes, or linked by hydrogen bounding (STEVENSON 1985). Complexes of metals with fulvic acids are more soluble, because of the lower molecular weight and the higher acidic functional group content (STEVENSON 1985), but both acid fractions also can form insoluble complexes with metals, depending on the saturation degree. Connected with the strong affinity of organic matter to Hg(II), it has been observed that fulvic acids can promote volatilization of mineral bound Hg(II), where the extent is strongly dependent on complex capacity and stability of the organic material (YAO et al. 2006). Due to the high sorption capacity of organic matter material, SOM is also effective in binding Hg(II) (QUIAN 2001; SCHUSTER 1991; YIN et al. 1996). Especially soils with a high organic matter content, such as peat, can provide a sink for Hg(II) (DREXEL et al. 2002).

Generally the presence of soil organic matter (SOM) increases soil stability and its sorption capacity. Sorption on clays and oxides can provide a sink for organic matter (AIKEN and COTSARIS 1995). Due to mobilization by water, organic matter can reach groundwater and surface waters as dissolved organic matter < 0.45 µm (comprising the fraction < 1 nm, and colloidal organic matter (COM) with a size between 1 nm to 450 µm) and particulate organic matter > 0.45 µm (POM) (MACALADY and RANVILLE 1998). The DOM concentration and its qualities are related to the source soils in the watersheds, where the material was eroded (AIKEN and COTSARIS 1995). In general DOM does not affect drinking water quality negatively by itself, but because of its strong complexation capacity for toxic compounds such as trace metals (AIKEN and COTSARIS 1995), and its tendency to form disinfection by-products during chlorination.

Because of the complex structure of organic matter, it is very difficult to study their effects in natural systems. The isolation of dissolved organic matter using the XAD resin method (AIKEN et al. 1992) makes it possible to concentrate and purify a range of fractions from different source waters for use in experiments (Figure C 1). The use of isolated organic matter fractions is preferred over simple model organic ligands, better imitating the complexity occurring in the environment.

Studies with cinnabar (RAVICHANDRAN et al. 1998; WAPLES et al. 2005) have shown that DOM influences the dissolution of cinnabar, an insoluble mercury mineral (MORITA et al. 1998; RAVICHANDRAN et al. 1998; WAPLES et al. 2005). DOM has a range of functional groups that

can be involved in mercury complexation. There are reduced sulfur sites, such as thiols; these sites bind mercury very strongly, but are relatively few in number (HAITZER et al. 2002). Oxygen containing function groups, such as carboxylic acids, bind mercury weakly, but are quite numerous. Carboxylic groups have been shown to play a minor role in dissolution of cinnabar under conditions with a low mercury concentration (WAPLES et al. 2005). While the organic thiol groups bind mercury at low Hg(II) to DOM ratios, the carboxylic groups bind mercury at high and for natural systems untypical Hg(II) to DOM ratios (HAITZER et al. 2002) but also aromatic compounds preferring a dissolution of Hg(II) from cinnabar.

Mercury in the Bay-Delta Region

In the Region of the Sacramento-San Joaquin Delta and the San Francisco Bay (Bay-Delta region) in Northern California, methylmercury impairs the water quality. In several fish species from the Bay-Delta area, the EPA health guidelines for methylmercury are exceeded (CBDA 2005; WIENER et al. 2003a). To decrease the risk to human health and to protect the environment, the California Bay-Delta Authority (CBDA) convened a team of scientists to study mercury in this region and to work out management plans to (CBDA 2005).

In contrast to other regions were mercury contamination results from atmospheric deposition (according to MASON et al. (1994) estimations of global terrestrial wet and dry deposition are in the range of 15 µmol/year), the primary source of mercury in the Bay-Delta region originates from mining (Figure 2), both mercury mining and the processing of gold, and from natural thermal springs (CALFED 2005; MACLEOD et al. 2005; WIENER et al. 2003a).

As consequence of the historic gold and mercury mining in Northern California from the 1880s until the early 1960s, with a peak from 1852 to 1884, more than 13 million pounds of mercury were released into the environment (ALPERS and HUNERLACH 2000; CALFED 2005). The 'hot spots' of contamination are the mine and tailing areas itself and the surrounding sites (ALPERS and HUNERLACH 2000). By transporting of mercury with the rivers, areas located downstream the mines were contaminated. Mercury accumulated in soils, especially floodplain soils, river and lake sediments, and in reservoirs, where dams prevent the further distribution of the eroded mining material (CALFED 2005). With the mercury load run-off from the watersheds of Sacramento and San Joaquin rivers, huge amounts of mercury entered the wetland sediments of the Sacramento-San Joaquin delta and the sediments of the San Francisco-Bay (ALPERS and HUNERLACH 2000). CHOE et al. (2004) reported total mercury concentrations for surface sediments in the San Francisco Bay area in a range of 0.29 ± 0.25 mmol/g to 2.10 ± 0.90 mmol/g, with highest measured concentrations of 5 mmol/g in a depth of 9 – 10 cm (Consumnes

River), which are attributed to the mercury contamination after the 1950s (CHOE et al. 2004). The similar concentrations for sediments in the San Francisco Bay (1.7 ± 0.7 nm/g) and suspended particles (1.8 ± 0.6 nmol/g) reported in CONAWAY et al. (2003) indicate that resuspension and remobilization of finer material is an important process for continuous mercury distribution.

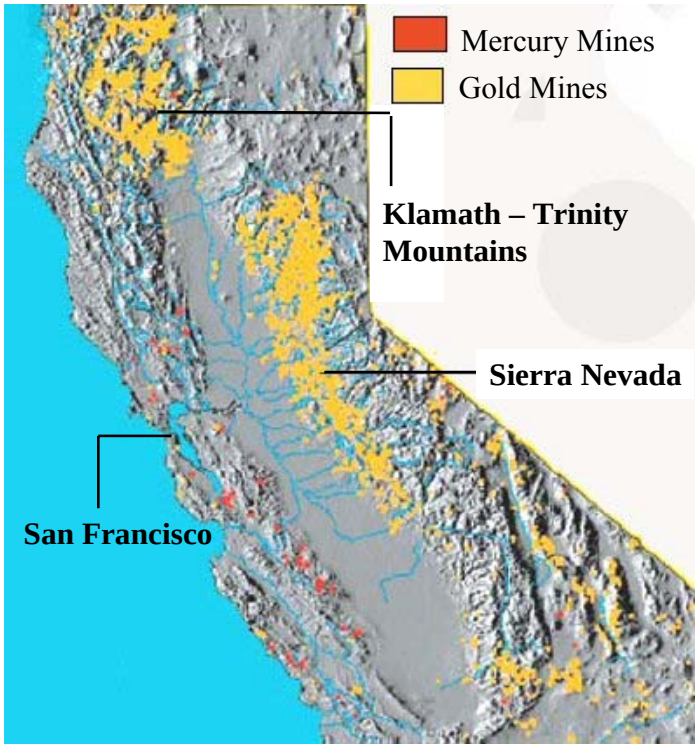


Figure 2. Gold and mercury mines in Northern California
Figure was modified, original from CALFED (2005).

The elevated actual concentration of mercury in mining drainage, river water and sediments indicate the enormous amount of remaining mercury, which will continue mercury transport and distribution in the future (ALPERS and HUNERLACH 2000). Estimations of the annual mercury transport into the Bay-delta are between at least 100 kg to more than 800 kg (CHOE et al. 2003; DOMAGALSKI 1998; DOMAGALSKI 2001). The actual total mercury concentrations in the water column of the San Francisco Bay are in a range of 100 pmol/L in the mid – estuarine region (salinity 15) to 50 pmol/L in rivers entering the Bay and 30 pmol/L in areas with high salinity (> 15) (CHOE et al. 2003). Obviously is salinity one of the factors controlling mercury distribution in the San Francisco Bay area (CHOE et al. 2003) as well as dissolved organic carbon diverting from the correlation of DOC with dissolved mercury (<0.45 µm) determined in studies of CONAWAY et al. (2003).

But the sedimentation of the eroded material does not inactivate the negative impacts of mercury. Under the right conditions, at the oxic-anoxic interface between sediment and water, mercury can be converted in to the highly toxic and bioavailable methylmercury by sulfate reducing bacteria (ALPERS and HUNERLACH 2000; CALFED 2005; CBDA 2005; WIENER et al. 2003a). Methylmercury in sediments of the San Francisco Bay ranged from 0.5 – 5.0 pmol/g and in the water column from 0.05 pM to 2.3 pM, reported in CONAWAY et al. (2003). Beside production of MeHg in the San Francisco Bay sediments, methylmercury is transported from the Sacramento-San Joaquin delta, where concentrations of MeHg are higher than in the Bay (CONAWAY et al. 2003). An important part of MeHg in the Sacramento-San Joaquin delta results from delivery by the tributaries entering the delta (CALFED 2005).

The focus of the study reported here was on six soils contaminated by historic gold and mercury mining. These soils were collected from different areas within the Sacramento-San Joaquin watershed in California. Mercury associated with these soils can be mobilized by erosion, solubilized by water, and transported downstream until the material is settled as sediment. The availability of mercury in these soils is controlled by various factors. These include the soil's own properties: the nature, origin, and geochemical composition of the soils; in addition, the amount of mercury, and the distribution and complexation of the mercury, especially by organic matter, in the soil. Water chemistry such as DOM concentration and quality, ionic strength, pH and other elementals like calcium, chloride, and iron can also affect mercury mobilization. DOM plays an important role in dissolution of Hg(II) from these soils under environmental conditions.

The aim of the recent study is to examine the impact of various factors influencing the dissolution of Hg(II) from these contaminated materials. This will be done through a series of batch experiments.

3. Methods and Material

3.1 Sampling sites and Sample preparation

Soil and sediment materials originated from six different sites in Northern California – four samples from the UC-Davis McLaughlin Reserve in the Coastal Range, 116 km north of San Francisco, and two samples from the Bear River watershed in the Sierra Nevada Range near Wheatland, CA. Both the Sierra Nevada and the Coastal Ranges are regarded as major mercury sources for the Bay-Delta area because of the historic gold and mercury mining (DOMAGALSKI 2001).

Four samples from the McLaughlin Reserve were collected by JoAnn Holloway (U.S. Geological Survey, Denver, CO) in March/April 2005. All these sampling sites were located in the Cache Creek watershed. This watershed contains several mercury mines, and is known as a main contributor for mercury contamination to the Bay-Delta system with the highest mercury loads reaching 2.25 ng/L in unfiltered water (DOMAGALSKI 1998; DOMAGALSKI 2001). The two samples from the Sierra Nevada Range are: 1) from the Camp Far West reservoir, an impoundment of the Bear River downstream from areas of historic gold mining, and 2) from the Starr Tunnel, a tunnel that contained a sluice box where elemental mercury was used to collect gold. These samples were collected by Jacob E. Fleck (U.S. Geological Survey, Sacramento, CA.) in March 2005. The Camp Far West sediment was collected in the Bear River Arm of Camp Far West Reservoir, where the Bear River flows into the reservoir. The sampling took place after a 1-week storm event. From the Starr tunnel, 2 cm of sediment overlaying the bottom sluice board was collected. The mineral fraction contained about 1 % of sulfide (verbal communication of Fleck J. E. 2005). Table 1 presents detailed information about all sampling sites.

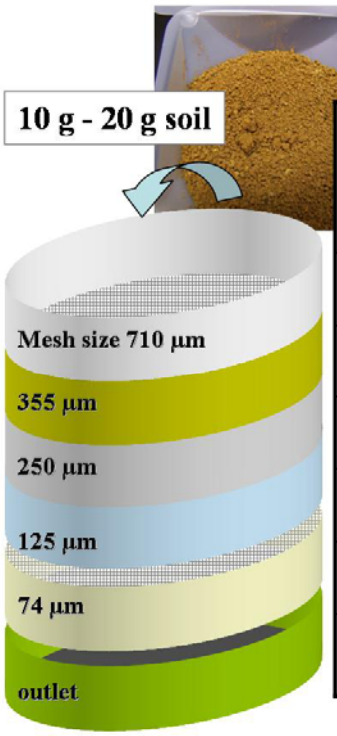
All soil and sediment samples were collected in clean glass containers and shipped in coolers to the USGS office in Boulder. The collected material was air-dried for 72 hours at room temperature and then sieved with a 24 mesh metal-sieve with 710 µm openings. The fraction < 710 µm was used for the leaching experiments. This fraction was selected because it was expected that mercury would be found primarily in the smaller size fraction, both bound to clay and oxide minerals and as small cinnabar particles.

Table 1. Summary of soil sampling site information

Sample name	Sample ID	Latitude	Longitude	Collection date	Site description	Soil sampling zone	Soil type	Reference
McLaughlin Reserve 107A	MCL107A (serpentine soil)	38°86'21"N	-122°36'97"W	5/30/2005	UC-Davis McLaughlin Reserve; hillslope serpentine soil along Blue Ridge.	A-horizon, 0-5 cm	gravelly silt loam	Holloway J., unpublished data
McLaughlin Reserve 131B	MCL131B (fluvent)	38°86'29"N	-122°37'24"W	5/31/2005	UC-Davis McLaughlin Reserve; fluvent on vegetated distal end of pt bar; transitional wetland vegetation, which is primarily dense; potentiometric surface at 22cm.	B-horizon, 26-60 cm	sandy silt loam	Holloway J., unpublished data
McLaughlin Reserve 134B1	MCL134B1 (wetland sediment)	38°86'21"N	-122°36'98"W	5/31/2005	UC-Davis McLaughlin Reserve; aquent in wetland where Davis Creek enters reservoir; vegetation includes cattails and willow; potentiometric surface at 15 cm.	B1-horizon, 45-67cm	sandy loam	Holloway J., unpublished data
McLaughlin Reserve 137	MCL137 (tailing)	38°86'80"N	-122°37'80"W	4/1/2005	UC-Davis McLaughlin Reserve; thin soil forming on mercury mining tailings; dominant parent material is altered serpentine.	A/C-horizon, 0-10 cm	gravelly silt loam	Holloway J., unpublished data
Camp Far West	CFW (lake sediment)	39°02'02"N	-121°16'22"W	3/24/2005	samples collected in the Bear River Arm of Camp Far West Reservoir; Bear River is upstream of dam, located in Wheatland, CA; sampling on first sunny day after a week of storms.	0-2 cm		Fleck J. E., unpublished data
Starr Tunnel	Starr (sluice sediment)	39°13'27"N	-120°54'2"W	3/29/2005	collected material is top sediment overlaying the bottom sluice board in the tunnel.	0-2 cm		Fleck J. E., unpublished data

3.2 Soil particle size analysis

Particle size fractionation was determined by the dry sieving of 10 to 20 g of air-dried soil material through a set of sieves (ASTM E11-04 specification, i.e. American Society for Testing and Materials - Standard Specification for Wire Cloth and Sieves for Testing). The sieves had openings with widths of 710 µm, 355 µm, 250 µm, 125 µm, and 74 µm, (Figure 3). The soil separation was examined using the classifications of the United States Department of Agriculture (USDA) and the common mineralochemical size fractions used in the USA (JACKSON 1956).



Particle size [µm]	Corresponding soil separate according to USDA classification (Jackson (1956))	Modified classification (mineralochemical size fractions (Jackson (1956)) and USDA)
> 710 µm	gravel > 1000 µm + coarse sand (1000 – 500 µm)	gravel and coarser sands (> 250 µm)
< 710 µm to > 355 µm	coarse (1000 – 500 µm) + medium sand (250 – 500 µm)	
< 355 µm to > 250 µm	medium sand (250 – 500 µm)	
< 250 µm to > 125 µm	fine sand (100 – 250 µm)	Fine and very fine sands (< 250 µm, > 50 µm)
< 125 µm to > 74 µm	fine sand (100 – 250 µm) + very fine sand (50 – 100 µm)	
< 74 µm	very fine sand (50 – 100 µm), silt (< 50 µm), clay (< 2 µm)	very fine sands, silt and clay

Figure 3. Particle size analysis procedure and size fractions according to the USDA and the commonly mineralochemical used fractionation (JACKSON 1956)

Each sieve was weighed before (tare weight), and after sieving, the difference giving the net weight of soil, used for the mass-percent calculation for each size fraction (Table 2). The calculation procedure was performed as shown in Table 2, the following interpretation and classifying occurred according to the details given in Figure 3.

A mean method error of 1 % was calculated as average over the relative percent difference (RSD) between the total soil input and the summarized net weights for each soil (Table 2).

Table 2. Mass-percent calculation scheme for particle size analyses by sieving

Mesh size [µm]	Size fraction	Net weight	Mass-percent of each size fraction
710	> 710 µm	_____ g	$\%\ fraction = 100\,\% * \frac{net\ weight\,[g]}{sum\ net\ weight\,[g]}$
355	710 µm to 355 µm	_____ g	_____ %
250	250 µm to 355 µm	_____ g	_____ %
125	125 µm to 250 µm	_____ g	_____ %
74	74 µm to 125 µm	_____ g	_____ %
outlet	< 74 µm	_____ g	_____ %
sum		**_____ g**	**100%**
total soil input		**_____ g**	
method error	$RPD\ [\%] = 200 * \frac{\lvert sum\ [g] - total\ input\,[g] \rvert}{(sum\ [g] + total\ input\,[g]}$		

3.3 Analytical methods

3.3.1 XRD analysis

To determine the mineralogical composition, X-ray diffraction (XRD) analyses were performed on freeze-dried, non-separated soil material using a Siemens D5000 powder diffractometer. The sample (1.000 g) was mixed with an internal standard (0.1111 g ZnO), and ground with 4 mL methanol in a McCrone mill for 5 minutes (SRODON et al. 2001). The suspension was dried overnight at 85 °C, and then sieved with a 500 µm sieve. The resulting powder was then packed into an XRD sample holder and tapped on a hard surface, to guarantee that the material distributed evenly (EBERL 2003). The X-ray diffraction occurred from the detector rotation (two-theta) 5 to 65 degrees using Cu K-alpha radiation (resulting K-alpha radiation after bombarding a copper anode with high energetic electrons) (EBERL 2003). The data were evaluated by Dennis Eberl and Zanden Frederick and the RockJock computer program was used to convert intensities into mineral content in weight % (EBERL 2003). The minimum detection limit (MDL) for all minerals analyzed with XRD is 1 weight % (verbal communication, Dennis Eberl, USGS Boulder)

3.3.2 Mercury analysis

Total dissolved mercury, which is according to the definition in the EPA method 1631 all the mercury that is reducible with BrCl in a 0.45 µm filtered solution (TELLIARD and GOMEZ-TAYLOR 2002), was determined with a Millenium Merlin Mercury Analyzer (PS Analytical, Kent, UK) following the procedure described in the PSA method manual (PSA 1997). About 10 mL of the sample filtrate were digested with BrCl to break down and oxidize all mercury to Hg(II). After an oxidation time of at least 30 minutes, pre-reduction with $NH_2OH*HCl$ removes surplus BrCl. By adding $SnCl_2$, Hg(II) in the prepared samples is reduced to gaseous Hg(0), which can be purged out of the solution by a carrier stream of argon. The detection of mercury is then done by cold vapor atomic fluorescence.

Standard solutions were prepared from NIST Standard Reference Material 3133 (U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD). During the analysis of samples, the standard series, consisting of four standards in the range of 0 - 100 ng/L Hg(II) was repeated every 14 samples. A minimum detection limit (MDL) of 5 ng/L was calculated for all experiments, based on the 3σ-criterion, which is three times the standard deviation (SD) above the average instrument response for the zero standards, MDL = 3*SD/n, n= 60).

3.3.3 DOC analysis

The DOC concentrations of the filtered samples (0.45 µm) were measured using persulfate oxidation method with infrared detection of the resulting CO_2. Measurements were performed on two instruments: an O.I. Analytical Model 1010 and an O.I. Analytical Model 700, (O. I. ANALYTICAL 2003; O.I. ANALYTICAL 1984). The detection range of the O.I. Analytical instruments for TOC is 2 µg C/L to 125 µg C/L for model 1010 (O. I. ANALYTICAL 2003) and 4 µg C/L to 10,000 mg C/L for model 700 (O.I. ANALYTICAL 1984). Samples containing chloride (e.g. experiment no. 9 from Table 3) were analyzed with a catalytic combustion TOC analyzer from Shimadzu Scientific Instruments. This alternate instrument was used because chloride interferes with wet-chemical oxidation methods at chloride concentrations higher than 0.02 M (AIKEN 1992), and to minimize corrosive effects on the detector. According to the manufacturer the MDL for Shimadzu TOC-V CPH for total carbon is 4 µgC/L (SHIMADZU 2006).

Table 3. Experimental conditions for leaching experiments

Detailed information about constituents of leaching and stock solutions, and pH buffers can be found in Table A 1 to Table A 5 (Appendix A – Tables).

No.	Experiment	Basic conditions	Additional settings	
1	Basic leaching conditions (background leaching)	0.25 g soil, pH 6.4 ± 0.06, I = 0.1 M, total volume = 50 mL (ultrapure water - UPW), equilibration time 24 h		
2	Leaching without buffers	0.25 g soil in 50 mL UPW, equilibration time 24 h		
3	Leaching with water from Sacramento River	0.25 g soil, pH6.4 ± 0.06, I = 0.1 M, total volume = 50 mL, equilibration time 24 h	used liquid: Sacramento River water	
4	DOM experiment (variable DOM concentration.)	0.25 g soil, pH6.4 ± 0.06, I = 0.1 M, total volume = 50 mL, equilibration time 24 h	DOM (F1-FA-stock) in conc. of 1 mg/L, 5 mg/L, and 10 mg/L	
5	pH experiment (variable pH)	0.25 g soil , I = 0.1 M, total volume = 50 mL, equilibration time 24 h	addition of 0.50 mL 1 M Phosphate buffer with pH adjustment by NaOH and HNO_3	
			buffer pH [± 0.01 pH units]	average pH in filtered leaching solution [± SD over all samples]
	pH 3	phosphate buffer - 0.1 M $Na_2H_2HPO_4*2H_2O$	3.0	4.7 ± 0.6
	pH 4	standard phosphate buffer - 0.3 M Na_2HPO4 and 0.7 M $Na_2H_2HPO_4*2H_2O$	4.0	5.4 ± 0.3
	pH 6	standard phosphate buffer	6.0	6.3 ± 0.1
	pH 8	standard phosphate buffer	8.0	7.9 ± 0.1
	pH 10	standard phosphate buffer	10.0	7.9 ± 0.4
	pH 12	phosphate buffer - 3 mM Na_2HPO_4 and 7 mM $Na_2H_2HPO_4*2H_2O$	12.0	11.3 ± 0.1
6	Ionic strength experiment (variable I)	0.25 g soil , total volume = 50 mL, equilibration time 24 h	ionic strength setup: 0.1 M, 0.01 M and 0.001 M with $NaClO_4$	
7	Isolates experiment (variable DOM)	0.25 g soil, pH 6.4 ± 0.06, I = 0.1 M, total volume = 50 mL, equilibration time 24 h	10 mg/L DOM: WL-HPoA, 2BSWCA-HPoA, F1-FA, F1-HPoA, CF06-0006-HPoA, , Suw-HA	
8	Model compound experiment	0.25 g soil, pH 6.4 ± 0.06, I = 0.1 M, total volume = 50 mL, equilibration time 24 h	separate experiment series with additional organic ligands: 20.8 µM EDTA, 69.4 µM mercaptoacetic acid, and 29.7 µM salicylic acid	
9	Chloride- and Calcium experiment	0.25 g soil, pH6.4 ± 0.06, I = 0.1 M, total volume = 50 mL, equilibration time 24 h	0.01 M chloride as NaCl , $2.5*10^{-4}$ M calcium as $Ca(NO_3)_2$ with and without 10 mg/L F1-FA	
10	Colloid experiment	according to settings from no. 1 and 4 (10 mg/L F1-FA) with additional spin at 12, 000 rpm to separate Hg(II) < 0.02 µm.		

3.3.4 UVA and SUVA

The UV absorbance was measured on a Hewlett-Packard Model 8453™ photo-diode array spectrophotometer at a wavelength of 254 nm. Deionized water was used as blank. The filtered samples were analyzed at room temperature, using a quartz cell with a path-length of 1 cm.
Because of the known interference of nitrate on the absorption of UV light (WEISHAAR et al. 2003), the results for the calcium experiment (Table 3, no. 9) had to be corrected with a separate blank. For that the average blank UVA from the calcium experiment without additional DOM was subtracted from the sample UVA's for both experiment series (calcium and calcium with DOM). Also iron in concentrations higher than 0.50 mg/L have a strong influence in UV absorbance (WEISHAAR et al. 2003) and SUVA, because UVA is one factor necessary for its calculation. ICP-AES analyses were performed to determine whether there is an influence of iron on UVA.

The specific UV absorbance (SUVA), an indicator for reactivity of organic matter material (WEISHAAR et al. 2003), was calculated by:

$$SUVA[L * mgC^{-1}m^{-1}] = 100 * \frac{UVA_{254nm}[cm^{-1}]}{DOC\,[mg * L^{-1}]} \qquad \textbf{Equation 1}$$

In this study the SUVA is used to determine a possible correlation between reactivity of organic material in the leaching solutions and release of Hg(II) from the soils. In addition, UVA and SUVA are used as control elements to show possible mistakes and uncertainties occurring during sample preparation and filtering.

3.3.5 Determination of Total organic carbon, Total mercury analysis, and Sequential extraction

The total organic carbon (TOC) analyses were performed on freeze-dried, ground and homogenized sub-samples by the Huffman Analysis Laboratories in Golden, CO.
Total mercury (THg) for each sample was determined by Jarrod D. Gasper using aqua regia digestion (Table 4). Digestion of the samples involved a series of steps: first, 40 mg of freeze-dried soil material was mixed with 13 mL aqua regia, this was allowed to digest overnight at room temperature (25 ± 2 °C), then heated in a 96 °C water bath for 3 h, and finally analyzed for mercury with CVAFS. The MDL calculated as 3 times the average mercury concentration over the experiment blanks (i.e. digests without soil) is about 18 ng Hg/g.

Sequential extraction to determine the speciation of mercury in the soil samples was also performed by J. D. Gasper, according to the reported method of BLOOM et al. (2003). A summary of this method is given in Table 4.

Table 4. Sequential extraction for determination of mercury speciation in soil samples and procedure for total mercury analysis
Extract, mercury fraction and extracted mercury species were summarized from the methods described in BLOOM et al. (2003) and LOWRY et al. (2004).

Fraction name	Extract	Mercury fraction	Typical extracted mercury species
F1	deionized water (DI)	water soluble	$HgCl_2$
F2	0.1 M CH_3COOH + 0.01 M HCl; pH 2	"stomach acid" soluble	HgO, $HgSO_4$
F3	1 M KOH	organic complexes	Hg-humics, CH_3Hg, (Hg_2CL_2)
F4	12 M HNO_3	strong complexed, elemental mercury	mineral lattice, Fe-, Mn-oxides, Hg_2Cl_2, Hg(0)
F5	aqua regia, $HCl:HNO_3$ = 10 : 3	Hg sulfide	HgS, HgSe, Fe-, Mn-oxides
THg (total mercury)	aqua regia, $HCl:HNO_3$ = 10 : 3	complete dissolution	residual mercury

3.3.6 Further analyses: IC, ICP-AES, and Fluorescence

Chloride, nitrate, and sulfate were analyzed at filtered leaching solutions (Table 3, no. 2, with and without 10 mg/L DOM), with a Dionex DX-120 Ion Chromatograph (IC) by Jennifer Schnackel and Kenna Butler, USGS in Boulder, CO. All results less then the MDL (0.03 mg/L for chloride and sulfate, 0.01 mg/L for nitrate, see Appendix D – Database) were replaced by 0.3*MDL for calculations and interpretations.

Selected metals (aluminum, boron, barium, calcium, copper, iron, potassium, lithium, magnesium, manganese, sodium, nickel, sulphur, silica as SiO_2, strontium, vanadium, and zinc) were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a Perkin Elmer Optima 3300™ dual view emission spectrometer. Filtered samples were acidified with 1 % trace metal grade HNO_3 and stored in high-density polyethylene (HDPE) cylinders, which were cleaned with aqua regia and ultrapure water, and rinsed with sample before filling.

For the ICP-AES analysis a 1:10 dilution of the sample solution was prepared with trace metal grade HNO_3. The MDL was calculated for each run and element by the standard deviation above the blanks multiplied with the t-statistic of the blank number at the 95 % level (MDL's can be found in Appendix D – Database). Results less than the MDL were replaced by 0.3*MDL.

The samples from the various leaching experiments (e.g. Table 3, no. 1 and 3) were additionally analyzed by fluorescence spectroscopy using a Jobin Yvon Fluoromax-3 instrument. The fluorescence index (FI) that reveals information about the origin of organic material in solution was calculated by:

$$FI_{(excitiation\ 370\,nm)} = \frac{Emission_{470\,nm}}{Emission_{520\,nm}} \qquad \textbf{Equation 2}$$

(MCKNIGHT et al. 2001).

3.4 Leaching experiments

The batch experiments were carried out with 0.25 g sample material (< 710µm) in a total suspension volume of 50 mL in polypropylene centrifuge tubes with polyethylene plug seal caps (Corning Incorporated) (see Figure 4). Ionic strength was set to 0.1 M with $NaClO_4$. The pH-value was adjusted to 6.4 ± 0.1 (standard deviation calculated over all experiments, n = 372) with a 1 M phosphate buffer made of 0.7 M $NaH_2PO_4*2H_2O$ and 0.3 M Na_2HPO_4. The difference in amount of leaching fluid to a total volume of 50 mL was compensated with ultrapure water (UPW), except the leaching with Sacramento River water (experiment 3, Table 3).

Depending on the particular experiment, the leaching setup (see Table 3, no. 1) was completed by the addition of either dissolved organic matter material (DOM) in various concentrations (experiment 4) and of different quality (experiment 7) or by addition of simple organic and inorganic ligands (experiments 8 and 9) as shown in Table 3. Each series of experiments was run in duplicate, with two blank replicates which contained everything but the soil samples.

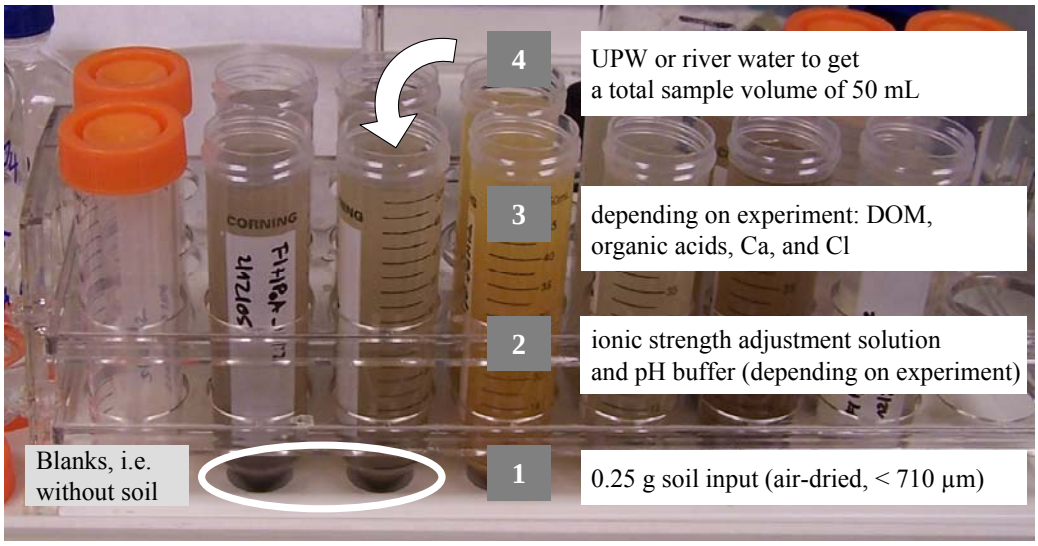


Figure 4. Preparation of leaching experiments

All DOM stock solutions (isolate origin and quality information in Table 5 and Table 6) were prepared of freeze-dried, fractionated organic matter material (separation by XAD-8/XAD-4 resin method (AIKEN et al. 1992), Figure C 1) in ultrapure water (Table A 4). In most experiments with added DOM (experiments no. 4, 8 and 9), the isolate F1-FA from a marshland in the northern Everglades (WAPLES et al. 2005) was used at a concentration of 10 mg/L (isolate description Table 5 and Table 6).

Table 5. Isolate origin information

Isolate ID	Collection date	Site description	Reference
Suw-HA	Jan-83	Suwannee River - Drainage of the Okeefenokee Swamp (Black water river), sampling site: Fargo, Georgia; vegetation types: southern floodplain forest (*Quercus*, *Nyassa*, *Taxodium)*	(HAITZER et al. 2003)
F1-FA	Jul-97	F1 – marshland in Water Conservation Area 2A (eutrophied) in northern Everglades; dominant vegetation: cattails (*typha latifolia)*	(HAITZER et al. 2003)
F1-HPoA	Jul-97		
2BSWCA-HPoA (WCA-HPoA)	Apr-96	marshland (pristine) in Water Conservation Area 2B, northern Everglades; dominant vegetation: saw grass	(HAITZER et al. 2003)
WL-HPoA	Oct-00	Williams Lake – seepage lake located in north-central Minnesota; organic matter dominated by autochthonous sources, e.g. algae, bacteria, and vegetation	(WAPLES et al. 2005)
CF06-0006-HPoA (CF06-HPoA)	Jan-06	Sacramento River –resulting drainage from watersheds with mercury and gold mine districts from Coast Range and Sierra Nevada by tributaries of Sacramento River, CA, entering in San Francisco Bay; diverse vegetation types: riparian scrub, woodland, emergent and seasonal wetlands; influence of tide cycles.	(ROBERSON 2003)

Table 6. Isolate location and quality information

			Elemental composition [wt%]						^{13}C-NMR analysis [% of total carbon]					
Isolate ID	**COOH[A] [meq/g]**	**SUVA [LmgC^{-1}m^{-1}]**	**C**	**H**	**O**	**N**	**S**	**Mol wt [Da]**	**Al-I [0-62 ppm]**	**Al-II [62-90 ppm]**	**Al-III [90-110 ppm]**	**Ar [110-160 ppm]**	**C-I [160-190 ppm]**	**C-II [190-230 ppm]**
functional carbon groups	carboxyl								aliphatic		acetal	aromatic	carboxyl	ketone
Suw-HA	4.49	6.56	53.42	3.89	40.88	1.14	0.68	1399	21.3[B]	7.3	6.6	35.1	20.7	9
F1-FA	5.60	4.17	52.94	4.37	39.67	1.43	1.60	850	43.4	15	5.4	20.1	13.8	2.2
F1-HPoA	5.45	3.93	52.24	4.64	39.86	1.53	1.73	1031	45	17	5.6	18.2	11.6	2.7
2BSWCA-HPoA	5.09	3.17	52.25	4.79	40.15	1.58	1.23	953	48.5	14.9	4.1	15.4	15.4	1.8
WL-HPoA		2.20[C]	52.70[D]	5.20	36.60	1.70	0.74	772[E]	50[F]	15	5.8	13.8	13.9	1.5
CF06-0006-HPoA		3.50[G]												

[A] RAVICHANDRAN et al. (1998)

[B] THORN et al. (1989)

[C] WEISHAAR et al. (2003)

[D] RAVICHANDRAN et al. (1999)

[E] CHIN Y., Ohio State University, in WAPLES et al (2005)

[F] WAPLES et al (2005)

[G] AIKEN G. R., U.S. Geological Survey, Boulder, unpublished data

The samples in the variable pH (pH 4.7 – 11.3, Table 3, experiment no. 5) and ionic strength (I = 0.1, 0.001 and 0.001 mol/L, experiment no. 6) experiments deviate in the content of the pH buffer and the amount of $NaClO_4$ than that described in the general experimental description (Table 3). Based on the results of the kinetic experiments, the leaching was carried out for 24 hours, while mixing the samples in an end-over-end mixing apparatus at 4.5 rpm. After this equilibration time the samples were spun at 2800 rpm (Beckman CPR Centrifuge) for 40 minutes. The sampling procedure after centrifugation is shown in Figure 5. To separate the particulate material from the liquid the samples were filtered with 0.45 µm membrane filters pre-cleaned with 140 mL UPW. The first 10 mL of the sample filtrate was used for pH-measurements (pH-meter Φ 210, Beckman Instruments, CA). The pH-meter was calibrated with VWR international pH buffer solutions with pH 4, 7, and 10. The relative accuracy of this instrument according to the manufacturer is 0.01 pH-units with a three-point calibration. The next 40 mL of filtrate was used for mercury, DOC, and ICP analysis as well as for UV absorbance measurements, IC, and fluorescence following a standardized scheme, to guarantee comparable results, as shown in Figure 5 .

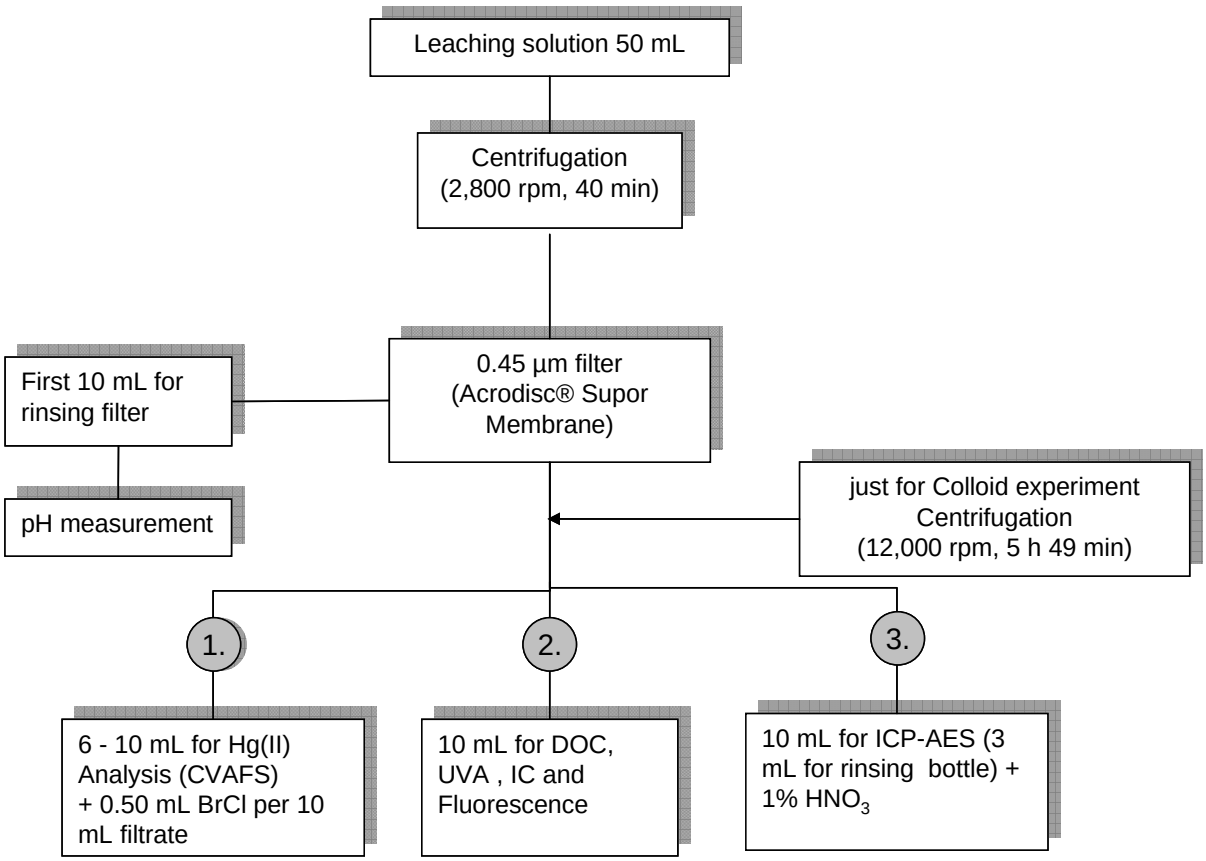


Figure 5. Overview filtering procedure

To estimate the content of dissolved mercury in the fraction < 0.02 µm, 0.02 µm Anotop® filters were tested (SHILLER 2003). Because low recoveries of Hg(II) spikes, observed while testing these filters, they were not suitable for these experiments.

Centrifugation at 12,000 rpm seemed to be another acceptable method to estimate dissolved mercury < 0.02 µm. To test the method within the colloid experiment (Table 3, experiment no. 10) two series of leaching solutions were prepared. After centrifugation and filtering as described for the other samples, a further centrifugation step was carried out at 12,000 rpm for 5 hours and 48 min (Figure 5). The time required for separating 0.02 µm colloids was calculated by the Stokes Law as follows:

$$v = \frac{d^2 * (\rho_p - \rho_L) * RCF * g}{18\eta} \qquad \textbf{Equation 3}$$

(JACKSON 1956),

with: $\nu = s/t$ = sink velocity [m/s]

d = particle diameter [m] = $0.02 * 10^{-4}$ m

ρ_p = particle density [g/cm^3] = 2.65 g/cm^3 (Quartz)

ρ_L = liquid density [g/cm^3] = 0.997071 g/cm^3 (water at 25°C)

g = earth acceleration [m/s^2] = 9.81 m/s^2

η = viscosity [Pa*s = kg*s/m*s^2] = 0.000894

RCF = relative centrifugal force = 11,854 for the Rotor JA-20, max spin 12,000 rpm (reference: see BECKMAN)

s = path length = centrifuge tube length [m]

t = resulting centrifugation time

For a path length of 10 cm, a time of 5 hours and 48 min was calculated. After centrifugation, preparation of the samples and mercury analysis was carried out in the same way as described for the other experiments. In addition to the mercury analysis, DOC, UVA, and ICP analyses were performed.

The amount of colloidal mercury in the leaching solutions can be estimated by calculating the difference of the amount of dissolved mercury < 0.45 µm, measured in the experiments no. 1 and 4 (Table 3) and the Hg(II) content < 0.02 µm, measured after centrifugation at 12,000 rpm (Table 3, experiment no. 10).

3.5 Calculations

All results for Hg(II) were corrected by the average from the experiment blank duplicates run at the same time as the samples. The UVA and DOC concentrations were also corrected for experiment blanks in experiments were no DOM material was added. For experiments with additional DOM the results for UVA and DOC were corrected by average blank values of four separate leaching experiments under conditions of pH = 6.4 ± 0.1 and I = 0.1 M (analogous to experiment no. 1 in Table 3) without soil addition. The SUVA was calculated from these corrected values. Several "background soil leachings" were performed, which means batch experiments with conditions corresponding to experiment no. 1 in Table 3. An average Hg(II) release from these background leachings was calculated from five separate experiments (n =10) and DOC, UVA, and SUVA values were calculated from four experiments (n=8). These results build a base for understanding the leaching processes, as the effects of changing the particular experimental variables (increase or decrease) can be calculated. Net increase of Hg(II), DOC and SUVA in various experiments were calculated by the difference between the results in the particular experiment and the background leaching results.

Because the experiments were performed in duplicate, average values, standard deviations (SD), and the relative percent differences (RPD) were calculated for each soil.

3.6 Preparation of stock solutions and approach to equipment operation, kinetic analysis, and matrix effects

3.6.1 General handling for mercury analysis and preparation of stock solutions

In order to reduce any mercury contamination by skin contact, powder free latex gloves were worn during all times when handling samples and chemicals. For all experiments, trace metal grade chemicals and mercury clean equipment were used. Stock and leaching solutions (Table A 1 to Table A 5) were prepared with ultrapure water (UPW) (Barnstead Nanopure purifier, resistivity 18.2 MOhm/cm), with a DOC of 0.2 ppm. For the DOM stock solutions freeze-dried, fractionated organic material (Table A 4) was used and dissolved in UPW.

Filters (0.45 µm Acrodisc® filters with Supor® membrane) were cleaned before use by rinsing with 140 mL ultrapure water to remove dissolved organic matter material from the filter membrane. Similarly, the plastic syringes (HSW Norm-Ject®, silicon oil and latex-free, 10 mL and 50 mL size) were rinsed with 60 mL to 180 mL UPW as described in Table A 11.

Any reference to "DOM" in the following text signifies the use of the stock solution of organic matter material from the isolate F1-FA (description in Table 5 and Table 6).

3.6.2 Equipments tests

The complete equipment used for the experiments (e.g. filters and centrifuge tubes) was tested for possible contamination or adsorption of mercury as well as dissolved organic matter. For the filter tests, different test solutions (e.g. with 10 mg/L DOM, spiked with 100 ng/L Hg(II), see Table A 7) were run through the filters (0.45 µm Acrodisc® filter with Supor® membrane, diameter: 25 mm and 32 mm, and 0.02 µm Anotop® filter with Anopore® membrane, diameter: 25 mm). The first 10 mL of the test solutions (total volume 50 mL) were used unfiltered for analyzing DOC and Hg(II), and for UVA measurements. Then the filtration was performed stepwise (in 10 mL steps), and each fraction of filtrate was collected and analyzed separately for DOC, Hg(II), and UVA.

For testing the tubes, test solutions (Table A 7) were stored for 24 h in centrifuge tubes. Afterwards the unfiltered solutions were analyzed for Hg(II), DOC and UVA.

Pipette tests (Fisherbrand® Finnpipetters® and digital Labsystems® finnpipettes) were performed by determination of the weight of definite pipetting volumes of UPW. The standard deviation was calculated between the specific volume which was set on the pipettes and the average weight of ten repeated pipetting steps.

For estimating contamination with Hg(II) during the experimental steps by the lab atmosphere, open test tubes filled with UPW were set at different places in the lab for a definite time of 2 and 4 hours. Afterwards prepared for Hg(II) by adding of BrCl and analyzed with CVAFS.

3.6.3 Kinetics

The dissolution kinetics of mercury from the soil material, i.e. the time necessary for reaching an equilibrium between solid and liquid phase, was determined in the absence and presence of 5 mg/L DOM F1-FA by leaching 0.5 g soil material from MCL131B (fluvent), CFW (lake sediment) and Starr tunnel (sluice sediment) in 100 mL ultrapure water. Setups for pH and ionic strength are according to the background leaching conditions given in Table 3. The kinetic leaching experiments were performed in duplicates with two additional blank replicates (i.e. no soil material was added). Sampling of the constantly shaken samples at room temperature (25 ± 2 °C) took place at 1, 2, 5, 8, 24 and 48 hours. Afterwards the samples were spun at 2800 rpm for 40 minutes (Beckman CPR centrifuge). Sediment was separated from liquid by filtration through a 0.45 µm filter (0.45 µm Acrodisc® filter with Supor® membrane) and then analyzed for mercury, DOC and UVA.

3.6.4 Matrix experiment, accuracy and precision of duplicates

Another control experiment was carried out to examine the accuracy and precision of duplicate samples, as well as to identify matrix interferences, following the procedure described in the EPA Method 1631, Section 9 (TELLIARD and GOMEZ-TAYLOR 2002). Two series of leaching solutions with and without added DOM were prepared as described in Table 3 for experiment no. 1 (series 1) and experiment no. 3 (series 2).

From each soil two separate leachings (1st and 2nd leaching sample) were performed. For each of them, two filtrates in duplicate (named as "sample" and "duplicate") (0.45 µm, each 10 mL) were diluted with BrCl for mercury analysis (description in section Mercury analysis). Two of the filtrates were spiked with a definite amount of a 100 µg/L Hg(II) stock solution to yield concentrations 30 to 200 % of their initial mercury concentration (see Table A 6). The mercury stock solution was prepared by dissolution of the NIST Standard Reference Material 3133 in BrCl. Both, spiked and non spiked samples were analyzed for Hg(II) with CVAFS.

To examine the accuracy and precision of the measurements, the relative percent difference (RPD) of the spiked samples was calculated by:

$$RPD = 200\frac{(|D1 - D2|)}{(D1 + D2)} \qquad \text{Equation 4}$$

where: D1 = Hg(II) concentration in spiked sample

D2 = Hg(II) concentration in duplicate spiked sample

(EPA Method 1631, TELLIARD and GOMEZ-TAYLOR (2002)).

The spike recovery (%R) was calculated after:

$$\%R = 100\frac{(A - B)}{T} \qquad \text{Equation 5}$$

with: A = measured sample concentration after spiking

B = measured sample concentration before spiking

T = calculated spike concentration

(EPA Method 1631, TELLIARD and GOMEZ-TAYLOR (2002)).

4. Results and Discussion

The complete experimental data, original instrument files, and calculated results can be found in the database on the CD attached to this thesis (see: Appendix D – Database and Appendix F – Instrument and data files). An overview over the experimental course of this Master thesis is presented in Appendix B – Table of performance; this includes a brief description of the work routine, notes on problems encountered, and a description of the experimental procedures.

4.1 Prepatory experiments: Equipment testing, kinetics and matrix effects

4.1.1 Equipment test – filters and centrifuge tubes

Initial experiments were performed to ensure that the experimental equipment was suitable for the experiments in the recent study. These control experiments were designed to investigate two difficulties often encountered in these types of experiments; first, the potential for mercury contamination from experimental equipment, and secondly, the potential for experimental equipment to cause the loss of mercury or DOM through processes such as sorption.

Soil leaching experiments were performed in 50 mL Corning centrifuge tubes (polypropylene with polyethylene plug seal caps). For the colloid experiment an additional spin was performed at 12,000 rpm, for that Nalgene® Oak Ridge 40 mL centrifuge tubes (polypropylene) were used. Prior to use, these tubes were investigated for mercury contamination and for the potential for Hg(II) and DOM sorption. For a variety of solutions, no significant levels of mercury were found to leach from the tubes (see Table A-13), particular in case of the Nalgene® tubes after the cleaning procedure (soak in UPW for 12 h and a final UPW rinse). Over a 24 hour period, with a test solution with Hg(II) and DOM, the sorption of mercury is less than 3 - 4 % and negligible for DOC (Table A 13). This indicates that the tubes were suitable for these experiments, and that no further cleaning was required.

During the course of leaching experiments it was found that it was necessary to filter the soil leaching solutions. As a result, it was necessary to test the filtration apparatus for interactions with either mercury or DOM. Two filter types were used, first were 0.45 µm Acrodisc® filters with Supor® membranes (25 and 35 mm diameter), and second were 0.02 µm Anotop® filters with Anopore® membrane. Both filters were single-use, syringe filters.

The mercury and DOC results for the stepwise testing of these filters are detailed shown in Table A 12. Figure 6 presents the Hg(II) results for testing with solutions spiked with Hg(II), DOM and HCl.

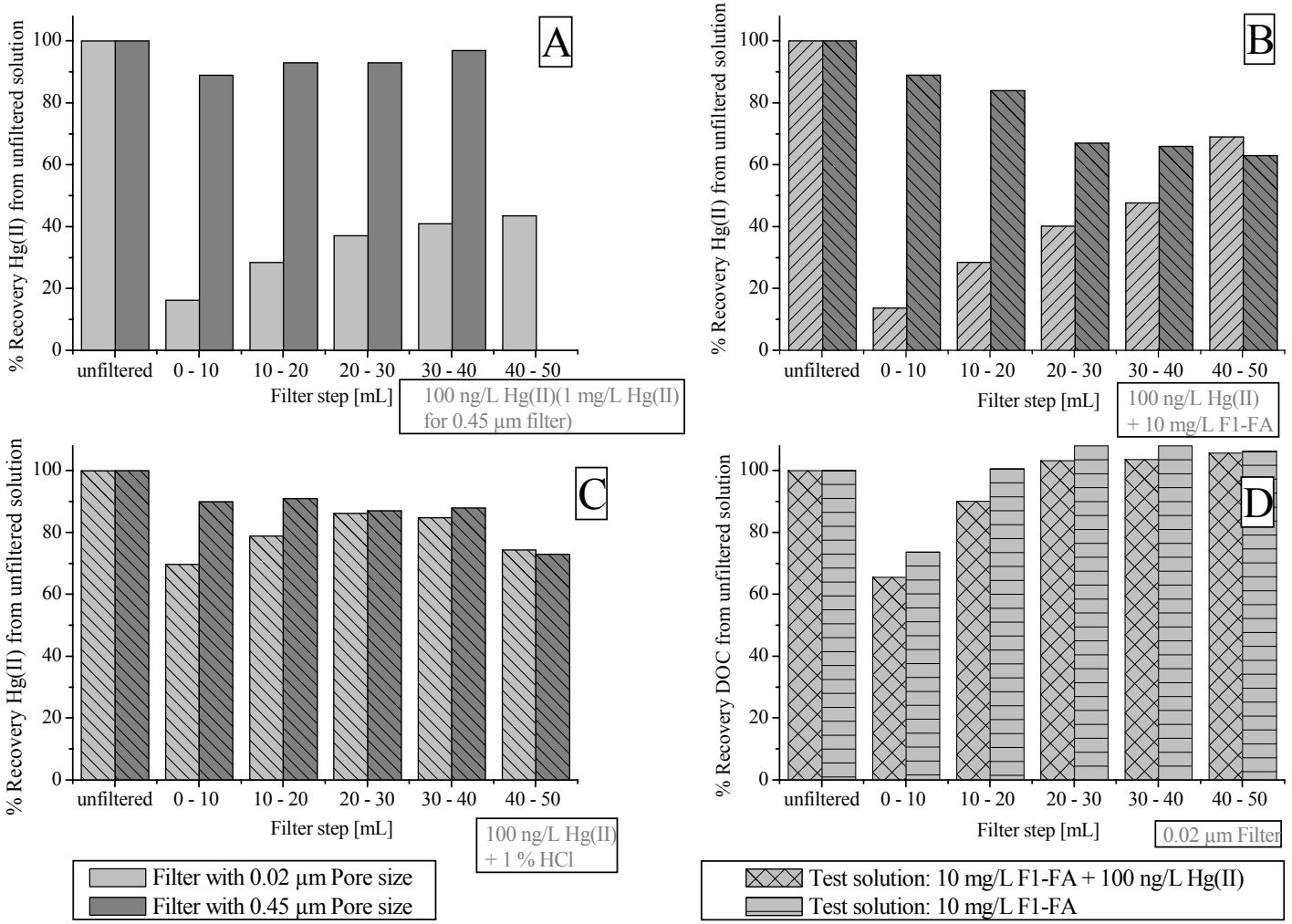


Figure 6. Hg(II) and DOC results for filter testing of filters with 0.45 µm (Acrodisc®) and 0.02 µm (Anotop®) pore size.

Results for Hg(II): A … test solution: 100 ng/L Hg(II) (1 mg/L Hg(II) for filter with 0.45 µm Pore size), B … test solution 100 ng/L Hg(II) and 10 mg/L F1-FA; C … test solution: 100 ng/L Hg(II) and 1 % HCl; Results for DOC: D … testing of filter with 0.02 µm Pore size with solutions containing 10 mg/L F1-FA and 100 ng/L Hg(II).

For the DOC containing test solution a loss of 26 % DOC (calculated as % of contents in the unfiltered solution) by the filter membrane was observed during the filter step 0 to 10 mL for the Anotop® filters (these steps were not performed for the Acrodisc® filters). The following filtrates (10 to 50 mL) showed a recovery of DOC between 96 % (Acrodisc®) and 90 -117 % for the Anotop® filters (Table 7 and Table A 12, Figure 6). These results indicate that regarding DOC both filters were suitable for the experiments.

Table 7. Mercury and DOC recovery from filter tests (filter steps 10 to 20 mL)

Test solution	Hg(II)	DOM + Hg(II)	HCl + Hg(II)	Mercaptoacetic acid + Hg(II)
Hg(II) recovery 0.45 µm filter	93 %	84 %	91 %	not measured
DOC recovery 0.45 µm Filter		96 %		
Hg(II) recovery 0.02 µm Filter	29 %	29 %	79 %	8 %
DOC recovery 0.02 µm filter		90 %		

For the Hg(II) containing test solutions both filters showed a loss of Hg(II) during the first filter stage in a range of 10 % for the 0.45 µm Acrodisc® filters and 92 % to 30 % for the Anotop® filters. This first loss has no influence for the experiments, because this solution will be used for pH-measurements and equilibration of the filter membrane. Whereas for the following filter step (10 to 20 mL) the recovery for the Acrodisc® filters is between 84 to 91 %, for the Anotop® filters the recovery does not exceed 75 % (range 8 % to 74 %), shown in Table A 12. Especially the test solution spiked with Hg(II) and DOM shows a low recovery for both filter types. Here possibly the competition of DOC and Hg(II) about binding sites on the filter membrane could be a reason.

Because of the standardized procedure of filtering the leaching solutions, the filtrate from the steps 10 mL to 20 mL was used for Hg(II) determination and from 20 mL to 30 mL for DOC analysis (results for filter tests summarized in Table 7). Because of the observed loss of Hg(II) of at least 30 % during the for mercury analysis important step, the Anotop® filters were not suitable for this experiments. The Acrodisc® filters were decided to use for filtration in the batch experiments, despite the calculated small loss.

From Figure 6 it can be estimated that the volume of 50 mL leaching solution is not enough to equilibrate the membrane, which leads to adsorption processes of mercury to the membrane in case of the Anotop® filter. The increasing Hg(II) for the 0.02 µm filter shows that probably if

using the double volume of solution passing the filter all sorption sites of the membrane are filled and Hg(II) can go through the membrane.

During the experimental course it was observed that for the sample MCL137 (tailing) the filtrate broke through the membrane, because of filter clocking with fine material and the resulting over-pressure. To avoid this, a second 0.45 µm Acrodisc® filter (Supor® membrane) with a diameter of 35 mm was used as pre-filter. Testing of this filter set shows similar results to the Acrodisc® filters with 25 mm diameter (Figure 7), whereas just filtering with the 35 mm diameter filter resulted in better recoveries. To get comparable results to earlier leaching experiments, which were done up to this date, the filter set with both filters (35 mm and 25 mm diameter) was used for following filtrations. In the matrix experiment an increase of Hg(II) with each filter step was observed due to break through of sample solution, despite using the filter set with the 35 mm pre-filter. This has no influence to other experiments, because in exception just for the matrix experiment the complete 40 mL of filtrate were used for Hg(II) analysis.

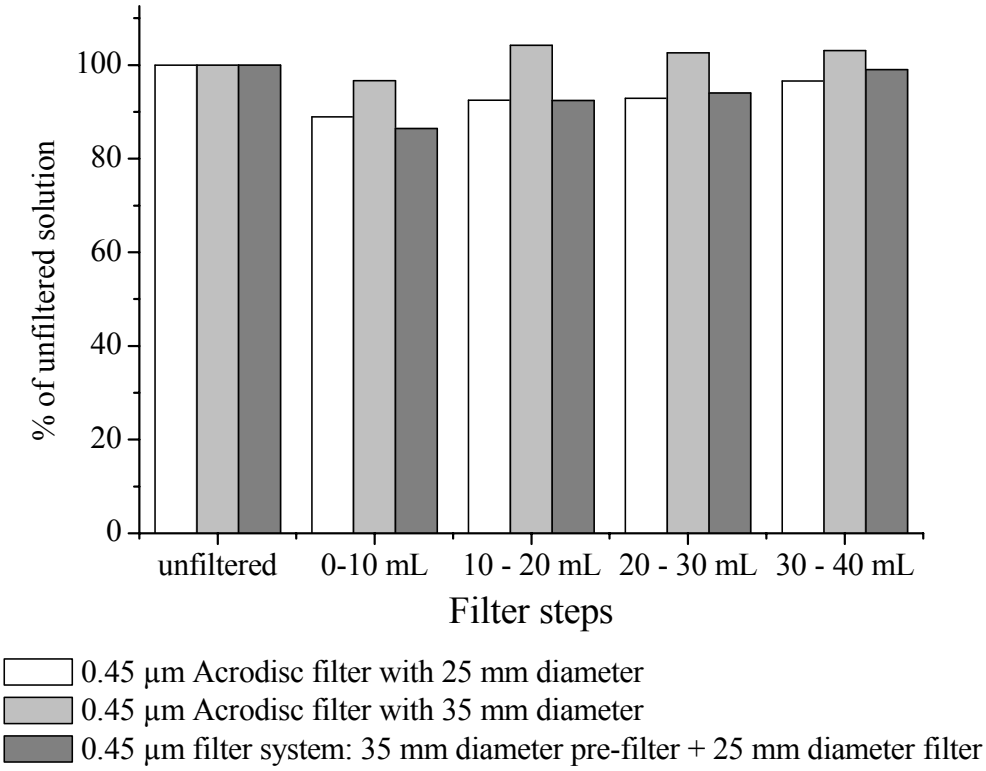


Figure 7. Comparison of mercury recovery from a test solution of 1 mg/L Hg(II) between 0.45 µm Acrodisc® filters with different diameters

Tests of pipettes were performed regularly; typical results are shown in Table A 17 and Table B 22. The recovery of definite pipetting volumes is between 0.5 to 1.5 % for the Fisherbrand® Finnpipetters® and 0.4 to 0.6 % for the digital Labsystems® finnpipettes.

Tests with test tubes allowing an exchange with the lab atmosphere proved that contamination by the lab atmosphere is below the MDL of 5 ng/L (< 0.3 ± 0.1 ng/L).

4.1.2 Kinetics

The optimum equilibrium time was determined experimentally. This was done by measuring Hg(II) release over a 48 h period. An equilibration time of 24 hours was estimated at a soil to liquid ratio of 5 mg soil : 1 mL solution (Figure 7). The first time point was collected at two hours, earlier time points were not feasible due to filtration constraints. These results are consistent with the reports of other researchers, who found an initial fast desorption of mercury during the first 100 minutes, followed by slower release over the next 8 hours (WANG et al. 1991; YIN et al. 1997b).

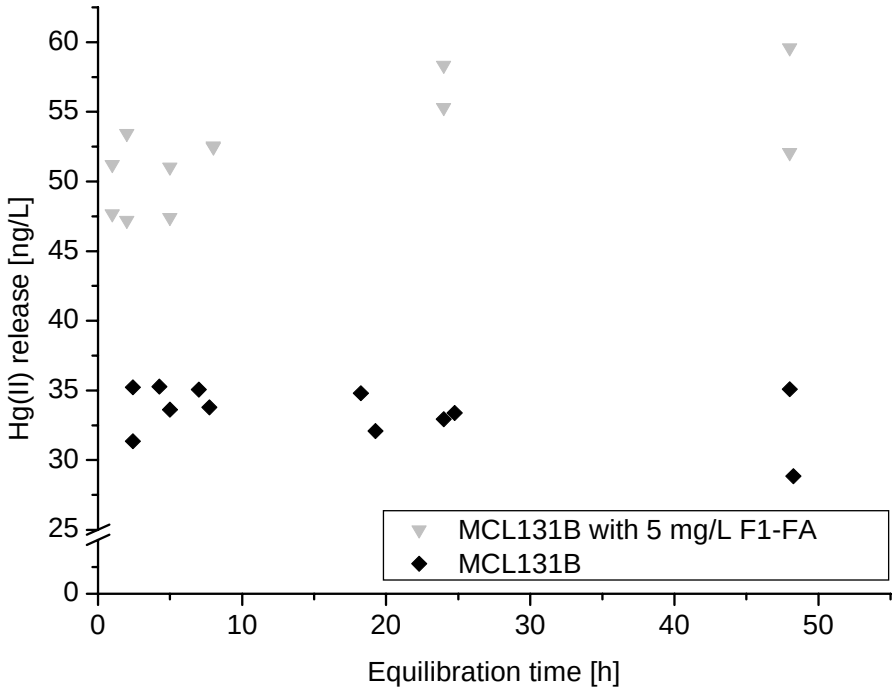


Figure 8. Desorption kinetics for MCL131B with and without 5 mg/L DOM

4.1.3 Matrix effects

To estimate effects of the solution matrix from the leachings on Hg(II) determination by CVAFS a matrix experiment was performed according to EPA Method 1631 (TELLIARD and GOMEZ-TAYLOR 2002). The results for the leaching with and without 10 mg/L F1-FA and Hg(II) concentrations after spiking (Table A 6) are shown in Table A 14 and Table A 15.

Accuracy and precision of Hg(II) measurements were determined by calculating RPD of duplicate spiked leaching samples. As shown in Table A 14 and Table A 15 the calculated RPD

was in all cases less than 24 %, the given quality control acceptance criteria in the EPA Method 1631.

For determining matrix effects the spike recovery was calculated (Table A 14 and Table A 15), which was for all samples, except sample MCL137 (tailing), between 92 % and 112 %. This is within the range (71 – 125 %) indicated as quality control criteria in the EPA Method 1631. In the case of the tailing (MCL137) break through of filtrate have lead to uncertain results. Comparison of the measured Hg(II) concentration of the spiked samples with the calculated mercury spike concentrations thus shows that the soil matrix has no significant influence on the Hg(II) determination.

4.2 Characterization of soil material – Particle size analysis, XRD, THg and TOC, and Sequential extraction

4.2.1 Particle size analysis

A basic experiment for soil related studies is to determine the particle size and to classify the soil texture by sieving and sedimentation. Depending on the particle size, the soil fractions can be assigned into different classes, which are shown in Table A 16 for both the US and German systems.

In this study, the soil was fractionated into different sizes as shown in Figure 3 by sieving through sieves with different mesh size. The percentages of soil material in the resulting mixed classes in comparison to standard classifications, due to the limitation of available sieve sizes, are shown in Table 8 and Figure 9.

Because the retained species from 710 µm to 250 µm sieves are a mixture of gravel and coarse to medium sands, they were summarized into one group "gravel and coarser sands" as shown in Figure 9. As Figure 9 shows, this is the dominant fraction in the tailing sample (MCL137) and the sluice sediment Starr tunnel (62 % and 78 %). This agrees with the observations of coarser material in these samples during soil input for the leaching experiments. The major class in the McLaughlin soils (MCL107A – serpentine soil, MCL134B1 – wetland, and MCL131B – fluvent, an expression for a floodplain soil) consists of fine and very fine sand in a range of 49 – 58 % (Figure 9). The wetland also contains a main fraction of very fine material < 74 µm (30 %), the dominant size of the soil material from CFW (57 %), the lake sediment.

The dominance of finer material in wetland and lake sediments is the result of settling of widely distributed finer material due to reduced flow velocity. This agrees with the fluvent data in respect that coarser material (sand), which is carried by the river, is deposited due to the reduced stream velocity at the floodplain.

Table 8. Results for particle size analysis

Net weight … difference between tare weight of the sieve and weight inclusive sieved sample material; % of each size fraction … mass-percent of each fraction referring to the total of the net weights for the soils; method error … RPD calculated between soil input for sieving and total of the net weights for each soil; explanations for separate classes in column two according to Table A 16: no. I - gravel and coarse sand, no. II - coarse and medium sand, no. III - medium sand, no. IV - fine sand, no. V - fine sand and very fine sand, no. VI - very fine sand, silt and clay)

			MCL107A		MCL134B1		MCL137		MCL131B		CFW		Starr	
Mesh wide [µm]	**No.**	**Size fraction [µm]**	**Net weight [g]**	**% of size fraction**	**Net weight [g]**	**% of size fraction**	**Net weight [g]**	**% of size fraction**	**Net weight [g]**	**% of size fraction**	**Net weight [g]**	**% of size fraction**	**Net weight [g]**	**% of size fraction**
710	I	> 710	0.10	1.0	0.10	0.5	0.50	36.9	0.90	4.4	0.10	2.0	2.30	11.5
355	II	710 - 355	1.50	15.2	1.00	5.0	2.50	16.8	1.90	9.3	0.50	10.1	10.70	53.4
250	III	250 - 355	1.30	13.1	1.90	9.6	1.20	8.1	2.30	11.3	0.30	6.1	2.70	13.5
125	IV	74 - 125	2.82	28.5	8.66	43.7	2.32	15.6	9.07	44.6	0.64	12.9	2.41	12.0
74	V	< 74	2.01	20.3	2.16	10.9	1.22	8.2	2.80	13.8	0.60	12.2	0.87	4.3
< 74	VI		2.16	21.8	5.99	30.3	2.16	14.5	3.37	16.6	2.81	56.7	1.08	5.4
Total weight [g]			9.89		19.81		9.90		20.35		4.95		20.05	
Soil input [g]			10.00		20.00		10.01		20.00		5.00		20.00	
Method error [%]			1.1		0.9		1.1		1.7		1.1		0.3	

In terms of particle size, the three non-tailing McLaughlin soils are similar. The tailing material from MCL137 consists mostly of raw rock and is dissimilar to the three other McLaughlin soils. As in the case of MCL137, soil formation starts as a thin layer of soil material dominated by coarser grain size is built over the rocky material, which indicates the beginning of the weathering processes. The coarser material from Starr tunnel is the result of out washing of finer material by the water flow in the sluice tunnel.

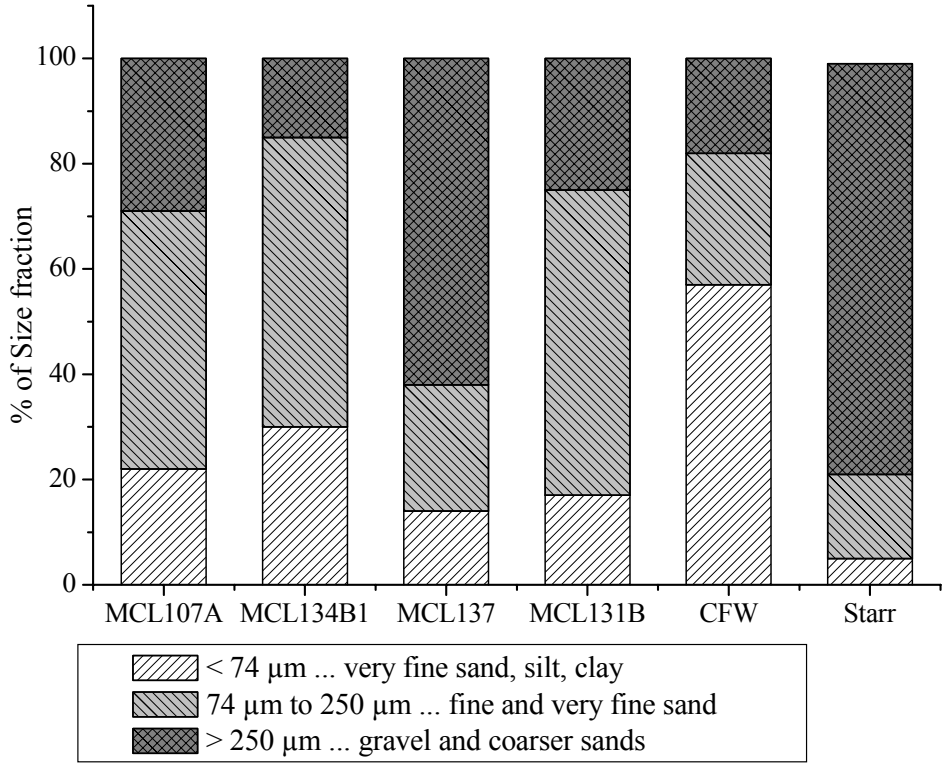


Figure 9. Particle size fractionation and classification modified by the separate classes of the USDA and the common mineralochemical used system.

The soil size distribution of the separated samples used in the leaching experiments (fraction < 710 µm) corresponds roughly to that of the un-separated bulk material (see Figure C 2), because the content of material > 710 µm is less than 4.4 % (Table 8), except for the Starr tunnel (11.5 %). Because of the dominance of particles in the size between 355 to 710 µm also for Starr the distributions of the un-separated and the material < 710 µm are comparable.

JoAnn Holloway (see Table 1) determined loam (a mixture of silt, clay and sand) as soil type for all McLaughlin soils, gravelly silt loam for MCL107A and MCL137 and sandy loam for MCL131B and MCL134B1 (sandy silt loam). This agrees roughly with the particle size analysis in this study, where soil material within all three soil classes, clay, silt and sand, was found as well as the coarser material for the tailing.

The general problem with the particle size analysis in this study was the lack of a standardized method for soil texture analysis (e.g. as described by JACKSON (1956)). Inadequate grounding and soil aggregates of particles with SOM or calcite could lead to further underestimation of the finer material, especially in strong weathered soils like the tailing. Standardized methods indent dispersion procedures after sieving with a mesh size of 2 mm, where soil aggregates of clays, oxides and SOM can be destroyed.

As a final statement regarding the soil size fractions, the results indicate that all soils, with the exception of CFW, are dominated by sandy material, with < 30 % silt and clay content. The CFW sample contains a greater percentage (57 %) of finer material (clay, silt and fine sand), 41 % sands and a minor content of coarser sands and gravel.

4.2.2 Mineral characterization by XRD

The mineralogy of the soils determined by XRD is shown in Table 9, indicating clay contents over 10 wt % for all samples. In particular, the wetland and lake sediments (CFW and MCL134B1) and the fluvent (MCL131B) have high clay contents (nearly 30 %), because clay minerals can be mobilized from soils by erosion and then be widely distributed by streams. When stream velocity decreases, as given in lakes, river banks and in wetlands, these clay minerals deposit. Also the tailing (MCL137) contains clay concentrations of about 36 wt %. Here, the clays are indicators for ongoing weathering processes were secondary minerals such as clays are formed, e.g. from feldspar and mica. Through the mining process, the surfaces of the minerals were uncovered, making the weathering processes easier.

The dominant minerals in the samples are bold marked in Table 9. Samples originating from the McLaughlin Reserve are dominated by serpentine, followed by clay minerals (ferruginous smectite, illite) and quartz, which is consistent with the geology of McLaughlin Reserve (ENDERLIN 2002). These loamy, clay-rich soils are mapped as the Henneke soil series (ENDERLIN 2002). Also, colluvials have a serpentinic character (Climara clays, Todos loams). The occurrence of other minerals can be explained by weathering of rocks from the Great Valley Sequence (with sandstone, shale, and greywacke) (ENDERLIN 2002).

The CFW (lake sediment) and Starr (sluice sediment) samples are dominated by quartz, which is a hard mineral and stable towards weathering. Furthermore the Starr tunnel sample contains feldspar minerals and just a few percent of secondary minerals, such as clays and chlorides. Because it is a sluice, the finer material (clay minerals) has been washed out, whereas the heavier material such as quartz and cinnabar remained. Cinnabar was not detected by XRD, because it occurred in trace concentrations below the XRD MDL (< 1 wt %).

Table 9. XRD results for mineralogy and silica content from ICP-AES analysis

The dominant mineral species are bold marked in the table.

Mineral classes	MCL107A	MCL134B1	MCL137	MCL131B	CFW	Starr
tectosilicates (feldspar) [wt%]	0.5	14.6	6.2	16.1	12.5	14.8
dominant feldspar species [wt%]		andesite 6.5	albite 4.5	albite 6.3, anorthoclase 3.1, andesite 5.6	albite 6.8, andesite 4.3	**microline 12.2**
carbonates [wt%]	0.4	1.6	1.1	1.3	1	0.2
dominant carbonate species	siderite	calcite, dolomite, siderite	calcite, dolomite, siderite	calcite, dolomite, siderite	calcite, dolomite, siderite	dolomite, siderite
silica oxides (quartz) [wt%]	0.6	**18.7**	**11.8**	**18.1**	**21.4**	**72.8**
neosilicates - (forsterite) [wt%]	0.3	0.2	0.6	0.7	0.2	0.1
inosilicates (amphibole, pyroxene) [wt%]	0	1.4	0.6	0.5	4	1.4
fe-oxides [wt%]	6.6	1	8.9	2.5	1.9	1.4
dominant oxide species	magnetite, maghemite	magnetite maghemite	maghemite	magnetite, maghemite	magnetite, maghemite	magnetite, maghemite
al-hydroxide (gibbsite) [wt%]	0	0.8	0.9	1.1	1.7	1.6
hydrosulfates (jarrosite) [wt%]	0	0	3.5	0	0	0
phyllosilicates -non clays [wt%]	74.5	31.9	31.5	35.8	16.1	4.4
dominant phyllosilica species [wt%]	**serpentine 70.4**, chlorites 4.1	**serpentine 19.8**, chlorites 12.1	**serpentine 15.5**, mg-chlorite 11.1	**serpentine 22.4**, mg-chlorites 12.7	**chlorites 13.2**	mg-chlorite 3.8
phyllosilicates – clays [wt%]	10.5	28.7	36	25.4	29	12
dominant clay species [wt%]	**ferruginous smectite (fe-smectite) 7.5**	**illite 19.1**, fe-smectite 8.1	**fe-smectite 29.9**, illite 4.1	**illite 15.2**, fe-smectite 9.8,	**illite 10.9**, halloysite 6.5, fe-smectite 6, kaolinite 4.1	illite 4.6, fe-smectite 4.1
organic material [wt%]	0	11.5	4.7	9.2	25.1	6.3
silica [mg/L]	6.0	4.9	9.0	3.9	4.3	1.8

The high occurrence of the Fe(III)-bearing smectite in the tailing MCL137 (29.9 wt %) causes problems regarding UVA measurements, because iron absorbs radiation at 254 nm (WEISHAAR et al. 2003). Concentrations higher than 0.5 mg/L can be critical for UVA measurements (WEISHAAR et al. 2003). For the background leaching of MCL137 the measured iron concentration is 0.69 mg/L (RSD between replicates 2 %). In the other experiments the iron content for the tailing varied between 0.05 mg/L (RSD 4 %) for experiment with pH 3 (DOC 0.9 ppm, UVA 0.04 cm^{-1}, SUVA 4.2 $L*mgC^{-1}*m^{-1}$, results based on blank corrected values) to 6.7 mg/L (RSD < 0.5 %) for the first experiment with chloride and calcium addition (see Performance Table B 16) (DOC 1.2 ppm, UVA 0.62 cm^{-1} and SUVA 53.5 $L*mgC^{-1}*m^{-1}$). For the other samples the average of iron in all experiments ranges from 0.06 mg/L (RSD 9%) (MCL107A, MCL131B, MCL134B1, and Starr) to 0.19 mg/L for CFW with a high variability in released iron depending on the experiment, which is between 0.03 mg/L (Sacramento River water leaching) and 1.48 mg/L (pH 12) (Appendix D – Database). The results for UVA for the tailing (MCL137) show clearly, how effective iron is in absorbing UV and thus influencing the calculation of SUVA. That a significant portion of the ferruginous smectite dissolves during the background leaching experiments is also confirmed by the positive correlation of smectite and dissolved silica (Table 9) determined by ICP-AES analysis ($R^2 = 0.76$, Pearson product moment correlation, significance level 95 % ($\alpha = 0.05$)).

As usual, amorphous organic material detected by XRD correlates significantly (significance level $\alpha = 0.05$) with the TOC ($R^2 = 0.82$) and DOC ($R^2 = 0.87$) contents measured in the background leaching experiments (Pearson product moment correlation).

There was no correlation between clay content and total phyllosilicate content with the size fraction < 74 µm in these minerals (no significance according to the Person product moment and Spearman rank correlation). Clay, calcite and organic matter can stick soil particles together and form coarser aggregates (SCHEFFER et al. 1998). Because aggregate destroying steps were not performed during the particle size analysis, this could lead to an insignificant correlation between XRD results and particle size analysis.

4.2.3 TOC and THg

The results for total organic carbon, ranging from 0.4 % to 5.4 %, and total mercury, in a range of 1 µg/g to 36 µm/g, are shown in Figure 10. As expected, the wetland sediment MCL134B1 and the lake sediment from CFW contain the highest TOC concentrations as well as the highest concentrations of DOC measured in the background leaching experiments (Table 10). This is because of the high bioactivity in these environments.

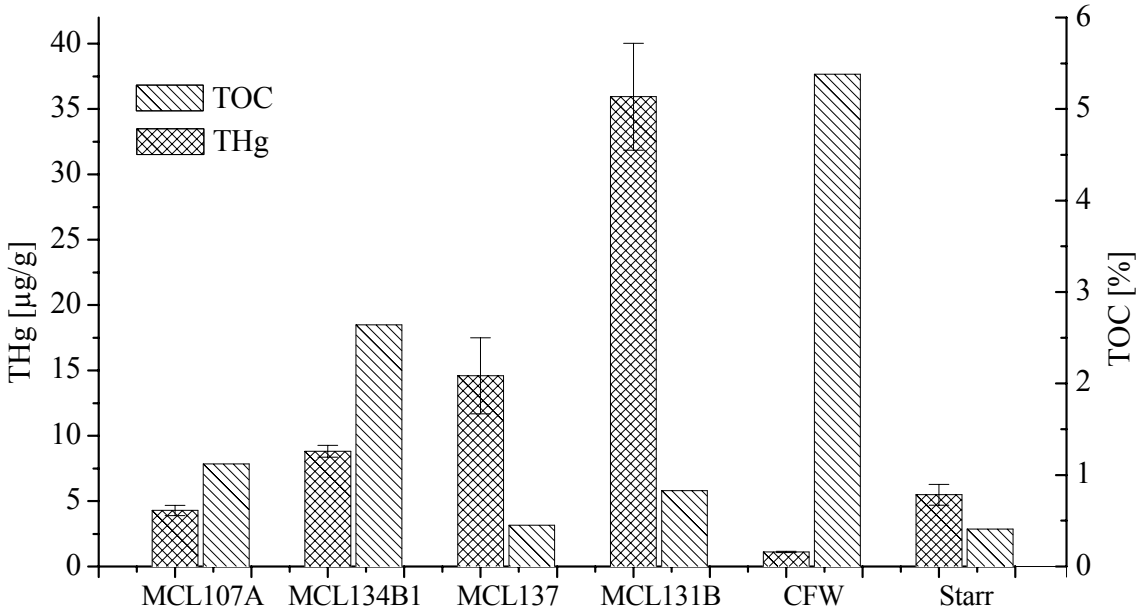


Figure 10. Total mercury content (THg) and total organic carbon (TOC)

As shown in Figure 10, the fluvent (MCL131B) and the tailing (MCL137) have the highest total mercury (THg) contents. There is no significant correlation between THg and mercury release from the background leaching experiments, nor is there a correlation between THg and the content of oxides, clay minerals, serpentine, and TOC or DOC. The results indicate that the major part of mercury in these soils is not associated with clays, humic substances or oxides, but occurs possibly as cinnabar. This agrees with other papers, from which it is known that eroded material from tailings is mainly cinnabar (WIENER et al. 2003a) and that cinnabar is an important mercury form in soils and sediments (MORITA et al. 1998; WIENER et al. 2003a).

Table 10. Background leaching results for (Hg(II), DOC, UVA and SUVA
Results for the soil samples are corrected by subtracting the blank values (line 1) for Hg(II), DOC, and UVA. SUVA was calculated from the blank corrected values.

Sample ID	Hg(II) [ng/L]		SD	n	DOC [ppm]		SD	UVA [cm^{-1}]		SD	SUVA [$LmgC^{-1}m^{-1}$]	n
Blank	6.0	±	1.4	8	0.3	±	0.1	0.01	±	0.00	3.46	8
MCL 107A	13.0	±	4.1	10	1.3	±	0.1	0.04	±	0.01	3.46	8
MCL 134B1	30.0	±	8.0	10	2.5	±	0.1	0.08	±	0.01	3.32	8
MCL 137	18.5	±	6.7	6	1.3	±	0.1	0.06	±	0.01	4.95	6
MCL 131B	45.4	±	12.9	10	1.8	±	0.1	0.06	±	0.01	3.59	8
CFW	8.8	±	1.8	10	9.8	±	0.4	0.38	±	0.02	3.84	8
Starr	349.7	±	90.5	10	1.4	±	0.2	0.05	±	0.01	3.75	8

4.2.4 Sequential extraction

Sequential extraction experiments (Table 11, Figure 11) to determine mercury speciation supports the predominance of mercury as Hg sulfides in the samples, because the majority of mercury (76 % to 97 %) was detected in the aqua regia extract (fraction 5), except in the fluvent (MCL131B), where a majority of mercury (85 %) is extracted in fraction 3. Fraction 5 is generally assumed to contain the sulfide fraction (Table 4). Additionally, this fraction can contain traces of oxides and hydroxides, however XRD analyses showed that oxide contents generally are low (Table 9).

Table 11. Sequential extraction data and contents of THg, TOC and amorphous organic matter detected by XRD
(F1 – water soluble mercury ($HgCl_2$), F2 – "stomach acid" soluble (HgO, $HgSO_4$), F3 – organic complexes, F4 – strong complexed (bound to oxides) and elemental mercury, and F5 mercury sulfides)

Sequential Extraction Fractions, THg, TOC	MCL107A	MCL134B1	MCL137	MCL131B	CFW	Starr
F1 [Hg wt%]	0.2 ± 0.0	0.3±0.0	0.9±0.1	0.3±0.0	2.9±0.6	0.1±0.1
F2 [Hg wt%]	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.1±0.1	0.0±0.0
F3 [Hg wt%]	1.1±0.0	0.2±0.0	4.8±0.8	84.6±0.1	8.1±0.1	3.2±1.9
F4 [Hg wt%]	2.2±0.2	3.3±0.4	3.0 ±0.6	4.2±0.3	13.0±1.9	1.0±0.8
F5 [Hg wt%]	96.5±0.1	96.2±0.4	91.2±0.3	10.8±0.2	75.9±2.6	95.7±2.7
THg [µg/g]	4.3±0.4	8.8±0.5	14.6±2.9	36.0±4.1	1.1±0.0	5.5±0.8
Hg(II)from background leaching [% THg]	1.2	1.4	0.5	0.5	3.2	25.5
TOC [%]	1.1	2.6	0.4	0.8	5.4	0.4
Amorphous organic matter detected by XRD [wt%]	0	11.5	4.7	9.2	25.1	6.3

Nearly no mercury seems to occur as HgO and $HgSO_4$ (fraction 2). Low sulfate concentrations determined by IC (< 0.03 mg/L (serpentine soil MCL107A, RSD between replicates 8 %) to 1.46 mg/L (wetland sediment MCL134B1, RSD 6 %)) confirm that sulfate is not a major species in these soils. It was not expected that the major mercury source in MCL131B would be organic

complexes (fraction 3 extractable with KOH, see Table 4). The fluvent contains eroded material from which it is known that mercury exists mostly as cinnabar (WIENER et al. 2003a). On the other hand, the fluvent has a high TOC content and it would not be unusual for the dissolved mercury in the river to sorb to the organic matter in the fluvent. Also DOM-Hg complexes could have settled down in this area, explaining the mercury dominance in fraction 3.

CFW also contains organic bound mercury (8.1 %) and mercury bound to oxides or of elemental nature (13.0 %), possibly resulting from settling of these complexes and minerals.

In earlier studies a correlation between mercury in fraction 3 and methylation potential was found (BLOOM et al. 2003), according to which the fluvent (MCL131B) is the most critical site in respect for methylation.

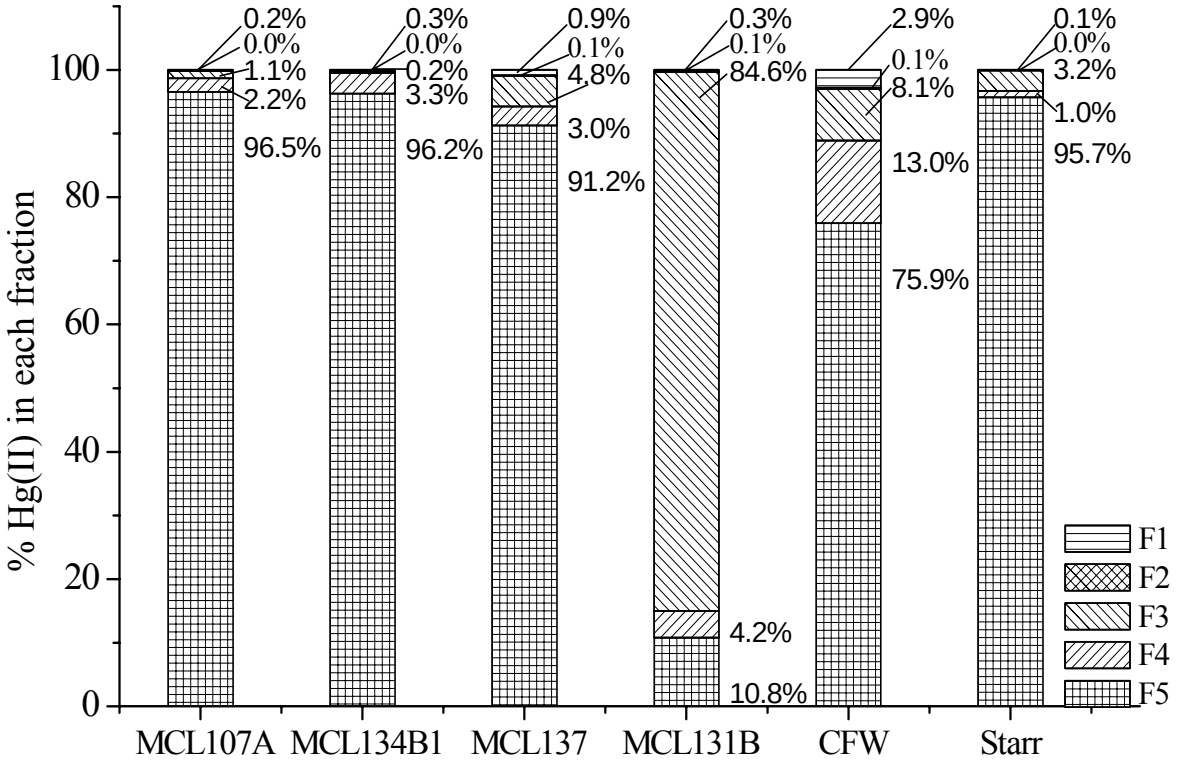


Figure 11. Results for mercury speciation by sequential extraction
(F1 – water soluble mercury ($HgCl_2$), F2 – "stomach acid" soluble (HgO, $HgSO_4$), F3 – organic complexes, F4 – strong complexed (bound to oxides) and elemental mercury, and F5 mercury sulfides)

Because of the high volatility of elemental mercury, a loss during the performance of the extraction procedures can not be excluded. However, for contaminated soil and sediment material, as well as for tailings, the loss is expected to be small with respect to the total mercury content of these samples.

In looking at the percentage of the THg released in the background leaching experiments (Table 11), however, it is evident that only a small amount of the THg was dissolved: Starr (25.5 %), CFW (3.2 %), and MCL134 (1.4 %). Just 0.5 % of THg was leached for MCL137 and MCL131B, where the latter stands in disagreement with the results observed in the sequential extraction.

These results, which show only a small fraction of the THg gets released during the background leaching experiments, confirm that a majority of mercury is not in an easily dissolvable form, but probably exists as the relatively insoluble cinnabar (PEAKALL and LOVETT 1972).

The results in the present study, excluding the fluvent MCL131B, are in agreement with the general supposition that the majority of mercury in soils and sediments occurs as cinnabar (PEAKALL and LOVETT 1972; WIENER et al. 2003a).

4.3 Background leaching in comparison to leaching with Sacramento River water

The background leaching values for Hg(II), DOC, UVA and SUVA under basic conditions with pH 6.4 ± 0.06 and I = 0.1 M, are shown in Table 10. For the mercury content, an average from the results of five separate background leaching experiments (n = 10, including duplicates) was calculated (Table 10). Inhomogeneity of sample material and the low soil to liquid ratio lead to an average RSD of 28 %. The mean results provide a basic mercury release value (comprising the water soluble fraction) that can be used as a standard for comparison when analyzing the results from other experiments (e.g. in assessing whether adding more DOM causes increases or decreases in mercury release). Average data for DOC and UVA (mean RSD's = 5 % and 12 %) are based on a calculation from four experiments (n = 8, Table 10).

Under the given experimental conditions (Table 3, no. 1) Hg(II) ranging from 8.8 ± 1.8 (CFW) to 350.0 ± 90.5 ng/L (Starr tunnel) can be removed from the soil samples (Table 10, Figure 12). In comparison to the total mercury content, this dissolved mercury presents only a small fraction (Table 11). Nevertheless, it is environmentally important regarding methylation and transport processes. The percentages of dissolved mercury reach from 0.5 % THg for the highest contaminated sites (tailing MCL137 and fluvent MCL131B) to 3.2 % (lake sediment CFW) to 25.5 % for Starr tunnel. This indicates that there is a high percentage of water soluble mercury in

Starr tunnel (which is in contrast to the observed mercury speciation measured by sequential extraction), whereas in the other samples just a small amount is easily dissolvable.

According to WILKEN (1992) the majority of water soluble mercury is bound to SOM. This, combined with the results of the sequential extraction experiments for MCL131B (in which most of the mercury was assumed to be bound to SOM), leads to the assumption that the background leaching provides a majority of the mercury dissolved in the leaching experiments for MCL131B.

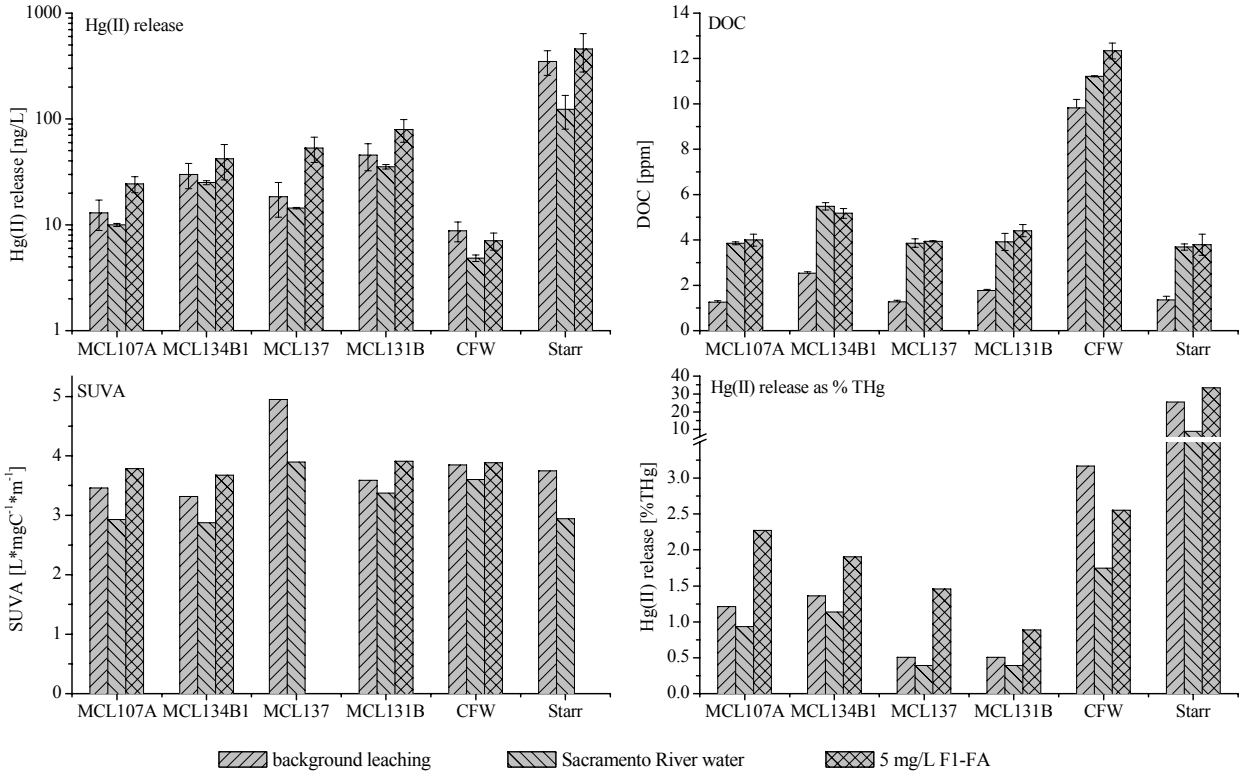


Figure 12. Comparison of Hg(II) release, DOC and SUVA after leaching with ultrapure water, Sacramento River water, and ultrapure water with additional DOM (5 mg/L).
The error bars represent the SD for duplicate samples. All Hg(II) values are corrected for experiment blanks. The results for DOC and UVA were corrected for the average blank value from the background leaching (despite the results from the Sacramento River water experiment, because no UPW was used in the experimental set up), as well the SUVA calculated from these corrected values.

Excluding the results from Starr tunnel, there is a significant correlation between the total mercury content and the released mercury ($R^2 = 0.81$). Possible explanations for the contrasting results with Starr tunnel are that the values for THg and Hg(II) release could be underestimated by volatilization of mercury if the sample contained a significant amount of Hg(0) or due to inhomogeneity of the sample material during leaching. Alternatively, if the majority of the

Hg(II) in the Starr tunnel sample occurs as HgS, a relatively insoluble mineral, no correlation is expected between Hg(II) release and THg.
A significant rank correlation between any of the particle size fractions with the Hg(II) release from the background leaching could not be observed (Figure C 3). Thus the water soluble Hg(II) can not be assigned to a mineral or particle size fraction.

Figure 12 shows Hg(II) and DOC contents, as well as SUVA values for the background leaching experiments, leaching experiments with Sacramento River water, and leaching experiments with 5 mg/L F1-FA (which represents typical DOM levels of the Sacramento River water). The background results for Hg(II), DOC and SUVA for the solution with 5 mg/L F1-FA and for Sacramento River are shown in Table 12, determined by the duplicate experiment blanks.

Table 12. Blank values for Hg(II), DOC, and SUVA for Sacramento River water and a solution of 5 mg/L F1-FA
blank values … average experiment blanks in Sacramento River water experiment and leaching with 5 mg/L F1-FA, without soil input

Solution	Hg(II) [ng/L]	DOC [ppm]	SUVA [$LmgC^{-1}m^{-1}$]
Sacramento River water	5.9 ± 0.4	2.8 ± 0.1	2.8
5 mg/L F1-FA	8.7 ± 0.5	3.0 ± 0.3	3.8

The results for SUVA from Sacramento River in Table 12, calculated from the blanks, equal the measurements performed on the whole water sample of Sacramento River by Kenna Butler, the measured DOC concentration from the leaching results (2.8 ppm) is slightly lower (3.3 ppm to 3.4 ppm).
The composition of the DOC in Sacramento River water is dominated by the hydrophobic acid fraction (as shown in Figure 13), which comprises the fulvic acid as major component (AIKEN et al. 1992).

Statistical tests (Wilcoxon signed rank test, because samples are not normal distributed according to Shapiro-Wilk) with a p-value of 0.04 indicated differences between the mercury release from background leaching and river water leaching, and to the leaching with 5 mg/L DOM. Although the DOC concentrations from the Sacramento River water and the F1-FA (DOM 5 mg/L) are not significantly different (p-value = 0.2), the DOM addition causes a higher mercury release (see Figure 12). This can be explained by the higher reactivity of the added DOM isolate relative to

the river water sample, due to increasing the amount of reactive hydrophobic acid, as determined by SUVA (WEISHAAR et al. 2003). Results of SUVA analyses are shown in Table 12 and Figure 12. In contrast to the added fulvic acid, the Sacramento River water contained just 41 % of this reactive HPoA form, which is the important fraction in the dissolution of Hg(II).

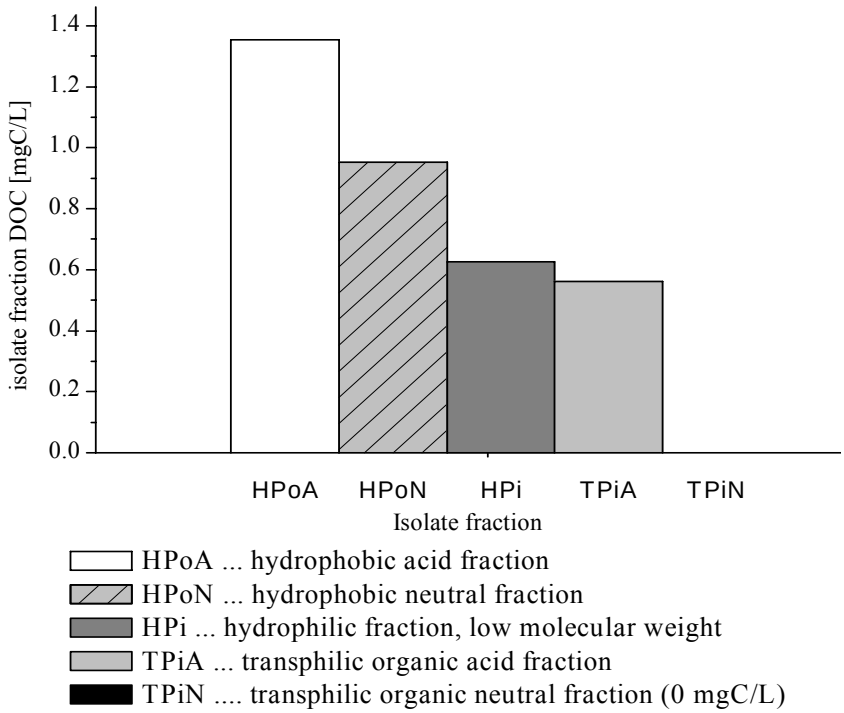


Figure 13. Fractionation of DOC from Sacramento River water
Measurements and fractionation (XAD-4/XAD-8 isolation method according to AIKEN et al (1992), Figure C 1) performed by Kenna Butler (02/2006). The isolate fraction DOC is calculated by multiplication of the percentage of each fraction with the DOC measured for the whole water sample of Sacramento River.

For the samples, excluding MCL137, the measured SUVA values fall within a tight range of about 3 to 4 $L*mgC^{-1}*m^{-1}$ (Figure 12). Because the SUVA values did not vary much, even small amounts of iron in the samples could skew the analysis.

The variability between Sacramento River water leaching and the average for the background leaching can be due to variations between the five background leachings. If including the 28 % of RSD for the average Hg(II) release, the leachable amount of Hg(II) with Sacramento River water falls into the range of the background leaching.

Most of the water soluble mercury is supposed to be complexed with soil organic matter (SOM) in colloidal form (WILKEN 1992). Also BLOOM et al. (2003) suggested that mercury mobilized

by DI water could include some colloidal mercury, possibly as colloidal organic mercury complexes.

For all three experiments (background and river water leaching, and leaching with 5 mg/L F1-FA), no significant correlation between SUVA and DOC with Hg(II) release could be observed. This was also true even if the tailing MCL137 (because of strong iron influence at UVA and SUVA) and the Starr tunnel (because of its high results variability) samples were excluded from the analyses.

Thus, the leachable soil organic matter and the DOC from the river water seem to play minor role in increasing the mercury dissolution under the given conditions, although the leached amount is not negligible for environmental health.

Implications for the environment are that if the soil particles come in contact with water from the Sacramento River, e.g. during erosion, water soluble mercury can be mobilized. Changes in dissolved organic carbon content, more so in terms of the quality and reactivity (i.e. aromaticity) than in concentration, can causes changes in the amount of mercury leached from these soils. This can happen, e.g. when the particles enter the wetlands in the delta. Given the right set of conditions for sulfate reduction, methylation of Hg(II) can be facilitated.

4.4 Origin of organic matter and leaching without buffers

To determine the origin of organic matter the fluorescence indices (FI) were determined from several leachings as exemplary shown in Table 13.

Table 13. Fluorescence indices for background leaching, leaching with Sacramento River water and 10 mg/L F1-FA

	Background leaching	Leaching with Sacramento River water	Leaching with 10 mg/L F1-FA
Sample ID	**FI**	**FI**	**FI**
Blank	1.3	1.4	1.3
MCL107A	1.0	1.2	1.2
MCL134B1	1.1	1.3	1.2
MCL137	1.2	1.2	1.2
MCL131B	1.1	1.2	1.2
CFW	1.1	1.2	1.2
Starr	1.1	1.3	1.2

The average FI for these three experiments is 1.2 ± 0.1 (n = 21), which indicates that the DOC is composed of terrestrially-derived fulvic acids, which have a FI around 1.4 (which is also true for all other experiments for which FI was calculated, see Appendix D – Database, with the average FI of 1.2 ± 0.1 for n = 49), whereas typical microbial-derived fulvic acids have a FI of about 1.9 (MCKNIGHT et al. 2001).

To determine major anions that dissolve during the leaching process, another background leaching experiment was performed without the addition of buffers. The Hg(II) concentration did not vary significantly from leaching experiments that contained buffer. Anion concentrations generally are low (shown in Table A 18), ranging from 0.05 mg/L (Starr) to 0.10 mg/L (MCL107A) for chloride, 0.04 mg/L (MCL134B1) to 0.37 mg/L (Starr) for nitrate, and < 0.03 mg/L (MCL107A) to 1.45 mg/L (MCL134B1) for sulfate. Sulfate also has higher concentrations in CFW (1.18 mg/L) and Starr (0.57 mg/L).
The expansion of the experimental setup to include an additional 10 mg/L DOM in the leaching solution did not show any significant influence of DOM on the release of chloride and sulfate. However, the results did show significantly lower values for nitrate, indicating adsorption by organic matter material from the soil matrix.

There was no significant correlation detected between Hg(II) release and the major anions for Spearman rank correlations.

4.5 Effect of pH-value and ionic strength

As expected, varying pH and ionic strength had an effect on the dissolution of Hg(II) from the soil samples (Figure 14, Figure 15). A significant increase of Hg(II) release was observed towards more alkaline conditions, as shown in Figure 14. Other studies have similarly reported significant desorption of Hg(II) above pH 5 (HAITZER et al. 2003; YIN et al. 1996). This contradicts the general assumption that with decreasing pH the competition of protons with cations for binding sites on clay minerals leads to an increase in Hg(II) release. However, increasing pH leads to the dissolution of soil organic matter (SOM) causing an increase in DOC in the leaching solution (Figure 14). Increasing values in UVA and SUVA analyses further indicate increased leaching of SOM at high pH-values. Because of the strong complexation of Hg(II) by DOM (HAITZER et al. 2002), releasing more SOM into the leaching solution also results in more Hg(II) being released. The Hg(II) complexation itself is also favorable at higher pH-values since at lower pH proton competition inhibits the mercury complexation; however this probably plays a minor role (YIN et al. 1997a). In the present study, Hg(II) release continuously

increased towards more alkaline conditions, with the release at pH 12 still being significantly higher than at pH 8. This is in contrast to previous studies (HAMILTON et al. 1995) where competition of Hg(II) complexes and hydroxide ions for sorption sites was found to yield decreasing Hg(II) sorption on illite with increasing pH.

All in all, significant positive correlation of Hg(II) release and UVA with pH could be determined for all samples except MCL137 and Starr tunnel, as well as for Hg(II) release versus SUVA. The DOC content correlated significantly in all cases with the pH-value (the correlation coefficients ranged from 0.79 to 0.96).

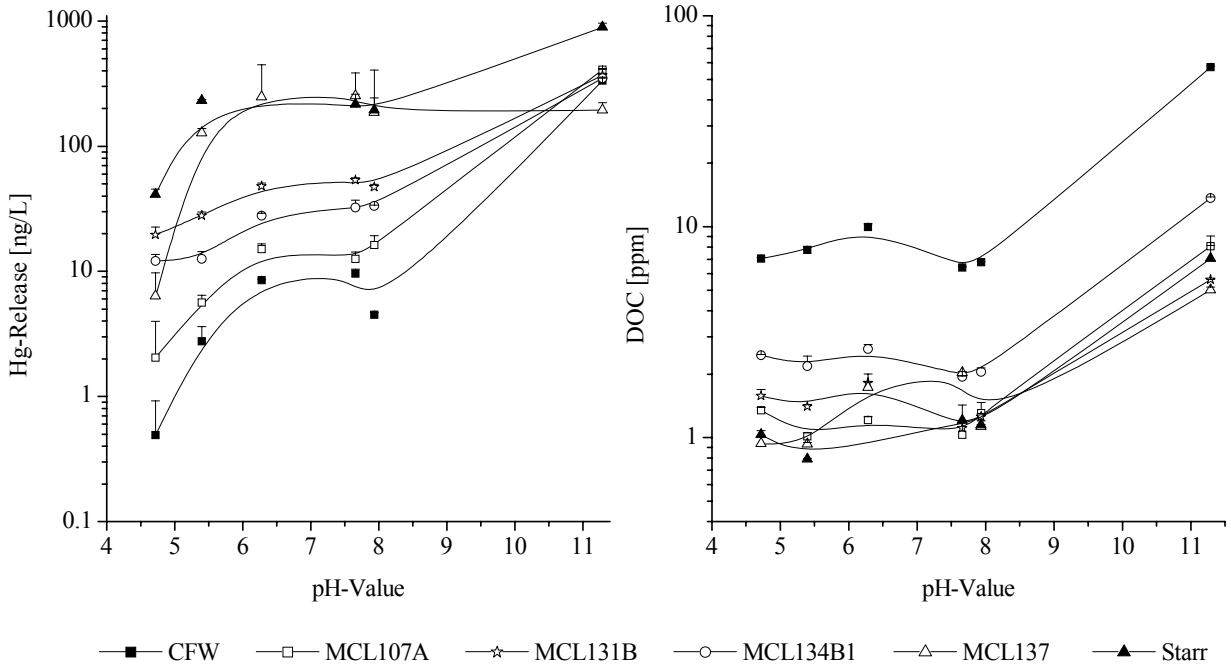


Figure 14. Mercury release and DOC content during variation of pH-value.

The ion exchange processes evident during the variable pH conditions are also reflected by some other elements (shown in the database attached to this thesis - Appendix D – Database). Thus, for barium, calcium, magnesium, manganese, nickel (except CFW), strontium, zinc (except the serpentine soil MCL107A and the wetland MCL134B1), and lithium (but just weak effect) a concentration increase was observed under more acidic conditions due to sorption competition with protons. For boron, copper (except Starr tunnel), iron, sodium, silica, and vanadium, higher concentrations were observed under alkaline conditions, probably due to increasing DOC complexation, but also because of their hydroxide complexes (SCHEFFER et al. 1998).

Varying the ionic strength (I) in a range of 0.1 mol/L to 0.001 mol/L an increase of Hg(II) release with decreasing ionic strength could be observed (Figure 15). Whereas the increase of mercury release is significant ($\alpha = 0.05$) from the steps I = 0.1 to 0.01 and I=0.1 to 0.001, a significant change of Hg(II) from I = 0.01 to 0.001 could not be observed.

UVA and SUVA also followed the observed increase with decreasing ionic strength (Figure 15)

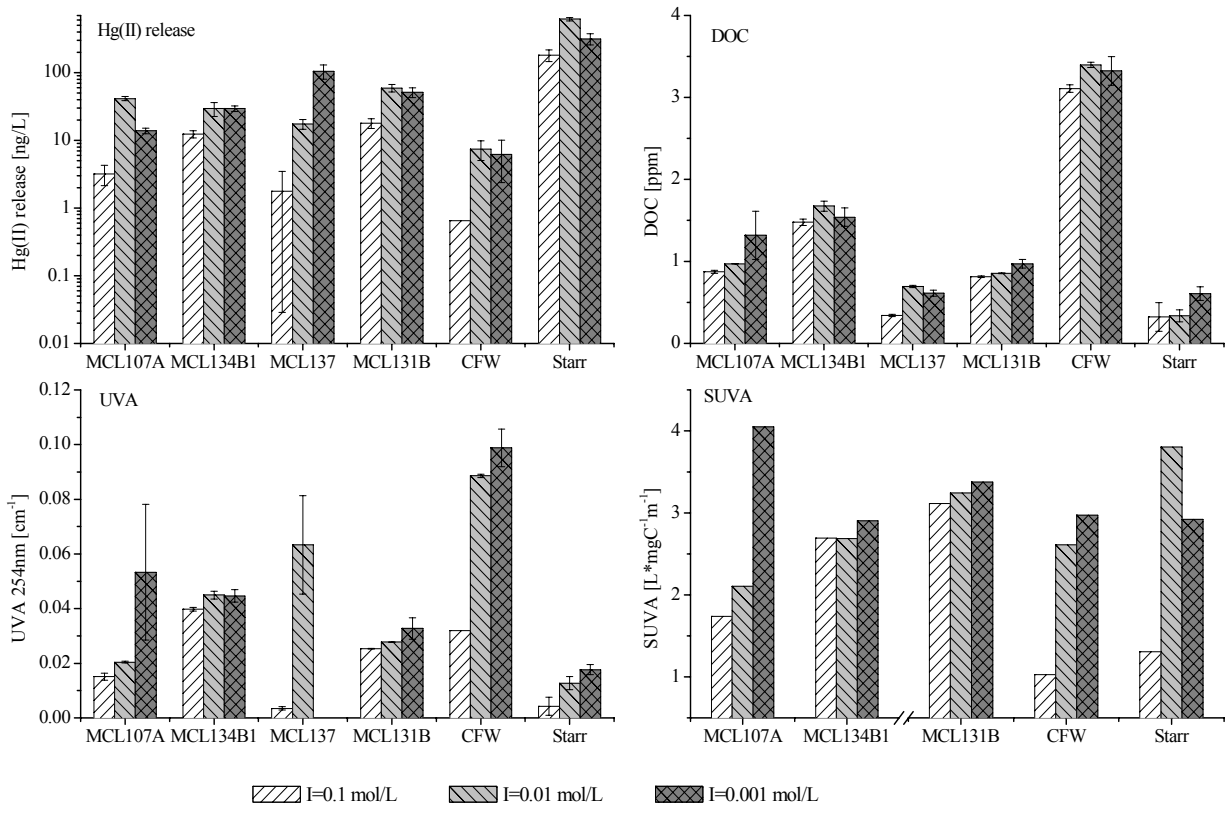


Figure 15. Hg(II), DOC, UVA and SUVA variation with decreasing ionic strength from 0.1 mol/L to 0.001 mol/L.

Error bars are the calculated standard deviation of duplicate analyses. All results, UVA, DOC and Hg(II) are corrected for the experiment blanks, and SUVA was calculated from the corrected values of UVA and DOC.

Increasing mercury desorption with decreasing ionic strength and increasing contact time was also observed in previous studies for contaminated coastal sediments in Portugal (DUARTE et al. 1991). In column experiments with tailing material (waste rock) from Sulphur Bank and New Idria Mine in California, lowering the ionic strength induced increased particle and colloid bound Hg(II) release (LOWRY et al. 2004). There the aqueous phase of the leaching experiments was analyzed for colloidal material by centrifugation. The results of this study indicate that the increase in Hg(II) was the result of colloidal materials, with very little Hg(II) in the dissolved phase (< 0.02 µm). Increased concentrations of mercury and other metals in the truly dissolved

phase (< 0.2 μm) were of minor significance. It was also observed that the colloids released during the ionic strength experiments are related to the soil material, but showed a different composition from those detected during preconditioning steps (where the released colloids consisted of weathered material from the mineral crusts). With respect to investigations on a calcine from Sulphur Bank mine, no significant ionic strength effect could be detected (LOWRY et al. 2004).

The increased Hg(II) release shown in most studies is attributed to colloidal stabilization of clay and organic matter as the ionic strength is lowered (DUARTE et al. 1991). Decreasing ionic strength increases the repulsive electrostatic forces between colloids (RYAN and ELIMELECH 1996), attributed to an increase of the thickness of the double layer (RYAN and GSCHWEND 1994). For the colloids to mobilize, the repulsive forces must exceed the attractive (van der Waals) forces between the colloid surfaces (RYAN and ELIMELECH 1996). At low ionic strength there are fewer ions in the solution to balance the surface charge, resulting in a thick double layer (RYAN and ELIMELECH 1996). If a certain separation barrier is exceeded, the repulsive forces exceed the attractive van der Waals forces, resulting in suspension of the colloids (OVERBEEK 1977; RYAN and ELIMELECH 1996). In contrast, high ionic strength solutions result in a thin double layer because the ions better balance the surface charges. Thus, the attractive forces are greater than the repulsive ones, leading to coagulation (RYAN and ELIMELECH 1996).

Lowering the ionic strength also results in increased UVA and DOC, indicating a higher colloid release, probably colloidal DOM, due to their ability to sorb UV radiation. Taken together, these results show that organic matter colloids are important in the complexation and release of Hg(II).

For the environment, the increase of colloid bound Hg(II) can mean a higher mobility of mercury, because colloids can be widely distributed because of their small size. On the other hand, when dispensed soil particles reach the brackish water region in the Bay-delta, which has a higher ionic strength because of sea water intrusion and the sediment content in this area, an increase of mercury release would not be expected. The higher ionic strength in these systems may also cause coagulation of small particles and colloids, resulting in immobilization by settling.

4.6 Effect of increasing DOC concentration

As expected, the DOC concentration showed a major effect on Hg(II) release from soils and sediment. The addition of fulvic acid from the site F1 in the Everglades (F1-FA, Table 5 and

Table 6) in various concentrations causes a significant (Wilcoxon signed rank test, $\alpha = 0.05$) increased in Hg(II) dissolution, as depicted in Figure 16.

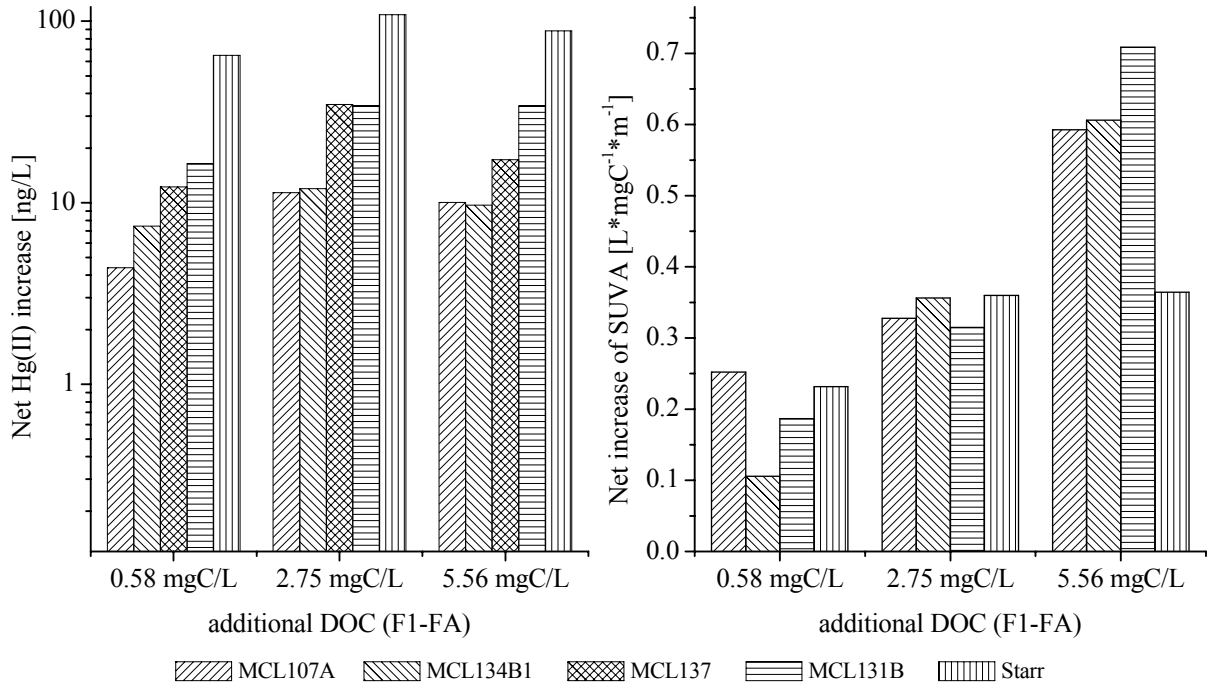


Figure 16. Increase of Hg(II) dissolution and SUVA during addition of DOM F1-FA in various concentrations.
Net Hg(II) and SUVA increase is calculated as difference of the measured and blank corrected Hg(II) (SUVA calculated from blank corrected UVA and DOC) from the present experiment and the average Hg(II) (SUVA) values from the background leaching experiments (Table 10). Results for CFW are not shown in this figure because of a decreasing Hg(II) release comparing to the background leaching, resulting in a negative net increase.

The only exception is the lake sediment CFW (not shown in Figure 16, because of negative values), where additional organic matter seems to inhibit mercury release. As shown in Table 14, the more dissolved organic matter added to the CFW sample, the bigger is the observed inhibition of Hg(II) dissolution

The net increase is calculated as the difference between the measured Hg(II) release with additional DOC and the Hg(II) content from the background leaching experiments (Table 10). The Hg(II) increase ranges from 4.4 ng/L for the serpentine soil (MCL107A) to 64.8 ng/L for the sluice sediment (Starr tunnel) for addition of 0.6 mg/L DOC as shown in Figure 16. The increase for addition of 2.8 mg/L DOC is in a range of 11.4 ng/L (MCL107A) to 108.7 ng/L (Starr tunnel). The Hg(II) release caused by a further DOC increase to 5.6 mg/L did not vary significantly from the step before, and in some cases (tailing MCL137 and Starr tunnel) an even

lower Hg(II) release was determined. Comparing of the DOC concentrations of these leachings there is no assumption that the additional DOC was sorbed by the soil.

Table 14. Mercury release from McLaughlin samples, CFW and Starr tunnel samples after addition of DOC in various concentrations

(% = increase of Hg(II) referring to Hg(II) release from leaching with 0 mg/L DOC, line 3)

	MCL107A		MCL134B1		MCL137		MCL131B		CFW		Starr	
DOC [mg/L]	Hg(II) [ng/L]	%	Hg(II) [ng/L]	%	Hg(II) [ng/L]	%	Hg(II) [ng/L]	%	Hg(II) [ng/L]	%	Hg(II) [ng/L]	%
0	13.0 ±4.1		30.0 ±8.0		18.5 ±6.7		45.4 ±12.9		8.8 ±1.8		349.6± 90.5	
0.6	17.4 ±2.9	33.8	37.5 ±13.2	24.9	30.7 ±1.1	66.3	61.8 ±11.6	36.1	5.9 ±5.8	-33.4	414.5± 112.5	18.5
2.8	24.3 ±4.6	87.4	42.0 ±18.4	39.9	53.3 ±14.2	188.3	79.6 ±23.2	75.3	7.1 ±1.2	-19.5	458.3± 159.1	31.1
5.6	23.0 ±3.4	77.4	39.7 ±6.6	32.4	35.8 ±10.1	93.7	79.7 ±9.7	75.4	5.1 ±2.5	-41.6	438.3 ±335.8	25.3

The lowest Hg(II) increase, calculated as % increase compared to 0 mg/L DOC, was observed for the sluice sediment Starr tunnel (18.5 - 31.1 %, see Table 14). The highest Hg(II) dissolution was observed for the tailing MCL137 (66 - 188 %, Table 14).

The increasing DOC is correlated with an increasing SUVA. Increasing addition of F1-FA caused a higher F1-FA to SOM ratio, which increased the contribution of F1-FA to the measured SUVA and causes its extent. It can be suggested that the reactivity of DOC in the leaching solution is also extended when greater amounts of the relatively reactive F1-FA are added. The net SUVA increase calculated as difference between SUVA from the background leaching experiments (Table 10) and calculated SUVA from the present experiment is shown in Figure 16. Not shown in Figure 16 are the results for CFW, because the SUVA did not increase significantly and for MCL137, because of the influence of iron on UV absorbance (as explained in chapter 4.2). The SUVA for the tailing MCL137 is in a range of 17 to 30 $L*mgC^{-1}*m^{-1}$, because of the absorption of UV by iron.

A significantly increased release of other elements triggered by a 0 to 2.75 mg/L DOC dosage was observed for boron, barium, calcium, copper, iron, magnesia, manganese, sulphur, vanadium, and zinc, whereas silica and strontium decreased and no change was observed for aluminum, potassium, lithium, and nickel. The results for the metals were also corrected by their concentrations in the experiment blanks (Appendix D – Database). For the statistical analysis, the sample CFW was excluded, because there is nearly no change for most elements.

Previous adsorption studies have shown that humic substances have the property to complex Hg(II) (DREXEL et al. 2002; HAITZER et al. 2002; YIN et al. 1997a). The results from this work agree with the observed complexation of Hg(II), which is shown by an increase of dissolved Hg(II) after DOC addition. Apart from the water soluble and soil organic matter (SOM) bound mercury, mineral bound mercury (RAVICHANDRAN et al. 1998) can not pass the 0.45 µm filter. With addition of DOC, the previously particulate Hg(II) fraction was partly bound to F1-FA. The organic mercury complex thus passed the 0.45 µm filter and was detected as increasing total dissolved mercury.

Observations for cinnabar (RAVICHANDRAN et al. 1998; WAPLES et al. 2005), which is regarded as relatively insoluble, showed a significant dissolution in the presence of DOC. For the present soil samples, a major part of mercury is expected to occur as cinnabar (except for MCL131B), as described before. The increase of dissolved Hg(II) compared to the background leaching experiment is thus assumed to be due to dissolution of cinnabar (RAVICHANDRAN et al. 1998; WAPLES et al. 2005). But other possibilities explaining the increased Hg(II) release can not be dismissed, e.g. mobilization of colloids containing mercury or mobilization of Hg(II) bound to other minerals.

In agreement with former studies, the data from this work show a non-linear increase of Hg(II) release relative to DOM concentration. This may be explained by the saturation of the mineral surface by DOM, which then hinders further increases in mercury dissolution upon addition of more DOM (RAVICHANDRAN et al. 1998). But other possibilities have to be considered, e.g. the removal of a major part of relatively easy to mobilize Hg(II) bound to SOM (up to the Hg(II) concentrations leached during the pH 12 dissolution experiments), at that point only the harder to mobilize Hg(II) (i.e. cinnabar) is available.

Because the calculated Hg(II) to DOM ratio for these experiments with additional DOC is below 0.4 µg Hg(II) per mg DOM, from former studies (DREXEL et al. 2002; HAITZER et al. 2002) it can be assumed that the binding between DOM and Hg(II) is very strong. Comparing the measured Hg(II)-DOM interactions by equilibrium dialysis ligand exchange with literature values, the thiol groups have previously been identified as being responsible for the strong binding (DREXEL et al. 2002; HAITZER et al. 2002).

The present studies show, that if the particles reach an aquatic environment, dissolution and complexation of Hg(II) by DOM increases transport mobility (DRISCOLL et al. 1995; MEILI 1991) and also the turnover of Hg(II) bound to DOM to Hg(0) by bacteria (WANG et al. 1997).

4.7 Effect of DOC quality

Isolates of varying chemical characteristics were added to the sediments, in an attempt to investigate the affects of DOM quality on the release of mercury (Table 3, no. 4, isolate information in Table 5 and Table 6). However, since the soils already contained some soil organic matter, it was possible that DOM could be released from the soils, or that the added DOM could be lost to the soils through sorption processes. Because of this, the effect of DOM quality on the dynamics of both Hg(II) and DOM were investigated.

With addition of the isolates also supplementary Hg(II) reached the system (Table 15), related to the isolates themselves in a range of 10 ng/L (WL-HPoA) to 43 ng/L (Suw-HA), which was subtracted from the measured Hg(II) release.

Table 15. Isolate associated Hg(II)
The isolate associated Hg(II) content was determined by Hg(II) analysis of the experiment blank, which were corrected for Hg(II) from UPW and buffers, i.e. average blank Hg(II) from the background leaching experiment without soil input.

Isolate ID	**Hg(II) [ng/L]** (measured Hg(II) from experiment blanks)	**Hg(II) associated to OM** (corrected for average blank value from background leaching experiment of 6.0 ng/L**)**
F1-FA	13.2	7.1
F1-HPoA	16.6	10.6
Suw-HA	43.2	37.2
2BSWCA-HPoA	12.8	6.8
WL-HPoA	10.0	4.0
CF06-0006-HPoA	14.9	8.8

Table 15 shows the high affinity of DOM with Hg(II), resulting in sorption of mercury by dissolved organic matter. It seemed that the more reactive the isolate is (shown by SUVA, Table 6) more Hg(II) is linked (Pearson product moment and Kendall rank correlations are significant, see Table A 19).
The DOC contents show clearly for all samples (Table A 20), that no dissolved organic matter was sorbed by the soils, except for the isolate Suw-HA. The statistical test results showed that DOC concentration measured in the background leaching experiments is not significantly

different ($\alpha = 0.05$) from the DOC content measured in the isolate experiment and corrected for the experiment blank, i.e. the additional DOC concentration. If there would be a sorption process of the added DOM material, as in the case of the Suw-HA isolate, blank leaching DOC concentrations were higher then the blank corrected DOC contents from the isolate experiments (Table A 20). Thus it indicates sorption processes of the added 10 mg/L DOC for the isolate Suw-HA.

The measured Hg(II) release is shown in Figure 18. The net increase (Figure 17) was calculated as the difference between the measured dissolved Hg(II) after DOM addition and the average Hg(II) from the background leaching without DOM.

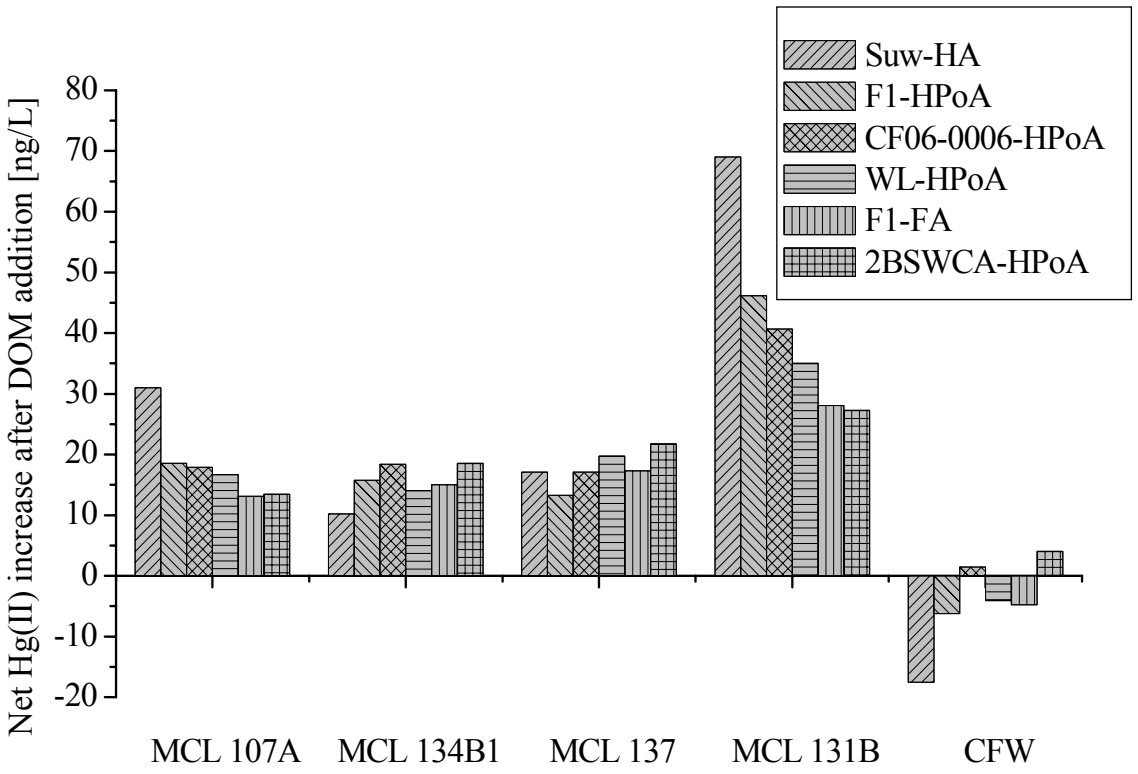


Figure 17. Net Hg(II) increase after addition of various isolates.
Net increase is based on the difference between measured Hg(II) in presence of DOM and the average Hg(II) from the background leaching (all values corrected for Hg(II) associated with the isolates themselves, given by the experiment blanks).

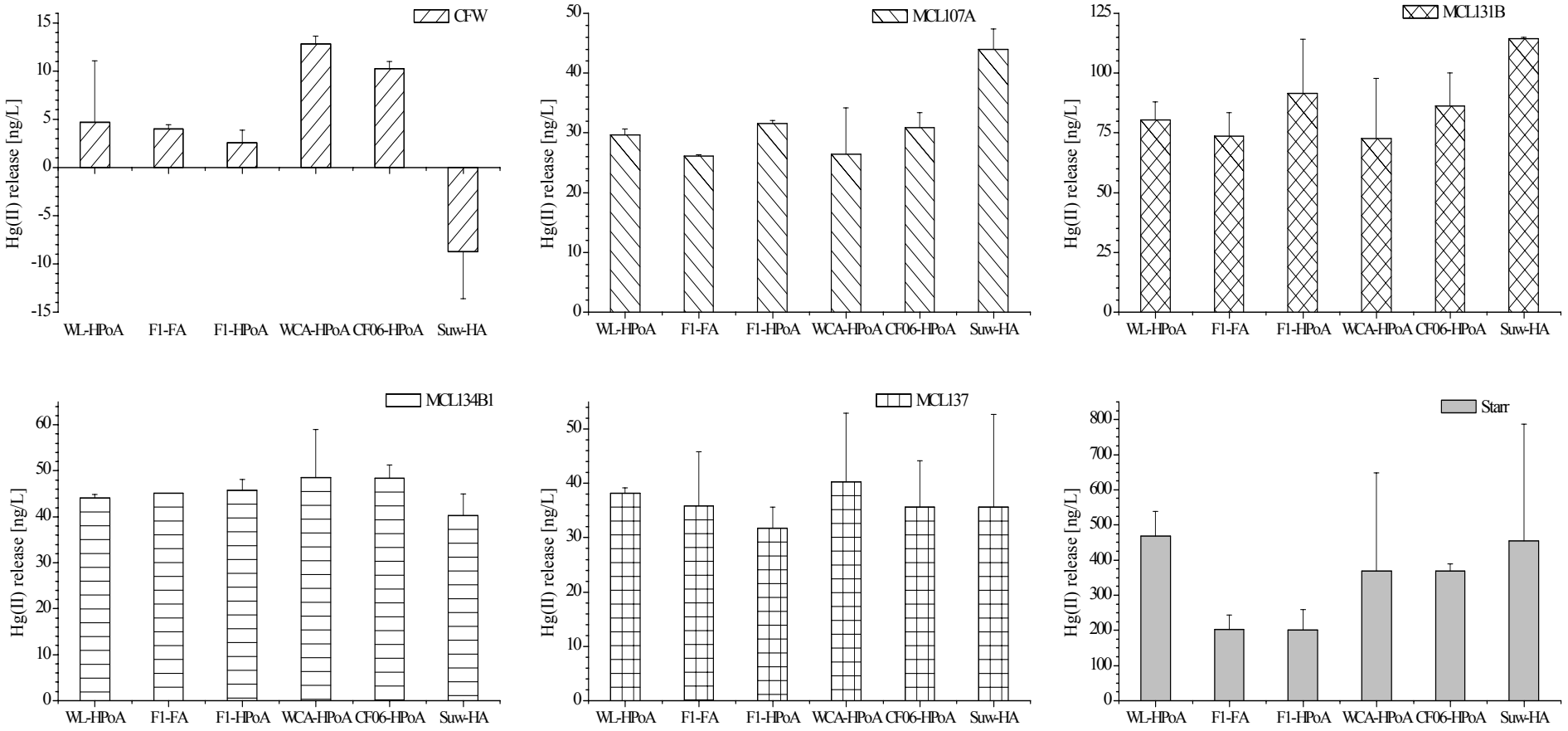


Figure 18. Mercury release from soil samples after addition of various DOM isolates.

The results for Hg(II) release in this figure were corrected for the experiment blanks. Error bars represent the standard deviation of duplicates.

It can be seen that the isolates, with varying chemical properties, cause a different response in the soils. For each soil sample the differences in Hg(II) release caused by the isolates are significant (t-test and Wilcoxon signed rank test, p-value < 0.05). In this experiment the lake sediment CFW shows the tendency for inhibition of Hg(II) release during isolate addition, which is expressed by a negative net increase of Hg(II) in comparison to the average from the background leaching. This also was observed for the experiment with addition of various DOM concentrations, were Hg(II) release from CFW also decreases in comparison to the background leaching (see section: Effect of increasing DOC concentration). Because of the comparison of the leached DOC content with the DOC from the background leaching, sorption of DOM can be excluded. The serpentine soil MCL107A and the fluvent MCL131B show the same behavior after DOM addition, with Suw-HA causing higher mercury releases. It is also clear form Figure 17 that addition of various DOM sources (regardless of their quality) mobilized more Hg(II) from MCL 131B than from any of the other soils.

Suw-HA is the most reactive isolate, i.e. most effective on dissolution of Hg(II) from the soils with the highest dissolution rate for cinnabar according to WAPLES et al. (2005), with a SUVA of 6.6 $L*mgC^{-1}*m^{-1}$ and an aromatic carbon content of 35.1 % of total carbon (TC) (RAVICHANDRAN et al. 1998). For the organic rich sediments CFW (lake sediment) and MCL134B1 (wetland sediment) it is conceivable that mercury, also in form of Hg-DOM complexes from Suw-HA was absorbed (Table A 20). WL-HPoA is the least reactive isolate (SUVA 2.2 $L*mgC^{-1}*m^{-1}$ (WAPLES et al. 2005)) with an aromatic carbon content of 13.8 % of TC (RAVICHANDRAN et al. 1998). Thus it was expected to yield the lowest Hg(II) release. This, however, was only observed for the tailing MCL137. Because of the large heterogeneity of the Starr tunnel sample, a high RSD between the different samples of up to 73 % was found. The mercury increase for Starr tunnel is in the range of -148 ng/L (F1-FA, F1-HPoA) to 104 ng/L (Suw-HA) and 118 ng/L (WL-HPoA).

In order to determine which isolate causes the biggest effect on Hg(II) dissolution, Hg(II) release with addition of isolates was plotted versus the dissolved Hg(II) from the background leaching experiments without DOM (Figure 19). The slope of the regression lines provides an indication of the effect of the isolate on Hg(II) release, with higher slopes indicating a greater propensity for Hg(II) release. The greatest effect is caused by Suw-HA (m = 2.67), followed by the isolate F1-HPoA (m =2.12). The slopes for WL-HPoA, CF06-0006-HPoA and F1-FA are in a range of 1.7 to 1.8, whereas the lowest slope was observed for 2BSWCA-HPoA. This trend regarding the influence of the isolates on the dissolution of Hg(II) from the soils as indicated by the slopes could be observed for the majority of the soil and sediment samples.

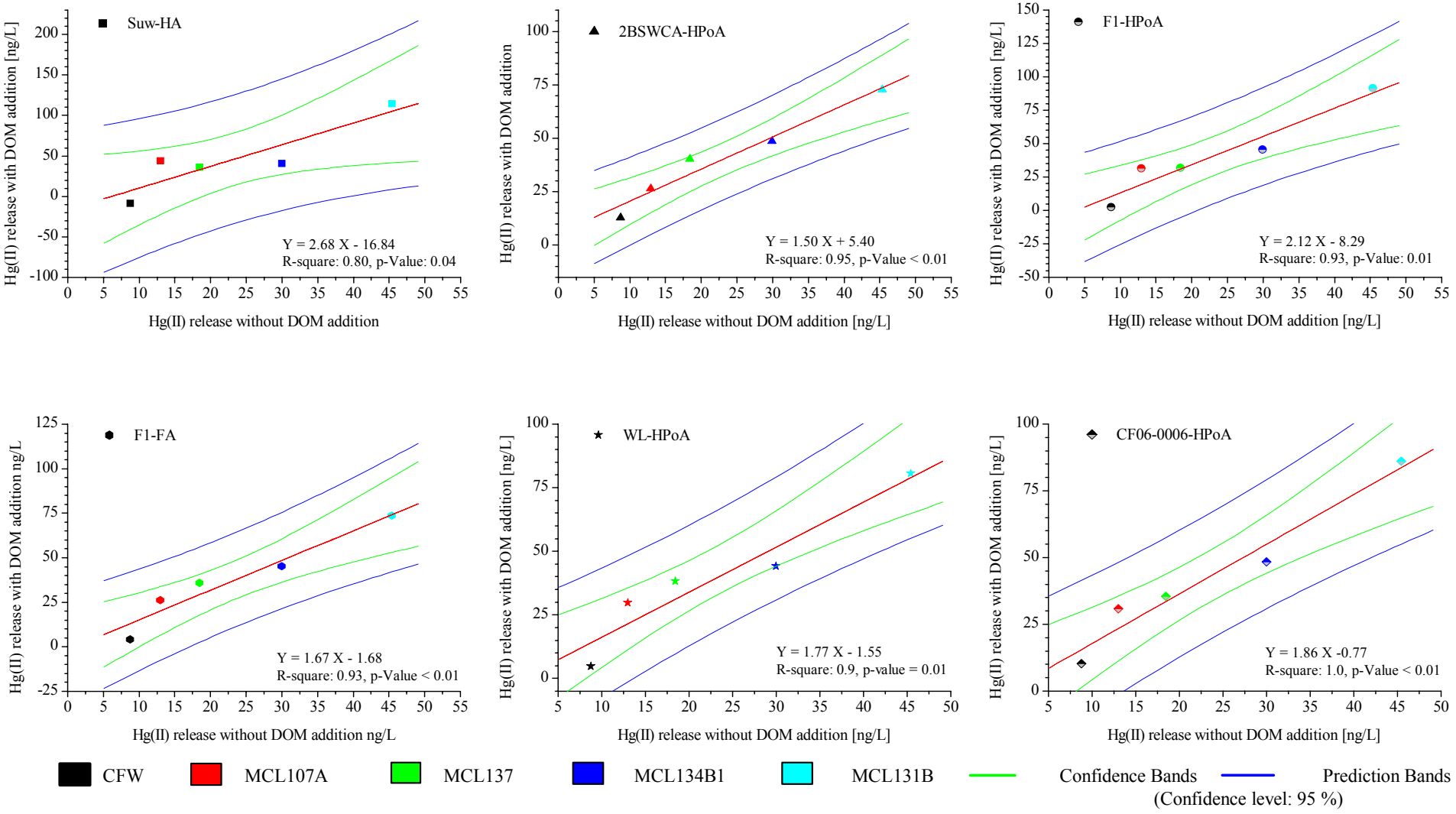


Figure 19. Hg(II) concentration with additional DOM versus Hg(II) release without DOM (excluding Starr tunnel sample)

All results were corrected for the experiment blanks.

The dissolved DOC content from the background leaching of the soils (see Table 10), in the range of 1.3 ppm (MCL107A, MCL137) to 2.5 ppm (MCL134B1), is less then the half of the added isolate DOC of about 5 mgC/L (see blank concentrations in Table A 20), except CFW which has a background leaching DOC content of 9.8 ppm. Clearly the final DOC is the sum of the SOM that dissolved and the DOC that was added. For the case of SUVA, the overall UVA of the sample is also the result of the contributions from the added DOC and dissolved SOM. This results in the SUVA of the final solution also being a combination of both the isolate DOC and the dissolved SOM. Clearly if DOC is added that has a greater SUVA - that is, it absorbs more UV than the SOM that dissolves from the soil, the final SUVA will increase compared to the solution with just the SOM signal. In this study the calculated SUVA for the leaching solutions increased significant with the isolate SUVA, which can be described by the following equation: Isolate SUVA = -1.6 + 1.4*$SUVA_{calc}$ ($p < 0.01$). It also would be possible, that the SOM would have a greater SUVA than the isolate being used in which case the final SUVA would decrease with added isolate.

A significant correlation (Pearson product moment correlation, because data of one and the same sample were according to Shapiro-Wilk normal distributed at $\alpha = 0.05$) between the isolate's SUVA and Hg(II) increase was observed for the serpentine soil MCL107A (Figure 20) and the fluvent MCL131B with R-square 0.62 and 0.56. Furthermore, the net increase correlates directly with the ratio carbon content to hydrogen content (Table A 21), aromatic and carboxylic carbon (Table A 21 and Table A 22) for MCL107A (shown in Figure 20) and MCL131B, which indicates that the carbon content affects the Hg(II) dissolution, especially aromatic carbon and carboxylic groups.

As shown in Table A 21 and Table A 22 the lake sediment CFW shows negative correlations between Hg(II) release and SUVA, molecular weight, UVA, aromatic and carboxylic carbon content. The dissolution seems to be controlled exactly by the opposite factors as for the serpentine soil and the fluvent (MCL107A, MCL131B). The results for all correlations between the Hg(II) release and the chemical properties of the isolates are shown in Table A 21 and Table A 22 in Appendix A – Tables.

The Hg(II) increase described in Figure 17, as well as the correlation results in Table A 21 and Table A 22, indicate that the Hg(II) release from the tailing (MCL137) is independent of the chemical properties of the isolates. The MCL137 leaching solutions have the highest iron content of all samples, 3.43 ± 0.72 mg/L. Iron oxidation is also one driving force for cinnabar dissolution, which is possibly the major factor causing Hg(II) release in MCL137 (WAPLES et al.

2005). Iron increases from the background leaching to isolate leaching experiments by a factor of 4.9, whereas, the Hg(II) increase was fewer than two times that observed for the blank soil leaching. In all other samples iron contents (corrected for the isolate own iron content – experiment blank) were < 0.13 mg/L after isolate addition and no significant changes could be observed in comparison with the iron release from the background leaching (results for iron contents see Appendix D – Database).

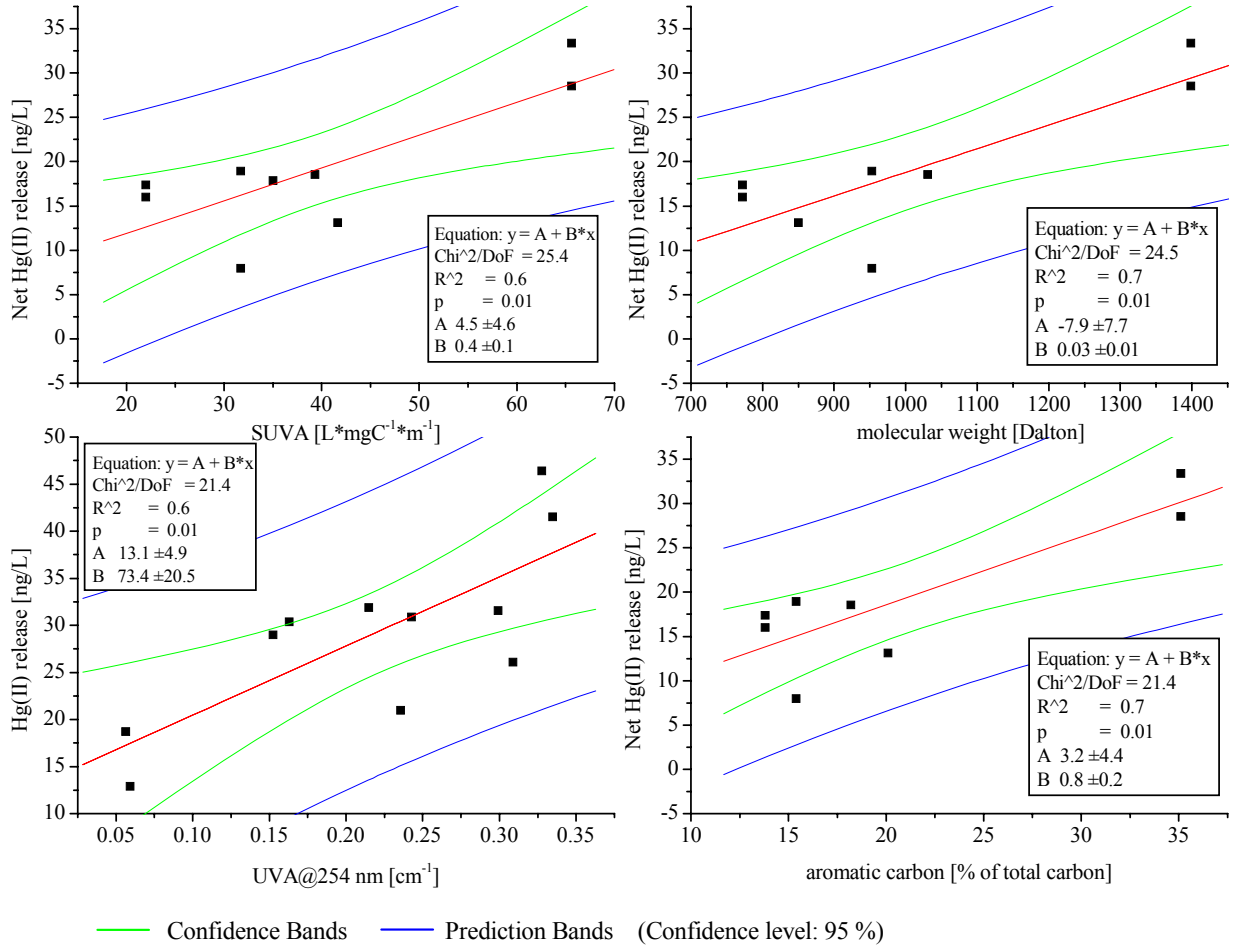


Figure 20. Correlation of isolates SUVA, molecular weight, aromatic carbon content, and UVA with Hg(II) release and net Hg(II) increase for the serpentine soil MCL 107A.
Net Hg(II) increase is calculated as difference between the measured and blank corrected Hg(II) release in the isolate experiment and the average from the background leachings. Hg(II) release was corrected by the experiment blank.

No correlation was noted for any of the soil samples between isolate sulfur content and Hg(II) increase, this is similar to what has been observed in cinnabar dissolution studies (RAVICHANDRAN et al. 1998; WAPLES et al. 2005). Nitrogen containing functional groups in DOM can play a minor role as ligands for Hg(II) (RAVICHANDRAN 2004), however, no correlation between Hg(II) release and nitrogen content nor nitrate could be observed for the

majority of the soil samples in this study (Table A 21). A significant correlation was observed between the isolate carboxyl and hydroxyl content and Hg(II) release for the serpentine soil, the fluvent and the lake sediment (MCL107A, MCL131B and CFW). These results are different from what has been observed in studies with cinnabar, where no correlations between cinnabar dissolution and these organic matter properties was detected (WAPLES et al. 2005).

Aromatic carbon content seems to be an important indicator of the reactivity of the DOM. This is based on the correlations of Hg(II) release and isolate aromatic carbon content and SUVA for the MCL107, MCL131B and CFW samples (Table A 21 and Table A 22). In some cases, the results indicate that the more aromatic the DOM, the more Hg(II) is dissolved (MCL107A and MCL131B). However, for the lake sediment (CFW) the more aromatic isolates result in adsorption to the sediment (Suw-HA) and inhibition of Hg(II) release. This could result from the interrelationships of organic matter molecules among themselves (STEVENSON 1985), where the added DOM sorbed to the SOM from CFW sediment, which has the highest TOC content of 5.4 % among the sample soils, or competes with SOM and is so not available for dissolution of Hg(II) from the sediment.

Because relationships between nearly all chemical properties were observed and Hg(II) increase for the samples CFW (lake sediment), MCL107 (serpentine soil) and MCL131B (fluvent), it can be assumed that the dissolution of mercury from soil and sediments is the result of a synergetic effect of several organic matter properties. A significant correlation with aromatic content of the organic matter suggesting, that this is an important parameter in predicting mercury release. The results, however, do suggest that DOM is quite effective at leaching or release of mercury from soils and sediments. But the soil and sediment own properties, occurring from their formation and origin, and the soil history, are important on the behaviour of Hg(II) release too as observed for the CFW sample. That is shown by the various effects the isolates cause in the different soil and sediments. One important soil own property is sorption capacity, which is strongly influenced by SOM, pH, and polyvalent cations which can compete with the added DOC. The results from this experiment show the complexities involved in the release process where the additional DOM quality and the soil characteristics are important.

4.8 Influence of specific organic acids on mercury release from soil samples and sediments in comparison to natural organic matter

In addition to investigating the effects of DOM on the mercury release from the soils, also the effects of a range of synthetic ligands on mercury release were studied. The organic ligands chosen were the well-known chelating agent EDTA, an aliphatic thiol containing ligand,

mercaptoacetic acid, and an aromatic and carboxylic carbon containing ligand, salicylic acid (Table 3, no. 8). These organic ligands are known to have strong affinities for complexing mercury, shown by the stability constants (log K^c) for their mercury ligand (Hg-L) complexes, which are 21.5 for EDTA and 34.5 for mercaptoacedic acid (RAVICHANDRAN 2004).

The results for Hg(II) release (Figure 21), reported as concentration per mg added DOC (to get a comparable base, because the DOC reaching the leaching systems differ between the added model compounds), show that addition of DOM F1-FA and mercaptoacetic acid caused the greatest increase in Hg(II) leaching. The effect of the strong ligand EDTA and salicylic acid is small in comparison to F1-FA and mercaptoacetic acid.

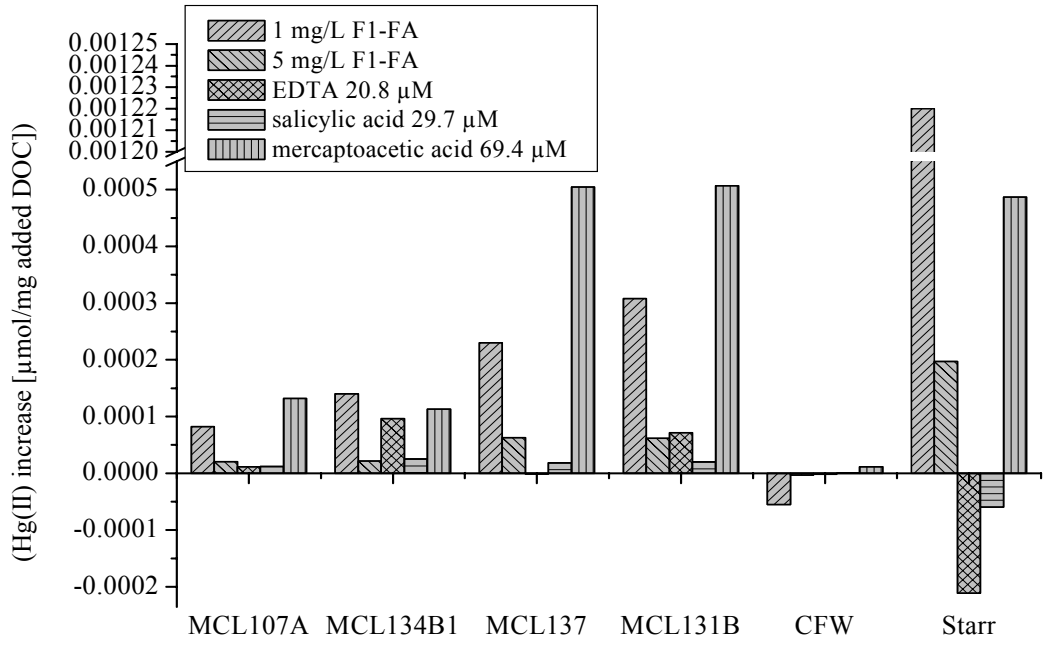


Figure 21. Competence of organic acids in dissolution of Hg(II) from soils and sediments in comparison to natural organic matter.

All results are corrected for experiment blanks. The Hg(II) increase is reported as µmol/mg DOC. Because the amount of carbon reaching the leaching system by addition of the model compounds differed, the results in µmol/mg are comparable regarding the DOC content. For that the Hg(II) increase in µmol/L was divided by the DOC content [mgC/L] from the experiment blank.

The binding constants for Hg-DOM complexes are in a range of $10^{11.5}$ M^{-1} (weak binding sites on peat) to 10^{23} M^{-1} (strong binding sites on peat) as reported in DREXEL et al. (2002) and are comparable with thus from the organic ligands. The results in Figure 21 show clearly that the effectiveness of Hg(II) release from the soils is not a simple process that can be described simply by using chemical constants, but a complex process were also soil and DOM properties are important.

The binding between mercury and sulfur in cinnabar is very strong and it needs a strong complexing ligand to remove Hg(II) from the mineral lattice. As reported before (DREXEL et al. 2002; HAITZER et al. 2002) reduced sulfur groups on DOM have a strong affinity for Hg(II) and are responsible for the Hg(II) release. Mercaptoacetic acid contains a thiol group, too, which also leads to a significant dissolution of Hg(II) in this study. Salicylic acid contains an aromatic carbon group and a carboxyl group and is much less effective at leaching mercury from the soil samples (Figure 21).

The results show that the chemical properties, e.g. thiol group content and aromaticity, of organic acids have a strong influence on dissolution processes. But the mercury release is not controlled by any simple processes like the binding of Hg(II) to the organic acids, but by more complex processes than that, which are influenced by a variety of factors such as soil own properties. The dissolution of mercury is also affected by the mineral type. Whereas for cinnabar, which is thought to be the main mercury source in the present soils based on sequential extraction analyses (except the fluvent MCL131B), the dissolution by high molecular weight acids containing sulfur groups plays an important role, for oxide dissolution low molecular weight acids promote the dissolution (RAVICHANDRAN et al. 1998). For modeling of environmental concerns the use of natural organic matter fractions can be important, because the various processes lead to strong and synergistic effects which can not be approximated by use of organic acids.

4.9 Effect of inorganic ligands and polyvalent cations

Among the inorganic ligands with a strong affinity for mercury, for example chloride (K^c=14.0 M), hydroxide (K^c=21.8), bromide (K^c=18.0) and sulfide (K^c= 37.7) as mercury-ligand (HgL_2) complexes, chloride and hydroxide are of special importance, because they are widespread in natural systems and form stable and mobile complexes with mercury across a wide pH range (MARTELL et al. 1998; RAVICHANDRAN 2004; SCHUSTER 1991). In this study chloride was chosen to investigate the effect of inorganic ligands on Hg(II) release from soils and sediments because of its ability to form strong complexes with mercury and because chloride is a major constituent of the brackish water of the San Francisco Bay, which can be reached by suspended soil particles.

The addition of 0.01 M chloride was found to cause a significant increase of Hg(II) release for all samples (Figure 22). However, the effect is not as strong as for mercaptoacetic acid and F1-FA. The addition of both 10 mg/L F1-FA and chloride expressed in Figure 22 increases Hg(II) dissolution, when compared to the average Hg(II) release from the DOM leaching experiment,

for three of the sediments, MCL107A, MCL134B1 and MCL131B. As observed in other experiments in this study, DOM addition to CFW causes an inhibition of mercury release also in the leaching with both, chloride and DOM. Assuming from oral communications of the Californian USGS group, the CFW sediment is very reactive, i.e. it has a high TOC content, the soil organic matter (SOM) can complex the mineral surface and prevent mineral dissolution, which inhibits the mercury release, as well as the additional DOC can sorb to the soil own SOM and thus the DOM binding sites are not available for releasing mercury. This is confirmed by the DOC measurements, were the DOC concentration for CFW after addition of chloride and both, chloride and DOM is more then 1 ppm lower then the DOC content determined in the background leachings (DOC: 8.4 ppm for chloride addition, 7.5 ppm for chloride and DOM addition, and 9.8 ppm in the background leachings).

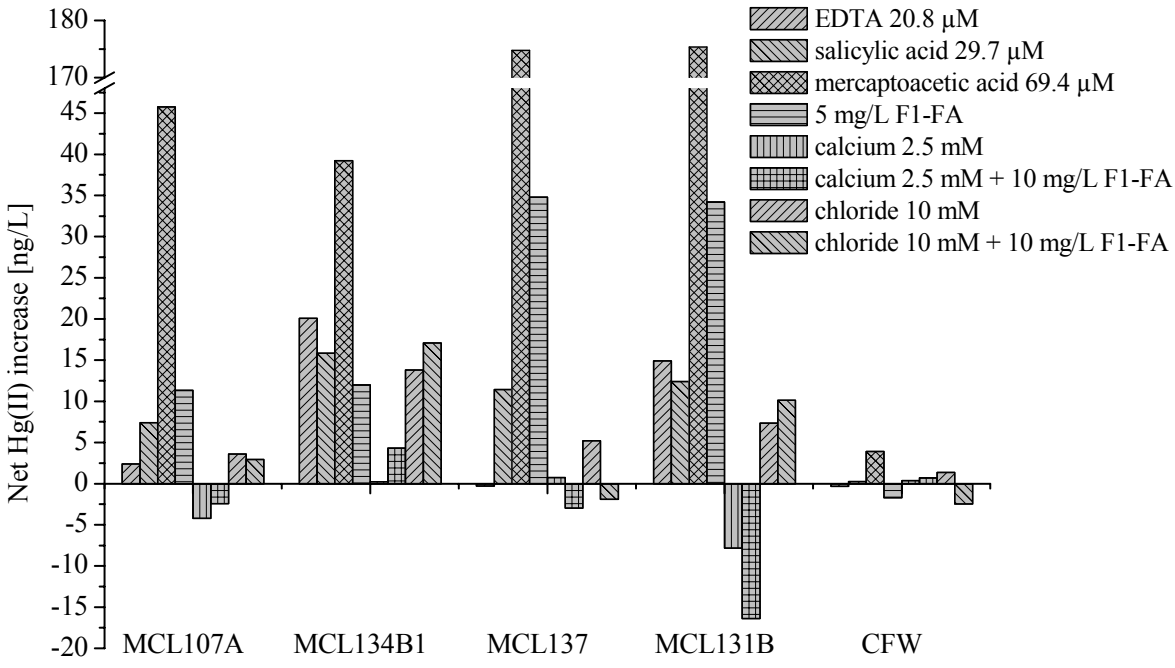


Figure 22. Net Hg(II) release from soils and sediments dependent on presence of organic and inorganic ligands.

Net Hg(II) increase in the figure is calculated as difference between Hg(II) release in the particular study and the average Hg(II) from the background leaching for the experiments with the organic acids, calcium and chloride. The Net Hg(II) increase calculation for the experiments CaDOM and ClDOM are based on the leaching with 10 mg/L F1-FA instead the background leaching. Thus the net increase is an indicator for effectiveness of Hg(II) release and increase related to the background leaching and the leaching with 10 mg/L F1-FA.

The statistics show that after addition of F1-FA and chloride together, the measured DOC is significant less compared to the background leaching. Just addition of chloride did not cause any differences. This indicates that some of the added DOM from the isolate F1-FA is sorbed to the soils or inhibits leaching of SOM.

Because of heterogeneity of the Starr tunnel sediment, the results show a large variability and were not considered for further interpretations for this experiment.

In the presence of chloride, stable and water soluble mercury-chloride complexes are formed with mercury from the sediments and soils, and these complexes may be dispersed into the liquid phase (SCHUSTER 1991; WANG et al. 1991), as observed as increasing Hg(II) release from the soil samples in this study. Additional Hg(II) dissolution can be generated by chloride complexes formed with sediment and soil bearing iron and manganese (WANG et al. 1991). SCHUSTER (1991) reported that at chloride concentrations about 0.1 mM, the solubility of $Hg(OH)_2$ and cinnabar increases about a factor of 55 and 408 respectively. For Canadian freshwater sediments a sharp increase in Hg(II) release was observed in the presence of chloride (WANG et al. 1991). In contrast to these observations, studies on cinnabar dissolution showed no significant increase in the presence of 0.01 M chloride (RAVICHANDRAN et al. 1998).

In addition to the increase of mercury release, an increasing manganese concentration (trace metal concentrations in Appendix D – Database), attributed to complexation with chloride (WANG et al. 1991) was observed for all samples. Especially for wetland MCL134B1, tailing MCL137 and lake sediment CFW a sharp increase of 68.2 ± 27.2 µg/L, 19.6 ± 0.9 µg/L and 168.8 ± 66.0 µg/L, respective, was detected with ICP-AES, whereas the increase for the other samples is approximately 5.2 ± 1.5 µg/L. Iron increased just for MCL137.

In contrast to chloride, for calcium a strong inhibition of mercury dissolution was observed (Figure 22). Addition of both F1-FA and calcium causes an Hg(II) increase in comparison to the leaching just with calcium, but yields lower Hg(II) releases than F1-FA leaching in the absence of calcium. This is indicated by a depression of Hg(II) for the serpentine soil (MCL107A), the fluvent (MCL131B) and the tailing (MCL137) in Figure 22, where Hg(II) increase for Ca-DOM leaching is expressed as the difference to leaching with 10 mg/L F1-FA. The presence of calcium probably inhibits colloidal stabilization as well as the release of SOM from the soils. This is confirmed by the DOC measurements, were DOC concentrations (blank corrected) for the experiments just with calcium and with calcium and added DOM are at least 0.5 ppm lower then the DOC concentration determined in the background leaching experiment, except for the MCL137 and MCL134B1. There the addition of calcium did not show any changes in DOC concentration, but calcium and DOM addition also caused lower DOC concentrations. For the

series CaDOM (calcium plus 10 mg/L F1-FA) the DOC content is significant ($\alpha = 0.05$) less than the DOC concentration form the background leaching (data are shown in the Appendix D – Database). The Hg(II) release from the wetland (MCL134B1) and lake sediments (CFW) is not affected by calcium, because there is nearly no difference to the results for background leaching. For these samples the addition of DOM and calcium tends to increase the Hg(II) release, in comparison to the leaching without calcium. This may also be the result of a reduction of the observed inhibition of Hg(II) release for CFW after DOM addition.

The inhibition of mercury release is consistent with previously observed inhibition of cinnabar dissolution in presence of calcium ($2.5*10^{-4}$ M) (RAVICHANDRAN et al. 1998). A change in surface charge of cinnabar to a less negative level was observed in these studies. This is a consequence of the interaction between calcium and the sulfur sites, resulting in a surface complexation against other dissolution agents (RAVICHANDRAN et al. 1998). The observed decrease of Hg(II) release in the CaDOM leaching in comparison to leaching just with DOM (F1-FA) can result from an interaction of calcium with organic matter, and the saturation of its active sites. The wetland and lake sediment (MCL134B1 and CFW) have a high TOC content. For these sediments the added calcium might react with the organic matter in the system so that an inhibition process can not be observed. This is because the calcium may complex with the SOM, and the additional DOC in CaDOM leaching, is still available to cause a Hg(II) release.

For the environment it can be assumed that polyvalent cations reduce the mobility of mercury in natural systems, while anions with a strong affinity for mercury, such as chloride and hydroxide, increase the mobility of mercury and consequently its distribution through the environment.

4.10 Mercury distribution between dissolved and colloidal state

It is likely that significant amounts of mercury may be released from the sediments as colloids. The use of 0.02 μm filters to separate dissolved mercury (<0.02 μm) from colloidal mercury (greater than 0.02 μm, but less than 0.45 μm) was investigated. However, it was found that the filtration method was unsuitable for the mercury studies because the 0.02 μm Anotop® filters sorbed mercury (the 0.45 μm filters, however, were deemed suitable for use).

Further, the potential usefulness of centrifugation as reasonable method for separating dissolved mercury < 0.02 μm from colloidal mercury, was investigated. According to Stokes law, the constituents in a solution can be separated by centrifugation, where the largest particles settle to the bottom during the spin. For these experiments, various sets of leaching solutions (background leaching and leaching with addition of 10 mg/L F1-FA, Table 3) were prepared, filtered through 0.45 μm filters, and centrifuged (Figure 5). The centrifugation was performed at 12, 000 rpm for

5 h 48 min after which time particles with an equivalent diameter > 0.02 µm should have settled on the tube bottom. The remaining clear solution should only contain dissolved matter < 0.02 µm. The colloidal fraction was estimated by the difference of the 0.45 µm filtered solution and the results after centrifugation at 12,000 rpm.

The distribution of mercury between the dissolved fraction < 0.02 µm and colloidal mercury indicates a significant amount of Hg(II) in the dissolved phase (Figure 23). The results from CFW and MCL137 are not shown in the figure, because the measured amount of Hg(II) < 0.02 µm exceeds the measured concentration for Hg(II) < 0.45 µm. Further development of the method is warranted.

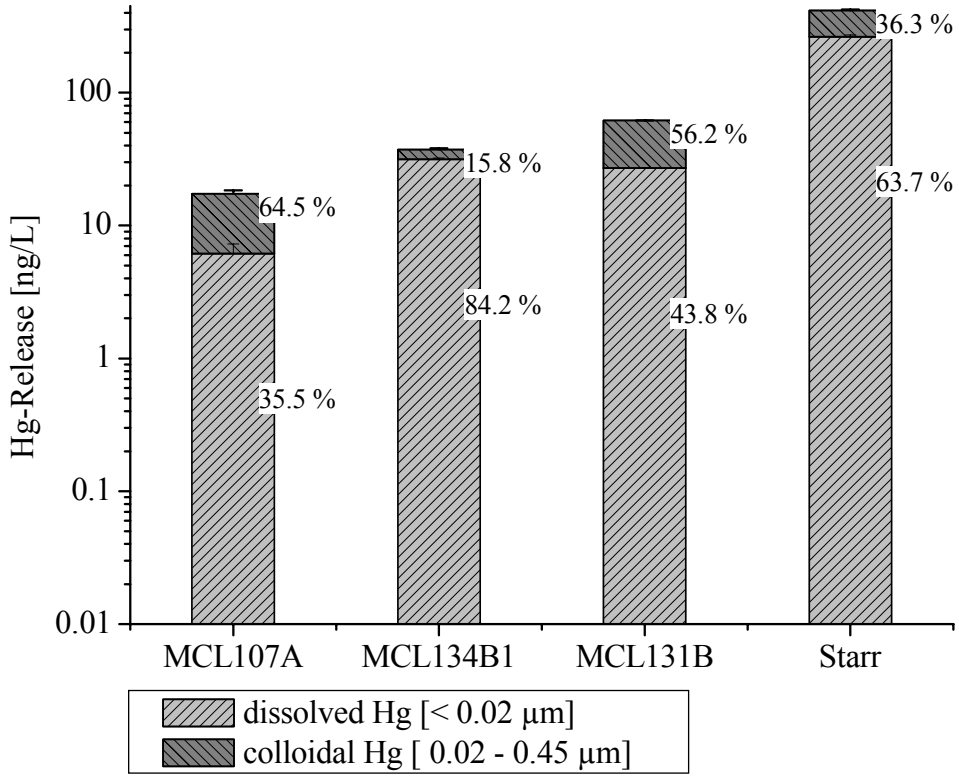


Figure 23. Distribution of mercury between the dissolved fraction (< 0.02 µm), obtained by centrifugation at 15,000 rpm, and colloidal fraction (0.02 - 0.45 µm)

The colloidal mercury was calculated by the difference between Hg(II) from the samples at 12,000 rpm and Hg(II) from the background leaching. Because the sum of both fractions reached > 110 % for CFW (124 %) and MCL137 (187 %), due to higher measured dissolved Hg(II) concentrations < 0.02 µm, these results are not presented here.

Also other researchers concern about the release of colloidal mercury, such as the soil column studies of LOWRY et al (2004). Although for the initially collected effluent about 50 % particle-related mercury was detected, the following solution after the first precondition steps shows the major mercury distribution in the dissolved phase < 0.02 µm (LOWRY et al. 2004).

The results for dissolved organic matter < 0.02 µ in the present study (Table 16) show slight differences between the measured DOC concentration (< 0.45µm) from background leaching and the DOC concentration measured after the separation process by centrifugation at 12,000 rpm (Wilcoxon signed rank test, p-value = 0.04). But assuming a MDL of 0.2 ppm and an accuracy of ± 0.1 ppm, the results suggest that there is no loss of DOC during centrifugation and that the vast majority of DOC occurs as dissolved fraction < 0.02 µm. Possibly for Starr tunnel and MCL131B there could be an amount of colloidal DOC (> 0.02 µm), but this requires further investigations.

Table 16. Results for DOC distribution between the dissolved fraction < 0.02 µm and the colloidal fraction between 0.02 - 0.45 µm after

Sample ID	DOC < 0.45 µm [ppm]	DOC < 0.02 µm [ppm]	DOC < 0.02 µm [%]	DOC 0.02 – 0.45 µm [ppm]
MCL107A	1.3	1.2	90.5	0.1
MCL134B1	2.5	2.3	92.1	0.2
MCL137	1.3	1.1	86.3	0.2
MCL131B	1.8	1.4	80.1	0.4
CFW	9.8	9.8	100.0	0.0
Starr	1.4	1.0	71.8	0.4

5. Problems encountered and Recommendations

For the batch experiments unhomogenized soil material (i.e. not the same particle size distribution - in this study coarse soil aggregates were crushed but not all the similar size), was used without using a method for randomly partitioning of the sample material (by sample splitter or sample dividers). This led to the problem, where the heterogeneity of the soil material resulted in an average relative standard deviation (RSD) for Hg(II) determination of 9.4 % in a range of < 0.1 % to 78.0 % calculated from RSD's of all sample replicates. Especially high RSD's were observed for Starr tunnel and the tailing MCL137. Starr tunnel material was relatively coarse grained (see Figure 9). Even a very small amount of cinnabar can cause a high variability in Hg(II). The difficulties encountered with the tailing samples were the result of filter clogging, resulting in over-pressure, and breaking of the filter membrane. This problem was solved using a 0.45 µm filter with 35 mm diameter as pre-filter before the regular used filter with a diameter of 25 mm (both filters were Acrodisc® filters with Supor® membrane and a pore size of 0.45 µm).

A further difficulty, encountered at the beginning of this study, was to complete the filtering without centrifugation. Initially, filtering of the samples occurred immediately after mixing. Filtering required one hour per sample. The first experiment was a kinetics experiment, and the results were significantly affected by this long filter time, resulting in a high variability between duplicate samples (average RSD 17 %). However for later experiments, a centrifugation step (2800 rpm, 40 min) was added prior to filtering. This decreased filtration difficulties and resulted in much better agreement of duplicate samples (average RSD 9.4 %).

Volatilization of mercury from the samples during the course of the experiments can not be completely excluded. However, it is likely that the amount of lost Hg(0) is small relative to the total mercury in these samples. The contamination of the experiments from the atmosphere or chemicals can be a significant problem in mercury studies, however, in the case of these experiments, contamination by lab atmosphere was found to be negligible (< 0.3 ± 0.1 ng/L). The average mercury concentration of the background leaching blanks (Table 10) was 6.0 ± 1.4 ng/L. When DOM isolates were added, the average Hg(II) increased to 18.4 ± 12.3 ng/L for blanks with additional 10 mg/L organic matter. All samples were corrected for the determined mercury from the blanks. For investigations with sediments low in Hg(II) it is recommended to use dissolved organic matter isolates with very low mercury contents.

When calculating SUVA, it is important to note that the UVA (necessary for the calculation) is strongly influenced by the iron concentration in a sample. To make conclusions using SUVA, as a measure for DOC reactivity and Hg(II) release for iron bearing samples, the UVA must be corrected for iron concentrations. For MCL 137, SUVA may not be a good parameter to analyze,

without correcting for iron influence, because the sediment contains high iron concentrations that may skew the SUVA measurement. The iron concentrations for MCL137 did correlate with the measured UVA (Spearman rank correlation, p-value < 0.05, R = 0.5), which might be a possibility to re-calculate the iron influence on UVA and thus the Hg(II) release, e.g. by using linear regression. For all other sediments iron concentrations were less than 0.5 mg/L, which is the reported iron concentration in WEISHAAR et al. (2003) for influencing UVA.

Because mercury is a soft and very reactive metal it tends to form complexes and sorb to surfaces, such as with membrane surfaces. During the filter tests for the 0.45 µm Acrodisc® filters and for the 0.02 µm Anotop® filters interactions of Hg(II) with the filter membrane were observed. Particularly strong interactions were observed for the Anotop® filters. Studies concerning filtering refer to problems like filter clogging and membrane interactions and recommend a standardized filtering procedure (SHILLER and TAYLOR 1996). The filter tests showed that the Anotop® filters were unsuitable for these experiments.

As a result of the difficulties with the Anotop® filters, a substitute method, centrifugation, was used for separating dissolved Hg(II) < 0.02 µm from Hg(II) < 0.45 µm. The results were encouraging, and the method needs further development. One suggestion is to centrifuge at 12,000 rpm without before filtering at 0.45 µm to exclude sorption of mercury to the filter membrane. Another possibility would be to reduce the filter size in a stepwise manner, testing filters with pore sizes in a range of 0.02 to 0.45 µm, to determine the fraction containing the highest amount of mercury, which can be compared with the centrifuge results. Ultracentrifugation, that is a centrifugation at high velocities (> 12,000 rpm to 60,000 rpm, (RALSTON)) to separate fine colloidal material under exploitation of centrifugal forces, was another possible method (realized in studies of BABIARZ et al. (2001), CHOE et al. (2003) and the USGS (2001)). For ultracentrifugation especially if the aim is to separate and analyze the colloids, a bigger leaching volume is necessary (at least 250 mL according to USGS studies USGS (2001)), because of the small size and low content of the colloidal material in a leaching sample.

It may also be possible to determine mercury retained by the filter membranes through a digestion in aqua regia, to estimate particulate mercury which was mobilized during leaching and did not pass the filter.

For particle size analyses it is necessary to use standardized sieves and methods, to get results that are comparable to other studies. And for the use in trace metal experiments, the sample sieves should be made with non-contaminating materials.

The results of the experiments in this study suggest the following experiments for further research:

- standardized analysis for soil characterization
- performance of digestions with defined particle size fractions, to determine the particle size fraction were the majority of Hg(II) is released
- variation of soil : liquid ratio
- batch experiments with varying dissolved organic matter (DOM) concentrations and DOM origin with previous extraction of soil organic matter (e.g. extraction with NaOH or destroying of SOM by addition of with H_2O_2 or heating (SCHEFFER et al. 1998), to exclude influences of SOM,
- extracting and analyzing of chemical properties (e.g. aromatic carbon content) of leached soil organic matter (leaching experiment with a bigger solution volume that extraction with XAD method is possible), to determine the effects of SOM on Hg(II) release, and interactions of Hg(II) with SOM, e.g. determination of binding constants of Hg(II) to SOM,
- measuring of Hg(II) release without filtering, and then stepwise using different filters with pore sizes between 0.45 µm and 0.02 µm to get Hg(II) concentrations related to definite size fractions,
- improvement of centrifuge technique for determination of dissolved mercury in various sizes <0.45 µm, e.g. centrifugation without beforehand filtering,
- test of ultracentrifugation for separation of Hg(II) colloids and dissolved mercury, i.e. spin at velocity higher then 12,000 rpm,
- analyzing of mercury sorbed to the filter membrane by dissolving the filter in aqua regia,
- use of soils from the San Francisco-San Joaquin delta for leaching experiments,
- determine methylation potential by incubation of the soil material, especially in the Bay-delta area with bacteria,
- repetition of pH, ionic strength, Ca and Cl experiments with using Sacramento River water instead of ultrapure water, to imitate natural conditions.

6. Summary, Conclusions and Environmental implications

The present studies have shown that Hg(II) dissolution from soils and sediments depends on a number of soil-specific factors and experimental conditions such as pH, ionic strength and the presence of polyvalent cations and inorganic ligands, and the presence of DOM. Under environmental conditions DOM can a cause significant dissolution of mercury from the samples. DOM addition causes a non-linear increase of Hg(II) release with respect to the DOM concentration. Besides the quantity of DOM, its quality also plays a major role for dissolution, especially the aromaticity which is a direct measure for the DOM´s reactivity (WEISHAAR et al. 2003). The results in this study suggest that areas with high DOM concentrations, such as the wetlands in the Sacramento River Delta, may be areas of high mercury release from deposited sediments.

Chloride occurs in a range of environmental systems, especially in the brackish water region in the Bay-Delta region. Chloride forms stable complexes with Hg(II) and increases its distribution in the environment, as observed in this studies. In contrast the presence of polyvalent cations, like the environmentally important elements calcium or magnesium, inhibits Hg(II) dissolution. This might be of special importance for contaminated calcite soils as well as calcite containing tailings, which occur in the Coastal Range (ENDERLIN 2002). Mercury release further increases with decreasing ionic strength because of the mobilization colloidal mercury, a very mobile mercury fraction. Downstream of the contaminated areas in the Bay-Delta region mixing with seawater causes a significant increase in ionic strength. Therefore it is assumed that the suspended soils do not release increasing amounts of Hg(II). However, the Bay-Delta region is a multi-factor system, where the above discussed factors, such as chloride and increasing DOM, can contribute to Hg(II) dissolution.

Although the results in the present study have shown that the amount of released mercury is small in comparison to the total mercury, this amount is of environmental importance because of its availability for methylation. Concentrations of mercury in a range of parts per trillion are sufficient for producing the neurotoxic methylmercury which has the tendency to accumulate and magnifies in the human and animal food chain (MOREL et al. 1998). But as shown in this and other studies, it is hard to control the system because of the influences of multiple factors. Understanding these factors is an important goal because the contaminated soils and sediments in California will provide a source of mercury for decades (ALPERS and HUNERLACH 2000).

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Appendix A – Tables

Table A 1. Experimental conditions for leaching experiments no. 1 - 4

No.	Experiment code	Basic conditions				Additional settings		Comments
		Soil input [g]	pH buffer [mL]	I buffer [mL]	UPW [mL]	Solution	[mL]	preparation of stocks and buffers see Table A 4 and Table A 5
1 Kinetics								
1A	K	0.50	1.00	2.70	95.30			standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M
1B	KDOM	0.25	0.50	1.35	47.65	F1-FA stock 1 g/L	0.50	standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M
2 Background leaching								
2A	BE	0.25	0.50	1.35	48.15			standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
3 Leachings without buffer								
3A	B	0.25			50.00			equilibration time 24 h
3B	IC	0.25			50.00			equilibration time 24 h
3C	ICDOM	0.25			49.5	F1-FA stock 1 g/L	0.50	equilibration time 24 h
Leaching with Sacramento River water								
4	SacRiver	0.25	0.50	1.35		Sacramento River water	48.15	standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
5 DOM experiment (variable DOM concentration)								
5A	F1FA_0 mg/L	0.25	0.50	1.35	48.15			standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
5B	F1FA_1 mg/L	0.25	0.50	1.35	48.10	F1-FA stock 1 g/L	0.05	
5C	F1FA_5 mg/L	0.25	0.50	1.35	47.90	F1-FA stock	0.25	
5D	F1FA_10 mg/L	0.25	0.50	1.35	47.65	F1-FA stock	0.50	

Table A 2. Experimental conditions for leaching experiments no. 5 - 8

No.	Experiment Code	Basic conditions				Additional settings		Comments
		Soil input [g]	pH buffer [mL]	I buffer [mL]	UPW [mL]	Solution	[mL]	preparation of stocks and buffers see Table A 4 and Table A 5
6 pH experiment (variable pH); I = 0.01 M, equilibration time 24 h								
						phosphate buffers		average pH in filtered leaching solution [± SD over all samples]
6A	pH3	0.25	0.50	1.35	48.50	pH 3 buffer		4.7 ± 0.6
6B	pH4	0.25	0.50	1.35	48.50	pH 4 buffer		5.4 ± 0.3
6C	pH6	0.25	0.50	1.35	48.50	pH 6 buffer		6.3 ± 0.1
6D	pH8	0.25	0.50	1.35	48.50	pH 8 buffer		7.9 ± 0.1
6E	pH8n	0.25	0.50	1.35	48.50	pH 8 new buffer		7.6 ± 0.4
6F	pH10	0.25	0.50	1.35	48.50	pH 10 buffer		7.9 ± 0.4
6G	pH12	0.25	0.50	1.35	48.50	pH 12 buffer		11.3 ± 0.1
7 Ionic strength experiment (variable I)								
7A	I_0.1	0.25		1.67	48.33			equilibration time 24 h; no pH buffer
7B	I_ 0.01	0.25		0.17	49.83			
7C	I_ 0.001 M	0.25		0.017	48.983			
8 Isolates experiment (variable DOM)								
8A	BDOM	0.25	0.50	1.35	48.15			standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
8B-8G		0.25	0.50	1.35	47.65	DOM stock 1 g/L	0.50	
	DOM stocks: WL-HPoA, (8B), 2BSWCA-HPoA (8C), Suw-HA (8D), F1-FA (8E), F1-HPoA (8F), CF06-0006-HPoA (8G)							

Table A 3. Experimental conditions for leaching experiments no. 9

No.	Experiment	Basic conditions				Additional settings		Comments
		Soil input [g]	pH buffer [mL]	I buffer [mL]	UPW [mL]	Solution	[mL]	preparation of stocks and buffers see Table A 4 and Table A 5
9 Model compound experiment								
9A	EDTA	0.25	0.50	1.35	47.763	EDTA 1 g/L	0.387	standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
9B	Mercaptoacetic acid	0.25	0.50	1.35	47.754	MercAcid	0.396	
8C	Salicylic acid	0.25	0.50	1.35	47.945	SaliAcid	0.205	
10 Chloride- and Calcium experiment								
10A	Ca ($2.5*10^{-4}$ M)	0.25	0.50	1.35	48.025	Ca-stock 0.1 M	0.125	standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
10B	CaDOM (Ca $2.5*10^{-4}$ M, DOM 10 mg/L)	0.25	0.50	1.35	47.525	Ca-stock 0.1 M	0.125	
						F1-FA stock 1 g/L	0.500	
10C	Cl (0.01 M)	0.25	0.50	1.35	47.817	Cl-stock 1 M	0.50	
10D	ClDOM (Cl 0.01 M, DOM 10 mg/L)	0.25	0.50	1.35	47.317	Cl-stock 1 M	0.50	
						F1-FA stock 1 g/L	0.50	
11 Matrix experiment								
11A	M, MD	0.25	0.50	1.35	48.15			standard pH buffer; pH 6.4 ± 0.06, I = 0.01 M; equilibration time 24 h
11B	MDOM, MDDOM	0.25	0.50	1.35	47.65	F1-FA stock 1 g/L	0.50	

Table A 4. Preparation of stock solutions and buffers: ionic strength, pH and DOM

Solution	Concentration.	Ingredients	UPW	Comments
ionic strength stock	3 M	$NaClO_4$ (sodium perchlorate)	X	after dissolving in ultrapure water (UPW) filtering through cleaned (140 mL ultrapure rinse) 0.45 µm filter
standard pH buffer	1 M	0.7 M $NaH_2PO_4*2H_2O$ (sodium phosphate, monobasic, dihydrate) plus 0.3M Na_2HPO_4 (sodium phosphate, dibasic, anhydrous)	X	pH = 5.95; after dissolving in UPW, filtering through a cleaned 0.45 µm filter
pH 3 buffer	1 M	8.5 mM H_3PO_4 (phosphoric acid) plus 91.4 mM $NaH_2PO_4*2H_2O$ (sodium phosphate, monobasic, dihydrate)	X	pH =2.98; after dissolving in UPW, filtering through a cleaned 0.45 µm filter
pH 4 buffer	1M	standard pH buffer plus certain amounts of 10 M NaOH (sodium hydroxide) and/or HNO_3 (nitric acid) for pH adjustment	X	pH =4.08
pH 8 buffer	1M	standard pH buffer plus certain amounts of 10 M NaOH (sodium hydroxide) and/or HNO_3 (nitric acid) for pH adjustment	X	pH =7.98 → precipitation of sodium phosphate
pH 8 new buffer	0.1 M	standard pH buffer (0.1 M) plus certain amounts of 10 M NaOH (sodium hydroxide) and/or HNO_3 (nitric acid) for pH adjustment	X	pH =8.01; dilution of standard pH buffer with UPW, then pH-adjustment
pH 10 buffer	1 M	standard pH buffer plus certain amounts of 10 M NaOH (sodium hydroxide) and/or HNO_3 (nitric acid) for pH adjustment	X	pH =10.00
pH 12 buffer	0.1 M	3.1 mM Na_2HPO_4 (sodium phosphate, dibasic, anhydrous) plus 6.8 mM $Na_3PO_4*12H_2O$		pH = 12.01; after dissolving in ultrapure, filtering through a cleaned 0.45 µm filter
DOM stock solutions	1 g/L	freeze-dried DOM material: F1-FA 7/97, F1-HpoA 7/97, Suw-HA Reference 1/83, 2BSWCA-HpoA 4/95, WL-HpoA, MN, 4/10/00, CF06-0006-HPoA	X	

Table A 5. Preparation of stock solutions: EDTA, MercAcid, SaliAcid, calcium, and chloride

Solution	Concentration	Ingredients	UPW	Comments
EDTA stock solution	1 g/L	$C_{10}H_{14}O_6Na_2N_2*2H_2O$ (EDTA disodium salt)	X	
MercAcid stock	1 g/L	$C_3H_3O_2SNa$ (thiogylcolic acid sodium salt – mercaptoacetic acid)	X	mercaptoacetic acid
SaliAcid stock	1 g/L	$2\text{-}HOC_6H_4COOH$ (salicylic acid powder – O-hydroxybenzoic acid)	X	salicylic acid
Ca-stock	0.1 M	$Ca(NO3)_2*4H_2O$ (calcium nitrate)	X	calcium
Cl-stock	1 M	NaCl (sodium chloride)	X	chloride

Table A 6. Matrix experiment: spikes

Sample ID	Average from background leachings without DOM	Spike = Hg(II)-stock 100 µg/L [mL]	Leaching with 10 mg/L DOM	Spike DOM sample = Hg(II)-stock 100 µg/L [mL]
Blank	6.0	0.003	13.15	0.003
MCL107	19.5	0.003	36.19	0.010
MCL134B1	37.8	0.010	52.87	0.010
MCL137	32.7	0.010	48.29	0.010
MCL131B	53.3	0.010	92.82	0.010
CFW	15.2	0.003	18.28	0.003
Starr	356.1	0.020	451.42	0.020
results are not corrected for experiment blanks				

Table A 7. Test solutions

Code	Test solutions	HCl [mL]	F1-FA g/L [mL]	MercAcid 1g/L	Hg(II)-stock 100 µg/L [mL]	UPW [mL]
A	ultrapure water					250
B	regular water					250 mL regular water
C	1 % HCl	2.50				247.50
D	1 % HCl + 1000 ng/L Hg(II)	2.50			2.50	245.00
E	5 mg/L DOM		1.25			249.75
F	5 mg/L DOM + 1000 ng/L Hg(II)		1.25		2.50	246.25
G	1000 ng/L Hg(II)				2.50	247.50
H	1 % HCl + 100 ng/L Hg(II)	2.50			0.25	247.25
I	100 ng/L Hg(II)				0.25	249.75
J	10 mg/L DOM		2.5			247.50
K	10 mg/L DOM + 100 ng/L Hg(II)		2.5		0.25	247.25
L	10 µM MercAcid + 100 ng/L Hg(II)			0.285	0.25	249.465

Table A 8. Chemical solutions for Hg(II) analysis with CVAFS

Chemical term	HCl [mL]	UPW [mL]	Chemicals	Total volume
KBr		125	2.98 g KBr (potassium bromide)	125 mL
KBrO3		125	0.70 g KBrO3 (potassium bromate)	125 mL
HH		50	4.68 g NH_2OH*HCl (hydroxylamine hydrochloride)	50 mL
BrCl	250		2.7 g KBr 3.8 g $KBrO_3$	250 mL
Reductant	100	1000	20 g $SnCl_2$*$2H_2O$ (stannous chloride)	1000 mL
Reagent blank (RB) for analyzer	50	1000	5 mL KBr 5 mL $KBrO_3$ 0.77 mL HH	1000 mL
Reagent blank (RB) for dilutions	50	1000	5 mL KBr 5 mL $KBrO_3$	1000 mL

Table A 9. Standard preparation for Hg(II) analysis with CVAFS

Standard concentration	Calculation	Comments
0 ng/L Hg(II)	RB (for dilution)	
5 ng/L Hg(II)	$\_\ mL\ Hg(II) - stock = \_\ mL\ RB\ (\ for\ dilution) * 5 * 10^{-5}\ mL$	tare balance, pour RB for dilution (Table A 8) into Hg(II) clean glass bottle, note weight and calculate amount of additional Hg(II) stock (100 µg/L)
20 ng/L Hg(II)	$\_\ mL\ Hg(II) - stock = \_\ mL\ RB\ (\ for\ dilution) * 2 * 10^{-4}\ mL$	
100 ng/L Hg(II)	$\_\ mL\ Hg(II) - stock = \_\ mL\ RB\ (\ for\ dilution) * 1 * 10^{-3}\ mL$	

Table A 10. Cleaning procedure for test tubes and vials
(ICP-AES sample bottles, DOC vials and TOC test tubes, and centrifuge tubes)

Equipment	Chemicals for cleaning	Procedure
ICP-AES bottles (HDPE cylinders with PE caps)	aqua regia (10 % HCl + 10 % HNO_3)	bottles soaked in aqua regia over night; afterwards rinsing for five times with ultrapure water
DOC boro silica vials and TOC Analyzer test tubes		rinsing three times with regular water and three times with ultrapure water, then for 4 h at 500 °C in oven
Nalgene® centrifuge tubes for 12,000 rpm spin		rinsing with ultrapure water , then soaked for 24 h in ultrapure water, afterwards additional rinse with ultrapure water

Table A 11. Cleaning procedure filters and syringes

Filter type	1.2 M HCL [mL]	0.024 M HCl [mL]	Rinse with UPW [mL]	Comment
syringes 10 mL			60 mL	
syringes 60 mL			180 mL	
0.45 µm Acrodisc® filter with Supor® membrane			140	leaching experiments; first rinse with HCl, then ultrapure water
0.45 µm Acrodisc® filter with Supor® membrane	40		40	filtration Anotop® filter test; first rinse with HCl, then ultrapure water
0.02 µm Anotop® with Anopore® (aluminum oxide) membrane		40	20	filtration Anotop® filter test; first rinse with HCl, then ultrapure water

Table A 12. Filter test results for 0.02 µm Anotop® and 0.45 µm Acrodisc® filters

Hg(II) and DOC results for stepwise testing of filters. The complete list of results can be found in the database (Appendix-D). Results in the table given as % Hg(II) or % DOC are the recoveries adopted to the unfiltered solution.

Filter	0.02 µm Anotop® filter with Anopore® membrane + 0.45 µm pre-filter (both diameter: 25 mm)						0.45 µm filter with Supor® membrane (diameter: 25 mm)				
Filter step [mL]	**Hg [ng/L]**	**SD [ng/L]**	**% Hg**	**DOC [ppm]**	**SD [ppm]**	**% DOC**	**Hg [ng/L]**	**SD [ng/L]**	**% Hg**	**DOC [ppm]**	**% DOC**
Test solution I (100 ng/L Hg(II)) and for 0.45 µm testing G (1000 ng/L Hg(II))											
unfiltered	109.4	0.2	100	DOC was not measured (n.m.) for this test.			1049.5	.	100	DOC was not measured for this test.	
0 - 10	17.8	8.1	16				933.5		89		
10 - 20	31.3	12.3	29				971.0		93		
20 - 30	40.7	13.9	37				974.7		93		
30 - 40	44.8	9.0	41				1014.1		97		
40 - 50	47.7	12.1	44				n.m.		n.m.		
Test solution K (10 mg/L DOM + 100 ng/L Hg(II)); for 0.45 µm filter testing for DOC: test solution F (5 mg/L DOM + 1000 ng/L Hg(II))											
unfiltered	107.6	6.5	100	4.5	0.1		123.9		100	2.7	100
0 - 10	14.8	10.2	14	3.0	0.2	66	110.2		89	n.m.	n.m.
10 - 20	30.8	16.2	29	4.1	0.1	90	104.2		84	2.6	96
20 - 30	43.4	18.2	40	4.7	0.3	103	83.6		67	n.m.	n.m.
30 - 40	51.4	20.0	48	4.7	0.00	104	81.9		66	n.m.	n.m.
40 - 50	74.4	0.1	69	4.8	0.2	106	77.8		63	n.m.	n.m.
Test solution H (1 % HCl + 100 ng/L Hg(II))											
unfiltered	91.6	9.5	100	DOC was not measured for this test.			112.8		100	DOC was not measured for this test.	
0 - 10	64.0	1.8	70				101.2		90		
10 - 20	72.4	0.4	79				102.9		91		
20 - 30	79.0	2.4	86				97.7		87		
30 - 40	77.7	4.2	85				98.9		88		
40 - 50	68.2	74.4	74				82.6		73		
Test solution J (10 mg/L DOM F1-FA)											
unfiltered	Hg(II)was not measured for this test.			5.25	0.05	100	14.0			DOC was not measured for this test.	
0 - 10				3.86	0.14	74	12.8		91		
10 - 20				5.28	0.03	101	15.0		107		
20 - 30				6.12	0.95	117	8.8		63		
30 - 40				5.69	0.01	108	10.8		77		
40 - 50				5.57	0.07	106	n.m.		n.m.		
Test solution L (10 µM MercAcid + 100 ng/L Hg(II))											
unfiltered	104.6	2.3	100	DOC was not measured for this test.			Hg(II)was not detected fort his test.			DOC was not measured for this test.	
0 - 10	8.1	1.1	8								
10 - 20	8.8	0.2	8								
20 - 30	7.6	0.6	7								
30 - 40	7.5	0.0	7								
40 - 50	8.6	0.4	8								

Table A 13. Results for DOC and Hg(II) from centrifuge tube test

Description	Hg (II) [ng/L]	DOC [ppm]	Hg(II) [ng/L], DOC [ppm] in test solution	% Hg(II), % DOC of test solution	Comments
Centrifuge tube: Nalgene® 40 mL					cleaning procedure: 6*UPW, 12 h UPW soak, 6*UPW
Hg-content in centrifuge tubes					
Hg(II) content in test tube (uncleaned)	20.6	0.17	DOC 0.14 – 0.2 ppm	% DOC 85 - 121.4	possibility to contaminate sample with Hg(II), if tube will not be cleaned before use; no influence on DOC, is in range of common measured UPW content
Hg(II) in cleaned vial: Hg(II) after cleaning with 6*UPW, 12 h soak in UPW, 6*UPW and 6 h centrifuging (12,000 rpm) in test solution UPW (Table A 7, A)	1.5 (< MDL 5 ng/L)	0.11			test tube clean – Hg(II) content corresponds with Hg(II) content from UPW - no contamination after cleaning
Hg(II) after soak in test solution					
Hg(II) after cleaning and centrifugation (6h at 12,000 rpm) in test solution with 100 ng/L Hg(II) (Table A 7, I)	99.5	0.11	Hg(II) 109.4	% Hg(II) 91.0	average for Hg(II) 96.3 %; Hg(II) sorption on material of test tube < 4 %; DOC no sorption detected
Hg(II) after cleaning and centrifugation (6h at 12,000 rpm) in test solution with 100 ng/L Hg(II) and 10 mg/L F1-FA (Table A 7 ,K)	109.2	4.62	Hg(II) 107.6 DOC 4.57	% Hg(II) 101.5 % DOC 101.1	
Blanks					
Hg(II) in UPW (Blank from HgAir experiment, Table B 21)	1.8				
Hg(II) from solution with 10 mg/L F1-FA (average blank from Matrix experiment)	13.4				
Centrifuge tube: Corning Inc. 50 mL					each leaching a new tube, no cleaning..
Hg(II) after soak (24 h) in UPW (Table A 7, A)	< MDL 5 ng/L				no contamination of leaching solutions from tube material.
Hg(II) after soak (24 h) in test solution with 1 mg/L Hg(II) (Table A 7, G)	1021.0		1049.5	% Hg(II) 97.2	sorption of Hg(II) on tube walls < 3%..

Table A 14. Results from matrix experiment without DOM addition

S … sample, D …. duplicate; 1st , 2nd … separate leachings; results for MCL137 (grey marked) have a high variability in results of successive filter stages resulting from damage of filter membrane; MCL137 results did not pass the EPA quality criteria for accuracy and matrix effects of a maximum RPD of 24 % and a spike recovery between 71 % and 125 % (TELLIARD and GOMEZ-TAYLOR 2002)

Reference	Hg(II) (B) ng/L		Hg(II) (A) ng/L after spiking		RPD spikes [%]	A-B	Calculated spike concentration (T) [ng/L]		Spike recovery (R) [%]	
	S	D	S	D			S	D	S	D
MCL107A	21.5		53.8			32.3	30.0		108	
1st	21.9	17.0	51.0	54.0	6		31.0	29.9	94	124
2nd	26.2	21.0	55.4	54.7	1		29.8	29.4	98	115
MCL134B1	48.0		144.0			96.1	100.3		96	
1st	48.4	41.6	139.1	139.8	1		98.4	100.3	92	98
2nd	54.3	47.7	144.9	152.4	5		100.3	102.2	90	102
MCL137	78.4		253.2			174.8	102.5		170	
1st	40.4	112.2	206.5	318.4	43		101.1	101.6	164	203
2nd	41.7	119.3	173.2	314.8	58		100.7	106.4	131	184
MCL131B	58.9		152.8			93.9	102.1		92	
1st	66.1	50.2	143.5	150.9	5		100.0	100.8	77	100
2nd	68.7	50.7	153.1	163.8	7		102.4	105.1	82	108
CFW	16.4		50.7			34.3	30.4		113	
1st	16.7	15.4	52.1	48.8	6		30.2	31.0	117	108
2nd	18.7	14.6	49.2	52.7	7		30.1	30.3	101	125
Starr	326.4		519.0			192.7	200.5		96	
1st	298.6	295.0	507.2	531.8	5		192.8	208.2	108	114
2nd	374.5	337.4	489.7	547.5	11		193.8	207.2	59	101

Table A 15. Results for matrix experiment with addition of 10 mg/L F1-FA

S … sample, D …. duplicate; 1st , 2nd … separate leachings; results for MCL137 (grey marked) have a high variability in results of successive filter stages resulting from damage of filter membrane; MCL137 results did not pass the EPA quality criteria for accuracy and matrix effects of a maximum RPD of 24 % and a spike recovery between 71 % and 125 % (TELLIARD and GOMEZ-TAYLOR 2002)

Reference	Hg(II) (B) ng/L		Hg(II) (A) ng/L after spiking		RPD spikes [%]	A-B	Calculated spike conc. (T) [ng/L]		Spike recovery (R) [%]	
	S	D	S	D	S		S	D	S	D
MCL107A	46.4		143.4			97.0	98.2		99	
1st	52.3	48.1	138.5	146.3	6		100.5	95.1	86	103
2nd	44.4	40.9	137.4	151.3	10		96.6	100.6	96	110
MCL134B1	72.0		165.0			93.0	100.8		92	
1st	73.9	66.2	157.7	162.0	3		101.2	102.4	83	94
2nd	76.5	71.4	161.2	179.0	10		98.5	100.9	86	107
MCL137	160.2		295.3			135.1	109.1		124	
1st	52.6	229.7	249.4	335.2	29		108.1	109.7	182	96
2nd	66.8	291.5	264.2	332.3	23		108.2	110.4	182	37
MCL131B	86.7		186.1			99.3	98.4		101	
1st	59.7	96.3	185.7	185.7	0		96.0	95.5	131	94
2nd	12.8	104.2	213.2	186.7	13		98.4	103.7	204	80
CFW	24.5		56.9			32.4	29.7		109	
1st	25.7	24.3	49.3	59.8	19		28.3	30.4	83	117
2nd	23.9	23.9	55.9	62.8	12		30.2	30.0	106	129
Starr	414.0		600.2			186.3	199.4		94	
1st	357.7	362.3	536.5	565.5	5		194.1	200.4	92	101
2nd	461.1	474.8	625.1	673.8	8		205.4	197.8	80	101

Table A 16. USDA and German particle size classification

Particle size classification	USDA equivalent diameter (JACKSON 1956)	Equivalent diameter for German nomenclature (SCHEFFER et al. 1998)
Gravel	< 12.5 mm	< 63 mm
Sand	0.05 mm - 2 mm	0.063 mm - 2 mm
Very coarse sand	1.0 mm - 2.0 mm	
Coarse sand	0.5 mm - 1.0 mm	0.63 mm - 2.00 mm
Medium sand	0.25 mm - 0.50 mm	0.20 mm - 0.63 mm
Fine sand	0.10 mm - 0.25 mm	0.063 mm - 0.200 mm
Very fine sand	0.05 mm - 0.10 mm	
Silt	0.002 mm - 0.050 mm	0.002 mm to 0.063 mm
Coarse silt		0.020 mm - 0.063 mm
Medium silt		0.0063 mm - 0.0200 mm
Fine silt		0.002 mm - 0.0063 mm
Clay	< 0.002 mm	0.002 mm

Table A 17. Results of pipette test

Pipette type	Accuracy [µL][1]	RSD[2] [%]	n
Fisherbrand® Finnpipette® 200-1000 µL	202.3 ± 1.1 to 995.3 ± 0.8	0.5	5*10 steps
Fisherbrand® Finnpipette® 100-1000 µL	104.8 ± 1.7 to 1004.5 ± 2.0	1.5	5*10 steps
Fisherbrand® Finnpipette® 20- 200 µL	20.3 ± 0.3 to 199.9 ± 0.1	0.7	3*10 steps
Fisherbrand® Finnpipette® 5- 50 µL	10.0 ± 0.1 to 49.4 ± 0.2 (start measuring at 10 µL)	0.5	3*10 steps
Fisherbrand® Finnpipette® 0.5- 10 µL	2.8 ± 0.1 to 9.8 ± 0.6 (start measuring at 3 µL)	3.8	3*10 steps
digital Finnpipette® Labsystems® 10 mL adapter	2004.1 ± 6.1 to 10094.9 ± 12.6	0.4	4*10 steps
digital Finnpipette® Labsystems® 5 mL adapter	994.5 ± 7.5 to 4968.8 ± 8.1	0.6	4*10 steps
digital Finnpipette® Labsystems® 200 µL adapter	15.1 ± 0.4 to 199.8 ± 0.2	1.9	4*10 steps
digital Finnpipette® Labsystems® 40 µL adapter	1.1 ± 0.1 to 39.5 ± 0.1	4.4	4*10 steps

[1]For accuracy ten pipetting steps for lowest and highest possible pipette volume.
[2] For RSD pipetting of different definite pipette volumes in each ten steps. Average RSD from measured mean pipetting volume and definite volume.

Table A 18. Major anion content in leachings with and without DOM

Sample ID	Cl^- [mg/L]	NO_3^- [mg/L]	SO_4^{2-} [mg/L]	Comment
MCL107A	0.03	<0.01	<0.03	with 10 mg/L F1-FA
MCL134B1	0.08	<0.01	1.49	with 10 mg/L F1-FA
MCL137	<0.03	0.04	<0.03	with 10 mg/L F1-FA
MCL131B	0.07	<0.01	0.11	with 10 mg/L F1-FA
CFW	0.07	0.04	1.19	with 10 mg/L F1-FA
Starr	0.04	0.31	0.54	with 10 mg/L F1-FA
MCL107A	0.10	0.09	<0.03	
MCL134B1	0.09	0.04	1.45	
MCL137	0.04	0.07	0.07	
MCL131B	0.07	0.05	0.16	
CFW	0.08	0.07	1.18	
Starr	0.05	0.37	0.57	

Table A 19. Correlation between Hg(II) associated with isolates and isolate reactivity given by SUVA

Isolate ID	Hg(II) associated with isolate	Isolate SUVA [L*mgC^{-1}*m^{-1}]
F1-FA	7.14	4.17
Suw-HA	37.20	6.56
2BSWCA-HPoA	6.83	3.17
WL-HPoA	3.95	2.20
CF06-0006-HPoA	8.84	3.5
F1-HPoA	10.59	3.93
Shapiro-Wilk normality test	not normal distributed at 0.05 level (p = 0.002)	normal distributed at 0.05 level (p = 0.410)
Pearson product moment correlation	significant non-zero correlation at 95 % confidence level R = 0.9, p = 0.01	
Spearman rank correlation	significant non-zero correlation at 95 % confidence level R = 0.83, p = 0.06	
Kendall rank correlations	significant non-zero correlation at 95 % confidence level R = 0.73, p = 0.04	

Table A 20. Examination of DOC sorption by soils after addition of 10 mg/L isolate

Isolate ID	DOC [ppm]	SD [ppm]	RSD	n[i]	Corrected sample DOC's in range of blank DOC[ii]	t-test[iii]	Wilcoxon signed rank
2BSWCA-HPoA					OK	< 0.05	0.2
blank[iv]	5.4	0.3	0.06	4			
average samples[v]	5.5	0.4	0.07	28			
CF06-0006-HPoA					OK	0.6	0.7
blank	5.5	< 0.1	0.00	2			
average samples	5.7	0.3	0.06	14			
F1-FA					except MCL137 out of range (6.8 ppm)	0.9	0.7
blank	5.5	0.4	0.07	2			
average samples	5.8	0.6	0.10	14			
F1-HPoA					except: CFW (6.6 ppm), MCL134B1 (5.7 ppm), and MCL131B (5.9 ppm)		
blank	4.4			1		0.1	0.7
average samples	5.6	0.9	0.15	11			
Suw-HA					OK	< 0.05	< 0.05
blank	5.0	0.2	0.03				
average samples	4.9	0.32	0.07	26		(tests indicate: avg. DOC background leaching > corrected Suw-HA DOC)	
WL-HPoA					OK	0.2	0.1
blank	5.4	0.16	0.03	2			
average samples	5.4	0.57	0.11	27			

[i] Because of experiment repetition n can be > 14; if there was too low sample for DOC analysis the result for the 2nd determination was removed, if much lower than the 1st determination, then n can be < 14 or 28.

[ii] Blank DOC range: examination, if the blank corrected average sample DOC`s under contemplation of their SD are in the range of the experiment blank average – SD and blank average + SD (comprises the added amount of DOM); possible differences also can be due to variability of added DOC stock solution volume

[iii] Tested was if there are differences between the blank corrected DOC content from the isolate experiment (corrected with the blank which contains just 10 mg/L isolate) and the average DOC from the background leaching (Table 10) of each sample. The null hypothesis was that the series equal each other, the alternative that there are differences. If there is no sorption of added DOM, the test should indicate no significant differences, i.e. p value > 0.05, what means that the null hypothesis will not be rejected. In the case of $p < 0.05$, the null hypothesis will be rejected, which indicates statistical significant differences.

[iv] Blank … comprises average of experiment blanks, leaching without soil.

[v] Average sample … comprises the average DOC of all samples in the particular experiment, corrected by the average DOC from the background leaching.

Table A 21. Correlation between Hg(II) release and net Hg(II) increase from the soil samples and chemical properties of isolates (molecular weight, SUVA, nitrogen, aromatic and aliphatic carbon content, carbon : hydrogen ratio)

Correlations which are significant, i.e. p-value < 0.05, are marked in grey. Hg(II) release … measured Hg(II) after leaching, net Hg(II) increase … difference between Hg(II) release measured in the particular experiment and the average Hg(II) release from the background leaching. The aliphatic II and III contents are less important regarding Hg(II) release from the soils, because they are a minor fraction the isolates.

Sample ID	a	b	R^2	p	n	a	b	R^2	p	n	a	B	R^2	p	n	a	b	R^2	p	n
Equation:	Net Hg(II) release = a*x + b;					Net Hg(II) release = a*x + b;					Net Hg(II) release = a*x + b					Net Hg(II) release = a*x + b;				
Characteristic x: Molecular weight [Da]						Characteristic x: C / H ratio					Characteristic x: Aliphatic II [% TC]					Characteristic x: Ar [% of TC]				
CFW	-0.02	19.79	0.52	0.04	8	-4.63	48.02	0.58	0.03	8	1.79	-29.66	0.59	0.03	8	-0.81	11.24	0.7	0.01	8
MCL134B1	-0.01	22.88	0.15	0.35	8	-1.56	32.61	0.17	0.30	8	0.69	5.33	0.23	0.23	8	-0.28	20.54	0.23	0.23	8
MCL107A	0.03	-7.88	0.69	0.01	8	4.25	-30.11	0.57	0.03	8	-1.82	43.41	0.7	0.01	8	0.77	3.2	0.72	0.01	8
MCL131B	0.01	-22.11	0.62	0.02	8	10.01	-74.15	0.51	0.05	8	-4.05	96.00	0.57	0.03	8	1.79	4.64	0.64	0.02	8
MCL137	-0.004	22.9	0.01	0.76	8	-0.87	28.61	0.02	0.72	8	0.10	17.14	< 0.01	0.92	8	-0.14	21.3	0.02	0.73	8
Starr	0.35	0.27	0.85	0.08	4	59.84	-329.55	0.82	0.09	4	-24.83	666.40	0.71	0.16	4	9.4	159.04	0.74	0.13	4
Characteristic x: Isolate SUVA [1000*L*mgC^{-1}cm^{-1}]						Characteristic x: N [wt%]					Characteristic x: Aliphatic III [%TC]					Equation: Hg(II) release = a*x + b; Characteristic x: SUVA [lL+mgC^{-1}*cm^{-1}]				
CFW	-0.4	10.96	0.59	0.02	8	30.21	-50.32	0.59	0.03	8	-8.04	38.44	0.77	< 0.01	8	-10.83	47.65	0.38	0.04	11
MCL134B1	-2.12	22.11	0.1	0.33	11	10.20	-0.49	0.18	0.30	8	-3.21	32.21	0.33	0.13	8	-2.11	52.10	0.10	0.33	11
MCL107A	0.37	4.52	0.62	0.01	8	-28.25	80.95	0.61	0.02	8	6.27	-15.27	0.55	0.03	8	4.11	13.64	0.20	0.17	11
MCL131B	0.88	7.43	0.56	0.02	8	-66.51	140.20	0.54	0.04	8	15.03	-40.55	0.51	0.05	8	9.50	44.60	0.20	0.20	11
MCL137	-0.08	21.3	0.02	0.69	9	5.48	10.38	0.02	0.73	8	-1.81	26.45	0.04	0.63	8	-0.30	36.20	< 0.01	0.85	11
Starr	4.99	130.6	0.5	0.18	5	384.40	930.40	0.82	0.09	4	24.90	203.20	0.05	0.77	4	55.90	291.30	0.28	0.26	6

Table A 22. Correlation between Hg(II) release and net Hg(II) increase from the sample soils and chemical properties of isolates (UVA, content of COOH and OH groups, sulfur, aliphatic carbon and ketone)

Correlations which are significant, i.e. p-value < 0.05, are marked in grey. Hg(II) release … measured Hg(II) after leaching, net Hg(II) increase … difference between Hg(II) release measured in the particular experiment and the average Hg(II) release from the background leaching. The ketone content is less important regarding Hg(II) release from the soils, because this is a minor fraction in the isolates.

Sample ID	a	b	R^2	p	n	a	b	R^2	p	n	a	b	R^2	p	n	a	b	R^2	p	n
Equation:	Net Hg(II) release = a*x + b;					Net Hg(II) release = a*x + b;					Net Hg(II) release = a*x + b					Hg(II) release = a*x + b;				
Characteristic x: COOH [meq/g]						Characteristic x: S [wt%]					Characteristic x: Carboxyl [% TC]					Characteristic x: UVA [cm^{-1}]				
CFW	13.2	-72.37	0.38	0.19	6	8.89	-15.36	0.19	0.28	8	-1.69	20.69	0.41	0.08	8	-34.17	24.51	0.22	0.15	11
MCL134B1	5.45	-12.88	0.16	0.43	6	4.7	9.47	0.14	0.36	8	-0.65	24.75	0.16	0.33	8	2.71	43.66	< 0.01	0.89	11
MCL107A	-15.72	99.23	0.60	0.07	6	-10.1	30.12	0.26	0.17	8	1.87	-10.11	0.58	0.03	8	73.44	13.12	0.95	< 0.01	11
MCL131B	-34.09	216.09	0.47	0.13	6	-20.04	63.71	0.18	0.30	8	4.07	-21.66	0.44	0.07	8	157.51	43.82	0.54	< 0.01	11
MCL137	-0.88	22.5	0.00	0.94	6	-2.13	20.77			8	0.04	17.77	< 0.01	0.97	8	16.85	26.4	0.16	0.22	11
Starr	-206.7	1412.25			2	1.4	341.2	< 0.01	1.00	4	31.7	-164.6	0.82	0.09	4	878.62	105.77	0.54	0.09	6
Characteristic x: OH [meq/g]						Characteristic x: Aliphatic I [% TC]					Characteristic x: Ketone [% of TC]									
CFW	-18.95	14.17	0.82	0.01	6	0.6	-30.35	0.71	0.01	8	-2.24	2.49	0.71	0.01	8					
MCL134B1	-7.64	22.97	0.32	0.24	6	0.21	5.77	0.24	0.22	8	-0.8	17.5	0.24	0.22	8					
MCL107A	17.58	1.06	0.77	0.02	6	-0.57	42.63	0.74	0.01	8	2.19	11.15	0.78	< 0.01	8					
MCL131B	39.75	1.45	0.66	0.05	6	-1.33	96.65	0.66	0.01	8	5.1	23.27	0.69	0.01	8					
MCL137	-1.88	20.99	0.01	0.87	6	0.09	14.57	0.02	0.74	8	-0.33	19.7	0.02	0.76	8					
Starr	129.17	265.95			2	-6.85	633.44	0.74	0.14	4	26.01	252.6	0.73	0.14	4					

Appendix B – Table of performance

Table B 1. Table of performance I

Date	Sample preparation	Analysis	Cleaning procedures	Additional experiments/ comments/ results
11/08/05 – 11/14/05 Soil preparation, XRD, sieving				
11/08/05	Description: Soils were air-dried for 72 hours at room temperature and then sieved with a 24 mesh metal sieve with 710 µm openings. Additional sieving was done with a set of sieves with different mesh width (710 µm, 355 µm, 250 µm, 0.125 µm, and 0.074 µm. Preparation of soil material for XRD (Siemens D5000 powder diffractometer, detector rotation (two-teta) from 5 to 65°, radiation source (high energetic electrons): CuK anode; (EBERL 2003; SRODON et al. 2001) Aim: Sieved soil fraction < 710 µm as material for all leaching experiments. Sieving with sieves of different size for soil particle size analysis. XRD to determine the soil mineralogy.			Possible loss of mercury during drying and sieving by volatilization. Dry sieving advantage versus wet sieving that mercury is not washed out. Disadvantage sieving with metal sieve – effect on trace metal determination by ICP-AES.
11/08/05	Wet soils into wave boats for drying, covered with paper towels, storage in a fume hood. Sample preparation for XRD from non-sieved freeze-dried (36 h) soil material. Weigh out exactly 1.0000 g sample and 0.1111 g ZnO into a plastic beaker.			 Samples in wave boats for drying. Left MCL137 (tailing), right MCL107A (serpentine soil).
11/09/05	Samples + 4 mL methanol in a McCrone Mill (5 min), fill into plastic beaker and rinse mill box for two times with methanol. Samples over night at 85 °C in dry-chamber.			Continuation of sample preparation for XRD.

Table B 2. Table of performance II

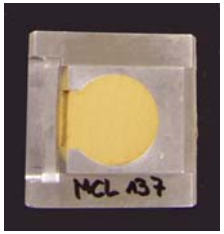
Date	Sample preparation	Analysis	Cleaning procedures	Additional experiments/ comments/ results
11/08/05 – 11/14/05 Soil preparation, XRD, sieving				
11/10/05	Samples out of dry-chamber. Sieving through a 500 µm sieve. Powder into slices (before clip slide and glass slide with the sleek side on top). Trapping on hard surface for even distribution of sieved material. Slides (see picture beside) into Siemens D5000 Diffractometer.		 **XRD slide with soil from MCL137**	Continuation of sample preparation for XRD. Data analysis by Zanden Frederick and Denis Eberl.
11/11/05	Dry soils into mercury clean glass beakers for sieving.			Soil aggregates after drying coarse and very hard. Ground with mortar and pestle.
11/14/05	Sieving for particle size analysis – 20 g of soil material, sieve sets like description above. The rest of the dried soil completely sieved through 710 µm sieve. Fraction < 710 µm for leaching experiments, rest storage in clean glass vials.			
	 **Sieved and air-dried soils for use in leaching experiments**. From left to right: MCL107A – serpentine soil, CFW – lake sediment, MCL137 – tailing material, MCL131B – fluvent = floodplain soil, Starr – sluice tunnel sediment, MCL134B1 – wetland sediment.			
	MCL107A white mineral particles (carbonate) visible. Rust colored iron bearing minerals visible in CFW. Red color of MCL137 conspicuous.			

Table B 3. Table of performance III

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 1010**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11**)**	**Others** (Table A 10)		
11/15/05 – 11/18/05 Kinetics (K) (Table A 1, no. 1A)												
	Description: Leaching solution (Table A 1, 1A) under definite conditions with pH 6.4 ± 0.06, I = 0.01 M using the soil samples: MCL137, CFW, and Starr; sampling after definite time steps Aim: Examine time for reaching equilibrium between solid and liquid phase.											All samples in duplicate. No blank was prepared. Filtering without centrifugation. Samples hard to filter (nearly 1 h per sample). Estimated equilibration time out of figures (e.g. Figure 8) is 24 h.
11/15/05	X	X(start)	X	labeling vials (each 36)					X (20)			set up samples for mixing on board (4.5 rpm), sampling after 2, 4, 7 h
11/16/05			X						X (12)			time steps 18, 24 h
11/17/05			X						X (6)			time step 48 h
11/18/05				X		X						reagent blank (RB), reductant for Hg(II) analysis (Table A 9), dilutions
11/22/05 – 11/25/05 Soil background leaching (BE) (Table A 1, no. 2A)												
	Description: Leaching experiment under definite conditions with pH 6.4 ± 0.06, I = 0.01 M (Table A 1, 2A) using all soil samples: MCL107A, MCL134B1, MCL137, MCL131B, CFW, and Starr; Aim: Background concentration for Hg(II) leaching = water soluble fraction.										.	Duplicates (i.e. leaching in separate tubes) for each soil and for experiment blank (i.e. no soil), used from here on and also for all following experiments. Hg(II) release between 9 ng/L (CFW) and 350 ng/L (Starr)
11/22/05	X	X (start)		labeling vials for DOC- and Hg(II)-filtrate (each 14)					X (14)		0.45 µm filters	test solutions: Table A 6, H, K; filtering in steps of 10 mL

Table B 4. Table of performance IV

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 1010**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
11/22/05 – 11/25/05 Soil background leaching (BE) (Table A 1, no. 2A)												
11/23/05			X									filtration of MCL137's: filter broken, i.e. break through of sample through membrane due to overpressure
11/25/06						X						sample dilution for Hg(II) analysis
11/27/05 – 11//30/06 Kinetics with DOM (KDOM) (Table A 1, no. 1B)												
	Description: Leaching solution (Table A 1), 1B) under definite conditions with pH 6.4 ± 0.06, I = 0.01 M using the soil samples: MCL137, CFW and Starr; sampling after a definite time steps. Aim: Examine time for reaching equilibrium between solid and liquid phase in a leaching system with additional DOM.											filtering with centrifugation (40 min); estimated equilibration time out of figures is 24 h (Figure 8). Better recovery between duplicate samples compared to experiments without centrifugation.
11/27/05	X			labeling vials (each 48)					X (35)		tube test (50 mL)	TubeTest1: centrifuge tubes Corning Inc., test solutions A, C, H, K, J, Table A 7)
11/28/05		X (start)	X	X					X (8)			set up samples for mixing on board (4.5 rpm), sampling after 1, 3, 5, and 8 hours; Hg(II) analysis BE, filter test, tube test
11/29/05			X		X				X (8)			time step 24 h; DOC analysis K, TOC analyzer O.I. Analytical Model 1010

Table B 5. Table of performance V

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 1010**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
11/27/05 – 11//30/06 Kinetics with DOM (KDOM) (Table A 1, no. 1B)												
11/30/05			X	X								time step 48 h; dilutions, KBr, $KBrO_3$, reagent blank (RB), reductant (R), standards for Hg(II) analysis (Table A 8, Table A 9) → analyzer broke down over night, samples 68-89 not analyzed
12/01/05 – 12/05/05 DOM experiment (Table A 1, no. 5)												
	Description: Leaching experiment with different DOC concentrations under definite conditions with pH 6.4 ± 0.06, I = 0.01 M (Table A 1, 5) using all soil samples (F1FA_0 mg/L, F1FA_1 mg/L, F1FA_5 mg/L, F1FA_10 mg/L). Aim: Determine effect of different DOC concentrations on Hg(II) release from soils.											DOC increase caused non-linear increase in Hg(II) release.
12/01/05	X			X	X							RB, R for Hg(II) analysis (Table A 8), rerun part of samples from KDOM (11/30/05); DOC for BE
12/02/05		X (start)		labeling vials (each 56)		X			X (60)			UVA KDOM
12/03/05			X			X						all MCL137 samples filter broken
12/05/05				X								vials for F1FA_1 mg/L MCL107A duplicate & MCL137 sample were broken during dilution, dilutions for Hg(II) analysis

Table B 6. Table of performance VI

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 1010**	**UVA**	**ICP - AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
12/06/05 – 12/12/05 pH experiment (Table A 2, no. 6B - F)												
	Description: Leaching experiment with variable pH, I = 0.01 M (Table A 2, 6B-F) using all soil samples (Table A 2, no. 6B - F). Aim: Determine effect of variable pH on Hg(II) release from soils.											With increasing pH, increasing DOC was observed, attributed to increased dissolution of soil organic matter (SOM), which in turn caused an increase in Hg(II) dissolution.
12/06/05	X											new pH buffer and ionic strength stock solution (Table A 4)
12/07/05		X (start)		labeling vials (each 70)					X (75)			pH adjustment buffers (HNO_3 , 1 M NaOH), buffer pH 8 precipitation new 0.1 M buffer solution (pH 8n)
12/08/05			X		X							all MCL137's – filter broken, DOC analysis KDOM, TubeTest1
12/09/05					X	X						UVA pH experiment, DOC analysis DOM experiment, Data processing DOC with Jennifer Schnackel
12/10/06					X	X						UVA pH experiment, DOC analysis DOM experiment and pH experiment
12/11/05												dilutions with RB for Hg(II) analysis pH experiment, standards for Hg(II) analysis (Table A 9)
12/12/05				X	X							RB, R for Hg(II) analysis (Table A 8), DOC analysis pH experiment

Table B 7. Table of performance VII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
12/14/05 – 12/16/05 Leaching without buffers (B) (Table A 1, no. 3A)												
	Description: Leaching experiment without adjustment of pH and ionic strength by buffers (Table A 1, 3A) using all soil samples. Aim: Comparison of leaching with and without buffers to exclude effects of pH buffer (phosphate) or ionic strength adjustment solution on Hg(II) release.											No significant difference between leaching with and without buffer and ionic strength adjustment.
12/14/06	X											
12/15/06		X(start)		labeling vials (each114)					X (16)			
12/16/06				X								RB, R for Hg(II) analysis (Table A 8)
12/19/05 – 12/22/05 Data processing Hg(II) analysis												
12/20/05						X						UVA B experiment
01/11/06 – 01/13/06 Filter test (FTII)												
	Description: Filter test of 0.45 µm filters with diameter 25 mm and 35 mm, and combination of both filters. Aim: In all experiments filters for sample MCL137 were broken because of filter clogging by fine material. Idea was to combine 0.45 µm filter with a diameter of 35 mm and a 0.45 µm filter with 25 mm diameter. Data from former experiments showed difference between filter of 35 mm diameter and 25 mm diameter; solution from 35 mm diameter was cloudy, reason: filter needs more rinses with ultrapure water (three times that of 25 mm filter). Filter test should show if there are differences in the resulting filtrate between these two filters of different diameters and a combination of both.											No significant differences between 0.45 µm filter (25 mm), filter combination 0.45 µm (0.25 mm + 0.35 mm), and 0.45 µm filter with 35 mm diameter detectable. For further experiments all MCL137 samples were filtered with filter combination of 0.45 µm filters (pre-filter 0.35 mm diameter + 0.25 mm diameter). Filter combination was used for additional safety, in case of pre-filter breaks

Table B 8. Table of performance VIII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
01/11/06 – 01/13/06 Filter test (FTII)												
01/11/06					X							DOC analysis – rerun all samples, because of high RPD's (previously analyzed with TOC Analyzer O.I. Analytical Model 1010) with instrument TOC Analyzer O. I. Analytical Model 700 (from here on used for all following DOC analysis)
01/12/06		X		labeling vials (each 70)					X(70)		0.45 µm filters	preparation of test solutions Table A 7, A-G ; DOC analysis B, FTII
					X							
01/13/06			X	X		X					0.45 µm filters	RB, R for Hg(II) analysis (Table A 8)
01/16/06 – 01/17/06 Data processing Hg(II) and DOC analyses												
01/16/06					X							DOC analysis FTII
01/18/06 – 01/20/06 Ionic strength experiment (I) (Table A 2, no. 7)												
	Description: Leaching experiment with variable ionic strength (I_0.1 M, I_0.01 M, I_0.001 M) (Table A 2, no. 7) using all soil samples. Aim: Determine effect of ionic strength on Hg(II) release from soils.											No pH adjustment; significant influence of ionic strength on Hg(II) release from soils. With decreasing I increased Hg(II) release; significant difference between I = 0.1 M and I = 0.01 M, 0.001 M; no sig. difference between I = 0.01 M and I = 0.001 M

Table B 9. Table of performance IX

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
01/18/06 – 01/20/06 Ionic strength experiment (I) (Table A 2, no. 7)												
01/18/06	X											
01/19/06		X(start)		labeling vials (42)					X (50)			
01/20/06			X	X	X							DOC analysis I_0.001, I_0.01; dilutions & Hg(II) analysis FTIII, RB, R
01/23/06 – 01/27/06 Isolates experiment (Table A 2, no. 8 A, C, D)												Hg(II) analyzer defect until 01/30/06
	Description: Leaching experiment with addition of various isolates (2BSWCA-HPoA, Suw-HA) (Table A 2, 8 A, C, D) in a concentration of 10 mg/L DOM under definite pH and ionic strength conditions (pH 6.4 ± 0.06, I = 0.01 M) using all soil samples. New filtration method: filtrate for Hg(II) analysis direct into test tubes for Hg(II) analyzer, plus ultrapure water (to get a total volume of 13 mL) and 350 µL BrCl. Aim: Determination effects of various chemical properties of different isolates on Hg(II) release.											Isolates caused a significant increase in Hg(II) release in comparison to leaching without DOM. A clear effect of certain properties could not be determined; for different soils, the isolates caused different effects.
01/23/06					X	X						UVA I, DOC analysis I_0.1; DOM stock solutions – 2BSWCA-HPoA, WL-HPoA, Suw-HA (Table A 4)
01/24/06	X	X(start)			labeling vials ICP, DOC (each 42)				X (50)	ICP bottles		ICP bottles (HDPE cylinders) filled with aqua regia, soaked over night.
01/25/06			X							ICP bottles		rinsing ICP bottles five times with ultrapure water
01/26/06					X							sample dilutions with ultrapure water for DOC analysis

Table B 10. Table of performance X

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
01/23/06 – 01/27/06 Isolates experiment (Table A 2, no. 8 A, C, D)												Hg(II) analyzer defect until 01/30/06
01/27/06					X	X						UVA isolates; sample dilutions with ultrapure water for DOC analysis
01/30/06 – 02//03/06 Isolates experiment – WL-HPoA, pH experiment pH 3, pH 12 (Table A 2, no. 6 A, G, 8 B)												
	Description: Leaching experiment with pH 3, pH 12 (I = 0.01 M), and with isolate WL-HPoA (I = 0.01 M, pH 6.4 ± 0.06) (Table A 2, no. 6 A, G, 8 B) using all soil samples. Aim: Determine effect of variable pH-value and various isolates on Hg(II) release from soils.											
01/30/06	X			X								Preparation buffers for pH 3 and pH 12 (Table A 4); Hg(II) analysis FTII – dilution samples with additional Hg(II), RB, R, standards Hg(II) analysis (Table A 8, Table A 9)
01/31/06		X(start)		X	labeling vials ICP, DOC (each 42)				X (50)	ICP bottles		Dilutions and Hg(II) analysis B and I experiments (no. 5, 7); RB, R for Hg(II) analysis
02/01/06			X	X						ICP bottles		Dilutions and Hg(II) analysis I experiment; RB, R

Table B 11. Table of performance XI

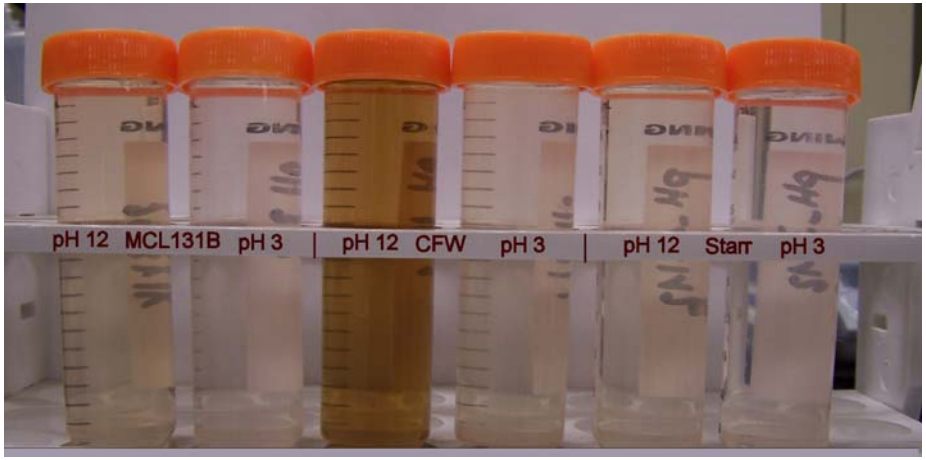
Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
01/30/06 – 02//03/06 Isolates experiment – WL-HPoA, pH experiment pH 3, pH 12 (Table A 2, no. 6 A, G, 8 B)												
02/01/06	 **Centrifuged samples from leaching with pH 3 and pH 12**											Visible leaching of soil organic matter at pH 12 (especially MCL131B and CFW), which causes a steep increase of Hg(II) dissolution from soils.
02/02/06				X	X							RB, R, standards for Hg(II) analysis (Table A 8, Table A 9); dilutions and DOC analysis for isolates and pH experiment. Measured Hg(II) concentration from pH 12 exceeds upper detection limit.
02/03/06				X								Dilution and rerun pH 12 samples.

Table B 12. Table of performance XII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
02/06/06 – 02/10/06 Model compound experiment (Table A 3, no.9)												
	Description: Leaching experiment with addition of organic ligands salicylic acid, mercaptoacetic acid, and EDTA (I = 0.01 M, pH 6.4 ± 0.06) (Table A 3, no.9) using all soil samples. Aim: Determination of effect of organic ligands (mercaptoacedic acid (MercAcid), EDTA, and salicylic acid (SaliAcid)) on Hg(II) dissolution from soils to compare the results with the effects of natural organic matter (NOM) (DOM experiment).											MercAcid acid shows strongest effect on Hg(II) dissolution from soils, because of significant complexation with Hg(II) comparable to DOM; minor effects for SaliAcid and EDTA.
02/06/06				X							salicylic acid	Test salicylic acid for Hg(II) content (solutions with 6.8 µmol/L and 68 µmol/L): Hg(II) < 1 ng/L < MDL. Preparation of stock solutions for EDTA, MercAcid, and SaliAcid (Table A 5).
02/07/06	X											
02/08/06		X			labeling vials ICP, DOC (each 42)				X (50)	ICP bottles		
02/09/06			X							ICP bottles		
02/10/06				X	X	X						RB, R, standards for Hg(II) analysis (Table A 8, Table A 9); UVA for pH 12, pH 3 and WL-HPoA; dilutions and DOC analysis model compounds

Table B 13. Table of performance XIII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	Preparat-ion of leaching	Sampling/ filtering (Figure 5)	Hg(II) CVAFS	DOC O.I. 700	UVA	ICP-AES	Fluor-escence	Filter, syringe (Table A 11)	Others (Table A 10)		
02/14/06 – 01/21/06 Repetition isolates experiment (Table A 2, no. 8 A-G)												Auto sampler working in two rows from here on.
	Description: Repetition of isolates experiment (01/24/06 + 01/31/06) and additional use of F1-FA and F1HPoA. DOM concentration of 10 mg/L, pH 6.4 ± 0.06, I = 0.01 M, with all soil samples. Aim: Repetition and extent of former isolate experiment to exclude variability in results - samples of 2BSWCA-HPoA, Suw-HA and BDOM from last isolate experiment stood for five days because mercury analyzer was defect.											Differences between blank corrected values for 2BSWCA-HPoA (samples MCL131B and Starr), WL-HPoA (CFW), Suw-HA (Starr), BDOM (MCL131B)
02/14/06	X											DOC stock solutions (Table A 4)
02/15/06		X(start)			labeling vials DOC (98)			X	X (115)			set up: BDOM, F1-HPoA, F1-FA, 2BSWCA-HPoA; start fluorescence B experiment - Blank,MCl107A, MCl134B1
02/16/06		X(start)	X									Set up: CF06-006-HPoA, WL-HPOA, Suw-HA
02/17/06			X	X								Hg(II) analysis BDOM, F1-HPoA, F1-FA, 2BSWCA-HPoA, problems with reductant flow at the beginning of analysis, problem solved before first standard row; RB, R for Hg(II) analysis
02/18/06					X							dilutions DOC analysis isolates
02/19/06					X							dilutions DOC analysis isolates
02/20/06					X							dilutions DOC analysis isolates

Table B 14. Table of performance XIV

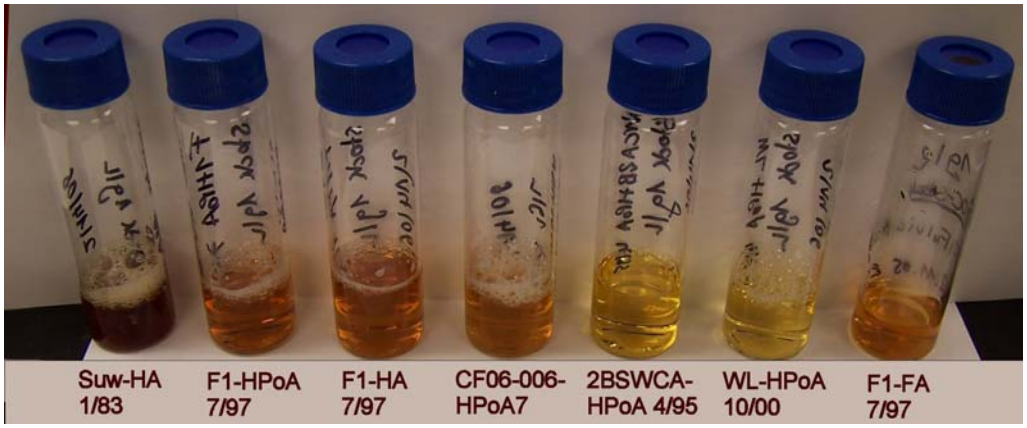
Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
02/14/06 – 01/21/06 Repetition isolates experiment (Table A 2, no. 8 A-G)												Problems with mercury analyzer, see above.
02/21/06				X		X						
	 **Isolate stock solutions in a concentration of 1 g/L freeze-dried DOM.**											Hg(II) analysis CF06-006-HPoA, WL-HPOA, Suw-HA. RB, R, and standards for Hg(II) analysis (Table A 8, Table A 9); UVA model compounds & repetition isolates; Problems with mercury analyzer: water bubbles in tube (to detector) pushed water level in gas/liquid separator under gas inflow level. No carrier gas could flow into gas/liquid separator and purge out the volatile mercury.
02/22/06 Filter test 0.02 µm Anotop® filters FilterTest III												
	Description: Filter test 0.02 µm filters (Anotop® filters with Anopore® membrane). Idea was to filter solutions with 0.45 µm filters and 0.02 µm filters. Hg(II) < 0.02 µm should give the dissolved fraction (< 0.02 µm), Hg(II) difference between 0.45 µm – 0.02 µm would be colloidal bound mercury. Aim: Test of these filter types for Hg(II) colloidal studies.											Hg(II) recovery < 30% for a test solution with DOM and Hg(II). Result: Filters do not fulfill the expectations for colloidal Hg(II) study.
02/22/06									each size 18 filters		0.02 µm filters	test solutions A, C, H, J, K (Table A 7); filtering in 10 mL steps

Table B 15. Table of performance XV

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
02/23/06 – 02/26/06 Leaching with Sacramento River water (SacRiver) (Table A 1, no. 4)												
	Description: Leaching experiment with water from Sacramento River (pH 6.4 ± 0.06, I = 0.01 M) using all soils (Table A 1, no. 4). Aim: Determine Hg(II) dissolution from soils using natural water.											Less Hg(II) release in comparison to leaching just with buffers and to leaching with 5 mg/L DOM (corresponds to the DOC of SacRiver). Reason: SUVA of 5 mg/L solution higher than SacRiver - not only amount of DOC also reactivity (explained as SUVA) is an important factor for Hg(II) release.
02/23/06	X	X			labeling vials DOC (14)				X(14)	ICP bottles		
02/24/06			X	X	X					ICP bottles		Hg(II) analysis FTIII and SacRiver, RB, R
02/25/06						X		X		DOC vials and test tubes		dilution and UVA for fluorescence; samples B experiment MCL137, MCl131B, and Starr Loss of digital DOC data from 02/24/06 – manual typing.
03/01/06 – 03/04/06 Filter test 0.02 µm Anotop® filters FilterTest III continuation												
	Description: Extension of filter test from 02/22/06, using the strong Hg(II) ligand mercaptoacedic acid and test solution with Hg(II) and DOM. Aim: Test of these filter types for colloidal Hg(II) studies.											

Table B 16. Table of performance XVI

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/02/06 – 03/04/06 Filter test 0.02 µm Anotop® filters FilterTest III continuation												
03/01/06		X	X			X			each size 6 filters		0.02 µm filters	test solutions K and L; filtering in steps of 10 mL
03/02/06					X							Complete loss of DOC data – printer defect and software was out of order.
03/03/06				X								exporting UVA files for fluorescence
03/04/06								X				pH adjustment, dilution, and UVA for fluorescence; fluorescence samples pH 12 blank, MCl107A
03/06/06 – 03/08/06 Calcium and Chloride experiment (Ca, CaDOM, Cl, ClDOM) (Table A 3, no. 10)												
	Description: Leaching experiment with addition of calcium ($2.5*10^{-4}$ M) and chloride (0.01 M) with and without presence of 10 mg/L DOM (I = 0.01 M, pH 6.4 ± 0.06) (Table A 3, no. 10) using all soil samples. Aim: Determination of polyvalent cations effect on Hg(II) dissolution from soils on the example calcium and effect of the inorganic ligand chloride.											Complete loss of data material for Hg(II) because of software error.
03/06/06	X											stock solutions for calcium and chloride (Table A 5)
03/07/06		X			labeling vials DOC, ICP (each 56)				X (60)			new type of ICP bottles, which are already cleaned with aqua regia and rinsed with ultrapure water
03/08/06			X									

Table B 17. Table of performance XVII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/08/06 – 03/10/06 Matrix experiment M, MDOM (Table A 3, no. 10)												
	Description: Leaching experiment with and without presence of 10 mg/L DOM (I = 0.01 M, pH 6.4 ± 0.06) (Table A 3, no. 11) using all soil samples, according to description in EPA method 1631 (TELLIARD and GOMEZ-TAYLOR 2002). Analysis of filtrate for Hg(II) and additional analysis of spiked filtrate with a definite concentration of added Hg(II) (Table A 6). Aim: Comparison of calculated concentration after spiking and measured Hg(II) content after spiking, to determine possible effects of the solution matrix on determination of Hg(II) with CVAFS.											RPD between spikes < 24% (EPA quality control acceptance criterion). Spike recovery between 71 and 125 % (EPA quality control acceptance criterion), except sample MCL137 (124 – 170 %). MCL137 seem to interact with filter – with each filter step increase of Hg(II) about 50 to 100 ng/L. Also possible that filter broke, which can cause increasing Hg(II).
03/08/06	X	X										
03/09/06			X	X								Hg(II) analysis Ca, CADOM, Cl, and CLDOM, RB, R → complete loss of all data, software error
03/10/06							X					Dilutions for ICP-AES – 1 : 10 with 1% HNO_3, samples isolates BDOM, SacRiver, SaliAcid, MercAcid, and EDTA
03/11/06								X				UVA, dilutions, and pH adjustment for fluorescence, samples pH 12 MCL134B1, MCL137

Table B 18. Table of performance XVIII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/12/06 – 03/14/06 Repetition of Calcium and Chloride experiment (Ca, CaDOM, Cl, ClDOM) from 03/07/06 (Table A 3, no. 10); **Spiking matrix experiment samples** (Table A 6)												
	Description: Leaching experiment with addition of calcium ($2.5*10^{-4}$ M) and chloride (0.01 M) with and without presence of 10 mg/L DOM (I = 0.01 M, pH 6.4 ± 0.06) (Table A 3, no. 10) using all soil samples. Aim: Determination of polyvalent cations effect on Hg(II) dissolution from soils on the example calcium and effect of the inorganic ligand chloride.											Calcium inhibits the Hg(II) release because of surface complexation of minerals, whereas chloride with a high affinity to Hg(II) increases Hg(II) release from soils.
03/12/06	X				labeling vials DOC, Hg(II) (each 56)			X	X (60)			stock solutions for F1-FA (Table A 4); fluorescence samples pH 12 MCL131B, CFW, Starr ; accuracy measurement balance Aiken Lab (± 0.001)
03/13/06		X		X								Hg(II) analysis matrix experiment, RB, R; spiking matrix experiment samples (see Table A 6)
03/14/06	X (for next exp.)		X	X	X							filtration into vials, so that repetition of Hg(II) analysis is possible; Hg(II) analysis matrix spikes → problems with reagent blank flow (pump takes not enough RB) on Hg(II) analyzer; problem was fixed after second sample group

Table B 19. Table of performance XIX

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/15/06 – 03/13/06 Leachings for ion chromatography analysis (IC, ICDOM) and repetition of DOM experiment (F1FA_1 mg/L, F1FA_5 mg/L) (Table A 1, no. 3B,C, and 5B, C)												
	Description: Leaching experiment without addition of buffers and ionic strength adjustment (Table A 1, no. 3B, C) with/without 10 mg/L DOM (IC, ICDOM) to use filtrate for analysis of anions chloride, sulfate and nitrate with IC using all soil samples. Repetition of leaching with additional DOM (F1-FA, Table A 1, no. 5B, C) in concentrations 1 mg/L and 5 mg/L DOM (I = 0.01 M, pH 6.4 ± 0.06). Aim: Determination of dissolved anions in leaching solution. Separate leaching just with ultrapure water, because addition of ionic strength adjustment solution (0.01 M $NaClO_4$) would overlay chloride peak.											Cl^- < 0.1 mg/L for all samples; highest $SO4^{2-}$ for CFW, MCL134B1, and Starr (2.0 mg/L, 1.6 mg/L, and 0.8 mg/L), rest < 0.2 mg/L; NO_3^- highest in Starr 0.7 mg/L, rest < 0.2 mg/L. No significant difference between solutions with and without DOM addition for $SO4^{2-}$ and Cl^-; differences significant for NO_3^- (addition of DOM causes lower NO_3^- dissolution)
03/15/06		X(start)		X	labeling vials ICP and DOC (56)				X (60)			dilutions and Hg(II) analysis Ca, Cl experiment; RB, R, standards (Table A 8, Table A 9)
03/16/06			X	X	X							DOC analysis and data processing Cl, ClDOM (from 03/08/06) with Shimadzu by Jennifer Schnackel; Rerun matrix spike samples for Hg(II), RB, R.
03/17/06					X	X	X					Dilutions for ICP 1 : 10 with 1% HNO_3 (samples pH3, pH12, Isolates: WL-HPoA, Suw-HA, CF06-006-HPoA;

Table B 20. Table of performance XX

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/15/06 – 03/13/06 Leachings for ion chromatography analysis (IC, ICDOM) and repetition of DOM experiment (F1FA_1 mg/L, F1FA_5 mg/L) (Table A 1, no. 3B,C, and 5B, C)												
03/17/06					X	X	X					DOC analysis and UVA of repeated Ca, CaDOM, F1FA_1 mg/L, and F1FA_5 mg/L by Jennifer Schnackel and Ryan.
03/18/06					X	X		X		DOC vials and test tubes		UVA, DOC analysis for Ca and CaDOM (from 02/08/06); UVA for Cl, ClDOM (from 02/08/06); dilutions and UVA for fluorescence samples BDOM CFW
03/19/06 – 03/21/06 Tube test Nalgene® tubes for 12,000 rpm spin (TubeTest2); experiment to determine Hg(II) contamination on sample material by air (HgAir); Repetition ionic strength experiment (I_0.001) (Table A 2, no. 7C)												
	Description: TubeTest2: Test of Nalgene® centrifuge tubes with different test solutions. HgAir: Set up of open test tubes filled with ultrapure water at different places in the lab (Aiken lab and Stallard lab) for a definite time (2 h and 8 h), to allow exchange with atmosphere and determine a possible Hg(II) contamination by the lab atmosphere. Repetition ionic strength experiment with definite I of I = 0.001 M, to compare results with the ones from first ionic strength experiment (01/18/06) Aim: TubeTest2: Test of these centrifuge tubes if there are any interactions with Hg(II) and DOM (i.e. sorption on tube wall) and if cleaning procedure is sufficient to remove all Hg(II) from solution of former spin. HgAir: Test, if there is a possibility of sample contamination by lab atmosphere.											No contamination of centrifuge tubes after cleaning procedure as described in Table A 10. Sorption of Hg(II) on tube walls < 3%. Contamination by lab atmosphere for an operation time of 2 h as usually necessary for sample preparation < 0.3 ± 0.1 ng/L.

Table B 21. Table of performance XXI

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results		
	Soil input	**Preparat-ion of leaching**	**sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)				
03/19/06 – 03/21/06 Tube test Nalgene® Oak Ridge tubes for 12,000 rpm spin (TubeTest2); experiment to determine Hg(II) contamination on sample material by air (HgAir); Repetition ionic strength experiment (I_0.001) (Table A 2, no. 7C)													**average Hg(II) contamination [ng/L]**	**SD**
												2h, Aiken lab	0.1	0.2
												8h, Aiken lab	0.9	0.3
												2h, Stallard lab	0.3	0.1
												8h, Stallard lab	0.4	0.1
03/19/06		X									tube test nalgene	Preparation of test solutions (Table A 1), I, K, and L); set up open test tubes filled with ultrapure water at different places in Aiken and Stallard lab		
03/20/06	X	X			labeling vials DOC (14)				X (14)	Nalgene test tubes				
03/21/06			X		X		X					Continuation TubeTest2; dilutions ICP – rerun samples from 03/17/06 plus Isolates: 2BSWCA-HPoA, F1-FA; DOC analysis and data processing Cl, ClDOM (from 03/12/06) with Shimadzu by Jennifer Schnackel		

Table B 22. Table of performance XXII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/22/06 – 03/31/06 Colloid experiment and pipette tests												
	Description: Colloids: Leaching experiments with and without 10 mg/L F1-FA (I = 0.01 M, pH 6.4 ± 0.06), with all soils (Table A 1, no. 5A, 5D), and leaching with additional 10 mg/L Suw-HA, Calcium and 10 mg/L F1-FA, mercaptoacedic acid and EDTA with the soils MCL107A, CFW and Starr. (Table A 2, no. 7D, Table A 3, no. 9A, B, and 10B). After filtration through 0.45 µm (Figure 5) centrifugation at 12,000 rpm for 5 h and 49 min. Pipette tests: Pipetting of three to five times of ten definite volumes of ultrapure water per pipette type on balance and calculating of average and standard deviation, giving the accuracy. Aim: Colloids: Separation of dissolved Hg(II) < 0.02 µm from colloidal Hg(II) 0.02 – 0.45 µm. Pipette tests: Pipettes were not calibrated during lab operating. Performance of test, to estimate the accuracy of pipetting.											Results pipette tests Table A 17. Recovery between adjusted and measured pipette volume for mostly used pipettes: Fisherbrand® Finnpipette®: volume range 200-1000 µL 0.5 % volume range 100-1000 µL 1.5 % volume range 20- 200 µL 0.7 % digital Finnpipette Labsystems®: adapter 10 mL 0.4 % adapter 5 mL 0.6 %
03/22/06	X	X		X	labeling vials DOC, ICP				X	Nalgene tubes		Set up leaching without DOM; Hg(II) analysis HgAir, TubeTest2, I_0.001, RB, R (Table A 8)
03/23/06		X	X	X					X			Set up leaching with/without DOM; Hg(II) analysis colloids, TubeTest2, RB, R
03/24/06		X	X						X		pipettes	Set up leaching with F1-FA and Suw-HA, pipette test
03/25/06		X	X						X		pipettes	Set up leaching with Suw-HA, MercAcid; new pH buffer (Table A 4); pipette test
03/26/06		X	X						X			Set up leaching with MercAcid, EDTA, and CaDOM

Table B 23. Table of performance XXIII

Date	Sample preparation			Analysis					Cleaning procedures		Tests	Additional experiments/ comments/ results
	Soil input	**Preparat-ion of leaching**	**Sampling/ filtering** (Figure 5)	**Hg(II) CVAFS**	**DOC O.I. 700**	**UVA**	**ICP-AES**	**Fluor-escence**	**Filter, syringe** (Table A 11)	**Others** (Table A 10)		
03/22/06 – 03/31/06 Colloid experiment												
03/27/06			X		X	X						DOC, UVA analysis colloid experiment
03/28/06			X						X 0.02 µm filters		0.02 µm filters	filter test Anotop® filters with test solution K, L
03/29/06				X	X			X				Hg(II) analysis colloid experiment; RB, R, KBr and $KBrO_3$, standards (Table A 8, Table A 9); Fluorescence pH 3 samples by Jennifer Schnackel; IC run & data processing by Jennifer Schnackel and Kenna Butler; dilutions and DOC samples for rerun
03/30/06				X			X	X				Hg(II) analysis colloids, TubeTest2, R, RB; dilutions and DOC samples for rerun; ICP dilutions 1: 10 with 1% HNO_3 samples F1FA_1 mg/L, F1FA_5 mg/L, colloids leaching with/without DOM, IC, ICDOM; Fluorescence pH 3 samples by Jennifer Schnackel;
03/31/06										DOC vials and test tubes		Introduction in ICP data processing with Quattro by Ronald C. Antweiler, USGS, Boulder; dilutions and DOC samples for rerun

Appendix C – Figures

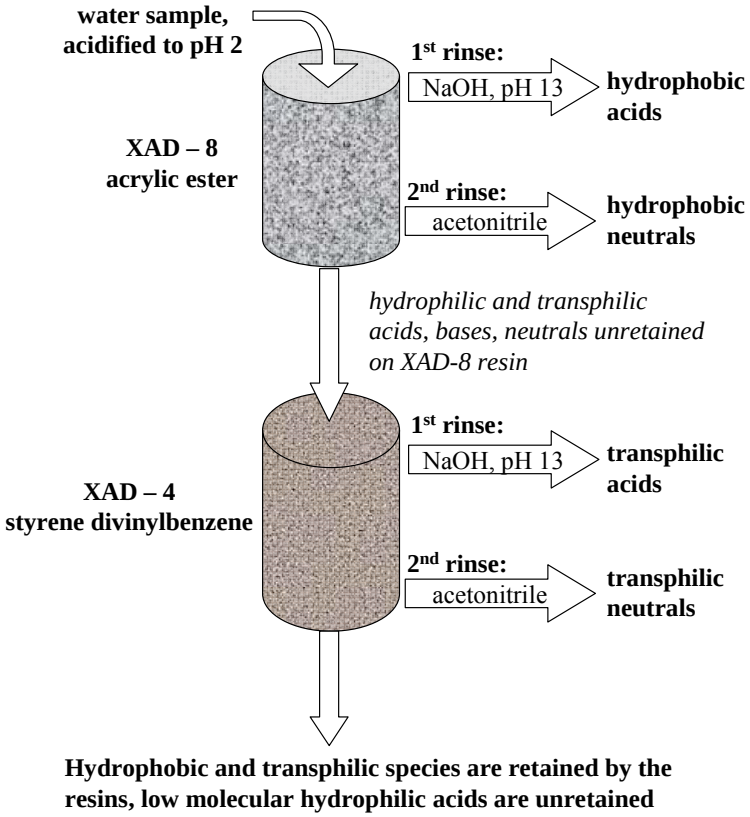


Figure C 1. Fractionation scheme for DOC according to AIKEN et al. (1992)

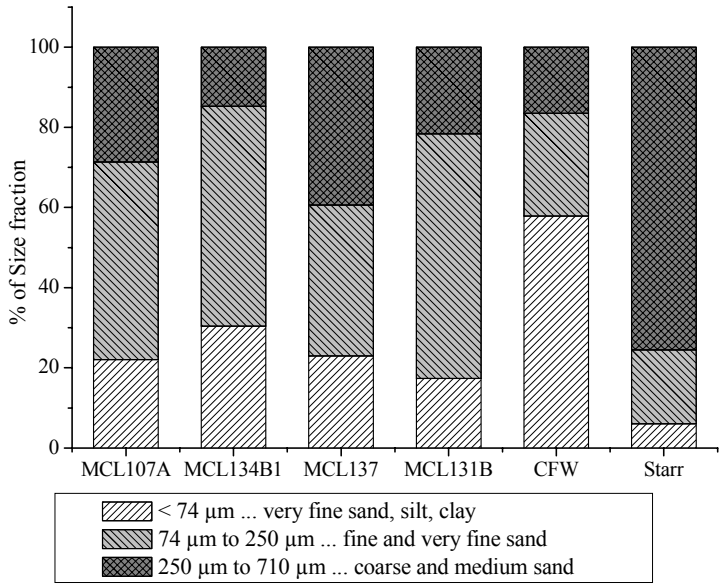


Figure C 2. Particle size distribution for soil material < 710 µm

Weightings for size fractions between < 74 µm and 710 µm were summarized and set as 100 %. Then the mass-percent of each fraction was calculated regarding to these 100% total soil < 710 µm. From the modified classification just the fraction > 710 µm was excluded, so that the resulting fraction comprises coarse and medium sand, no gravel.

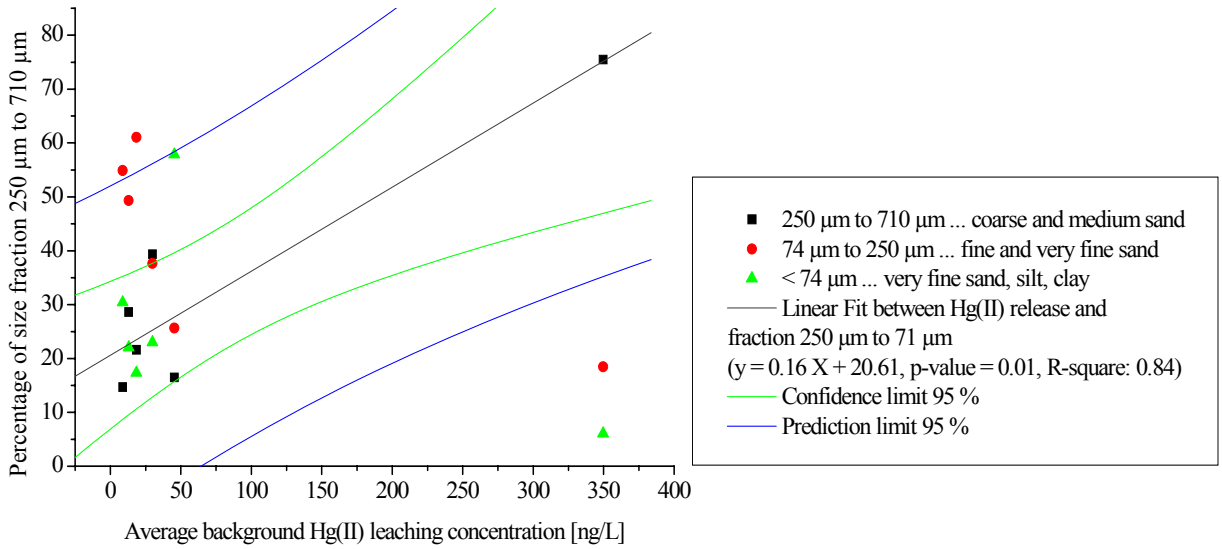


Figure C 3. Hg(II) release from background leaching versus particle size fractions for soil material < 710 µm with linear fit of Hg(II) release and percentage of fraction 250 to 710 µm

Spearman rank correlations not significant at p = 0.05, for Pearson product moment correlations were significant for particle size fraction 250 µm to 710 µm and Hg(II) release with R = 0.9 and p = 0.01; particle size fractions normal distributed at α = 0.05, Hg(II) release was not normal distributed (Shapiro Wilk)

Appendix D – Database

(Database with sampling site description, laboratory and experiment data attached on CD)

All digital data referred to in the following can be found in the database (Microsoft Access) on CD attached to this thesis.

The complete dataset of experimental results are summarized in the database (Figure D 1), which contains 59 tables, with references to the original data and files, and calculation files. In addition, information about the experiments with descriptions of experimental conditions, information about soil samples and sampling sites, and isolate information can be found in this database.

In Figure D 2 a brief description of the connections between the Access tables are presented and in the following tables (Table D 1 to Table D 37), the content of these tables are described. In these table columns marked with "🗗" are these columns were the particular table is connected to another one.

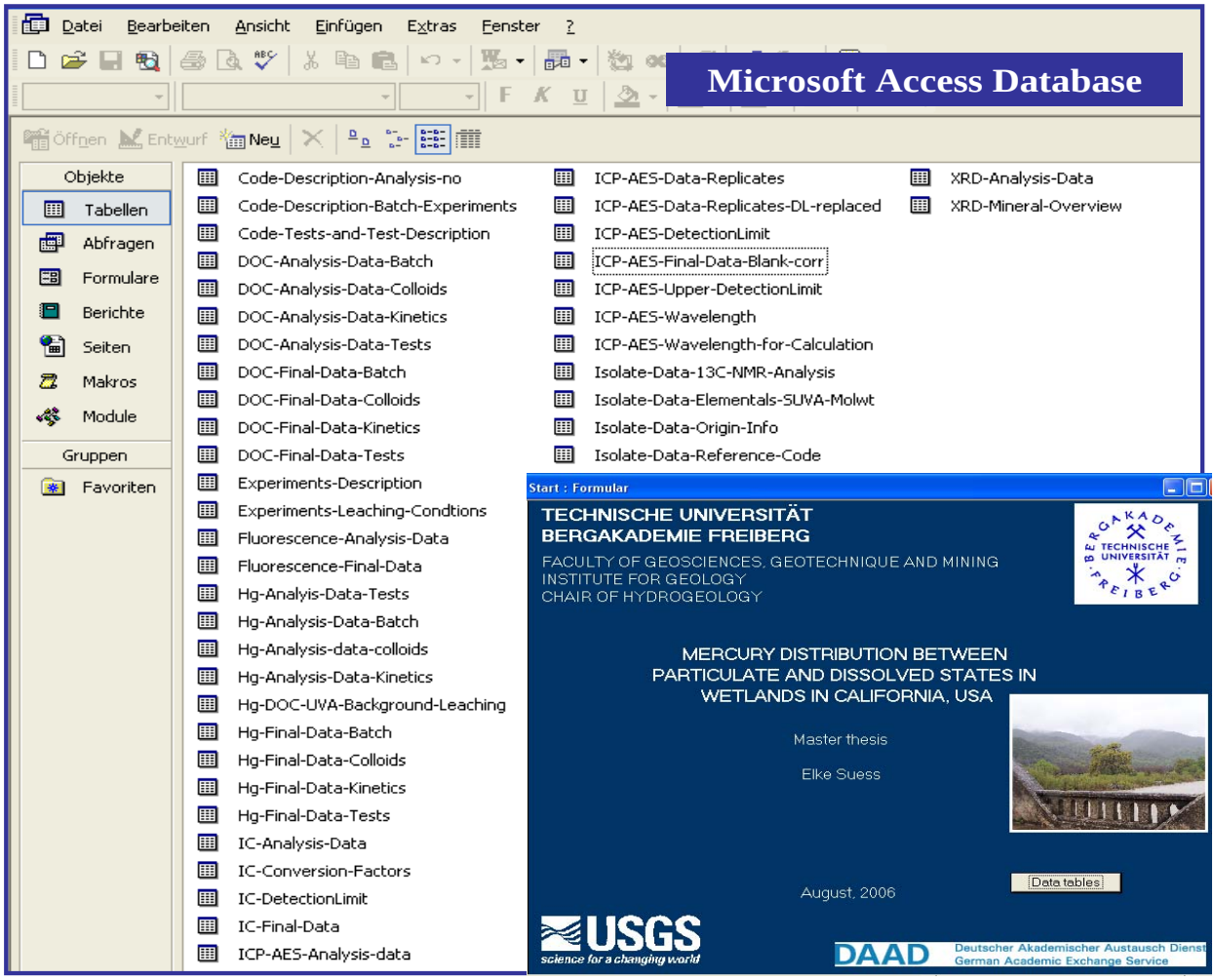


Figure D 1. Access database

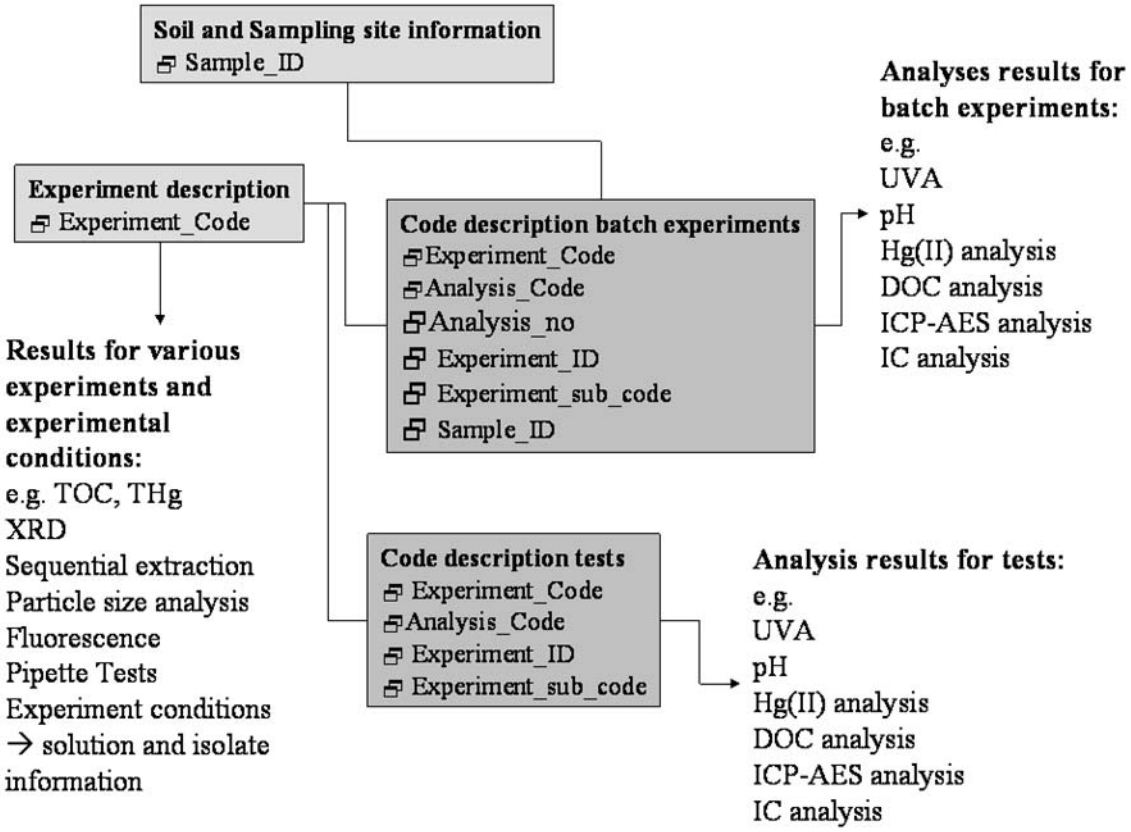


Figure D 2. Connections between tables in database

Code descriptions

Table D 1. Code description - analysis no.

Access table name: Code-Description-Analysis-no

Columns	Description	Example	
ID	primary key for Access (in each table)		
Analysis_no	no. which was attached to the abbreviation of experiment to identify the replicates of samples during the experiments and data analysis	no.	Sample ID
Sample_ID	identification of to analysis no. corresponding soil sample	0B1, 0B2 1, 2 3, 4 5, 6 7, 8 9, 10 11, 12	Blank MCL107A (serpentine soil) MCL134B1 (wetland sediment) MCL137 (tailing) MCL131B (fluvent) CFW (lake sediment) Starr (sluice tunnel sediment)
Description	connection between soil sample replicates and analysis no.	0B1 – Blank sample, 0B2 – Blank duplicate, 1 – MCL107A sample, 2 – MCL107A duplicate	

Table D 2. Code description for batch experiments and tests

Access table names: Code-Description-Batch-Experiments & Code-Tests-and-Test-Description

Columns	Description	Example
Analysis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	pH3_1, pH3_2, pH3_3, pH3_4
Analysis_code_abbreviation	analysis code contains experiment sub code (abbreviation of sub experiment) and analysis no.	Experiment_sub_code + Analysis_no (0B1, 0B2 = Blank, 1,2 = MCL107A, 3,4 = MCL134B1, 5,6 = MCL137, 7,8 = MCL131B, 9,10 = CFW, 11, 12 = Starr)
Analysis_no	no. which was attached to the abbreviation of experiment to identify the replicates of samples during the experiments and data analysis	1, 2, 3, 4
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH3_MCL107A pH3_MCL134B1
Experiment_ID_abbreviation	Experiment ID contains experiment sub code and sample ID	Experiment_sub_code + Sample_ID
Sample_ID	sample identification	MCL107A MCL134B1
Experiment_code	abbreviation for the main experiment	pH
Experiment_sub_code	abbreviation for the sub experiment	pH3
Description_test (just in table tests)	description of test experiment: identification of test (Filter test, tube test, HgAir for contamination test), test solution information, description of tested subject	FilterTestII, 5 mg/L DOM, Set1: 25 mm filter (0.45µm), filter step: 10-20 mL

Soil and sampling site information

Table D 3. Soil and sampling site information

Access table name: Soil-and-Sampling-Site-Info – contains information about sampling, sampling soil zone, collection area and site descriptions

Column	Description	Example
Sample_ID	sample identification	MCL107A
Site_No	site number	McL107A
Sample_Name	sample name	McLaughlin Reserve 107A
Latitude	Latitude	38.8621
Longitude	Longitude	-122.3697
Collection_Date	date of soil collection	5/30/2005
Site_Description	description of collection site	Hillslope serpentine soil along Blue Ridge. Site located in Cache Creek Watershed - major Hg source of the delta area.
State	State	CA
Country	Country	USA
Soil_sampling_zone	zone of which soil material comes from	0-5 cm
Soil_drainage	soil drainage degree	well-drained
Soil_defined_horizons	soil horizon from which sample was collected	A
Soil-Type	determined soil type	gravelly silt loam
Soil-Colour	visible soil colour in wet state	2.5YR3/1 wet
Sample_Preparation_On-Site	on site sample preparation	Soil samples were collected in clean glass containers, afterwards shipped frozen via FedEx to the USGS office in Boulder (Dr. George Aiken).
Reference_Site_information	reference for information about soil sampling and sampling sites	JoAnn Holloway (2005), USGS Denver, unpublished
Performance_Soil_sampling	performance of soil sampling	JoAnn Holloway, USGS Denver
Additional_Comments	comments and notes	

Experiment description

Table D 4. Experiment description and leaching conditions

Access table names: Experiments-Description, Experiments-Leaching-Conditions

Column	Description	Example
🗗 Experiment_code	abbreviation for the main experiment	pH
Description	experiment description	Leaching experiment with variable pH (buffer pH 3, 4, 6, 8, 10, 12), I = 0.1 M using all soil samples, Aim: Determine effect of variable pH on Hg(II) release from soils
Experiment_sub_code	abbreviation for the sub experiment	pH4
soil_input_g	soil input	0.25 g
soil_preparation	preparation of soil material before used in batch experiments	air-dried (72 h), sieved, fraction < 710 µm used for leachings
pH_buffer_mL	additional amount of pH buffer [mL]	0.5 mL
🗗 pH_buffer	name for used pH buffer	pH3 buffer
I_buffer_mL	additional amount of ionic strength adjustment solution [mL]	1.35 mL
🗗 I_stock	name for ionic strength stock solution	ionic strength stock
ultrapure_water_mL	amount of UPW [mL] to reach a total volume of 50 mL	48.5 mL
liquid_mL	amount of any else liquid [mL] to reach a total volume of 50 mL	
liquid	name of used liquid	e.g. Sacramento River Water
additional_DOM_mL	additional amount of DOM [mL]	
🗗 DOM-stock	name of DOC stock solution	e.g. F1-FA stock
additional_ingredients_mL	amount of additional ingredients [mL]	
stock-solution	name of stock solution	e.g. Ca stock
pH_conditions	Set up conditions for pH	4.7
SD_pH_conditions	SD from pH-values	0.6
Ionic_strength_conditions_M	set up conditions for ionic strength	0.1
Equilibration_time_h	time for equilibration	24 h (time in over-head shaker
Sampling_description	description of course after equilibration time	leaching for definite time, afterwards centrifugation at 2,800 rpm (40 min), then filtration through 0.45 µm filter
Hg(II)-Analysis DOC-Analyis UVA ICP-AES Fluorescence IC	performed analyses: X if analysis was performed for the sub experiment	X X X X X
Time_frame_experiments	begin and end of experiment	01/30/06 – 02/03/06
Time_frame_experiments_repetition	begin and end of experiment repetition	

Table D 5. Stock solutions

Access table names: Stock-solution-DOM, Stock-solution-additional-ingredients, Stock-solution-Ionic-strength, Stock

Column	Description	Example
DOM-stock I_stock pH_buffer stock-solution	Term for DOM, ionic strength or pH buffer stock solution	pH 3 buffer
DOM_stock_concentration_gL I_stock_concentration_M pH-buffer_concentration_M concentration_gL	concentration of stock solution, buffer [g/L or M]	1 M
Isolate_ID ingredients	Isolate ID, used for stock solution preparation, or chemical terms of ingredients	8.5 mM H_3PO4 + 91.4 mM $NaH_2PO_4*2H_2O$
buffer_pH_value (just for pH table)	pH-value for buffer solution	2.98
DOM_stock_preparation, preparation	brief description of preparation procedure	after dissolving 8.5 mM phosphoric acid plus 91.4 mM sodium phosphate monobasic, dihydrate in ultrapure, filtering through a cleaned (rinsed with 140 mL ultrapure water) 0.45 µm filter

Isolate information

Table D 6. Isolate information - elemental data

Access table name: Isolate-Data-13C-NMR-Analysis – contains element contents in isolates determined by ^{13}C-NMR analysis

Column	Description	Example
Isolate_ID	identification of isolate	F1-FA
Al-I_ %Total_0-62_ppm_13C-NMR	aliphatic carbon content in NMR range of 0 – 62 ppm as % of total carbon (TC)	43.4 % TC
Al-II_ %Total_62-90_ppm_13C-NMR	aliphatic carbon in NMR range of 62 – 90 ppm as % of total carbon	15 % TC
Al-III_ %Total_90-110_ppm_13C-NMR	acetal content in NMR range of 90 – 110 ppm as % of total carbon	5.4 % TC
Ar_ %Total_110-160_ppm_13C-NMR	aromatic carbon content in NMR range of 110 – 160 ppm as % of total carbon	20.1 % TC
C-I_ %Total_160-190_ppm_13C-NMR	carboxyl content in NMR range 160 – 190 ppm as % of total carbon	13.8 % TC
C-II_ %Total_190-230_ppm_13C-NMR	ketone content in NMR range of 190 – 230 ppm as % of total carbon	2.2 % TC

Table D 7. Isolate information - elementals and SUVA

Access table name: Isolate-Data-Elementals-SUVA-Molwt - contains information about acid groups, elementals C, H, O, N, S, and molecular weight of isolates

Column	Description	Example
Isolate_ID	identification of isolate	F1-FA
COOH_meqG	content of carboxylic groups [µeq/G]	5.6 µeq/G
OH_meqG	hydroxyl content of isolate [µeq/G]	0.88 µeq/G
SUVA_L mgC-1m-1	SUVA [$L*mgC^{-1}*m^{-1}$] calculated by measuring of UVA and DOC from liquid isolate before freeze-drying	4.17 $L*mgC^{-1}*m^{-1}$
C_wt%	content of C, H, O, N, S, and reduced S as weight %	45.94 wt%
H_wt%		4.37 wt%
O_wt%		39.67 wt%
N_wt%		1.43 wt%
S_wt%		1.6 wt%
red_S_mol%_totS		
ash	ash content [wt%]	7.31 wt%
mol_wt_Daltons	molecular weight of isolates [Daltons]	850 D

Table D 8. Isolate information – origin information and collection date

Access table name: Isolate-Data-Origin-Info – contains information about isolate origin and collection site

Column	Description	Example
Isolate_ID	identification of isolate	F1-FA
Location	location were sample was collected	F1
Isolate	DOC fraction	FA
Colletion_date	date of collection	07/01/1997

Table D 9. References for isolate information

Access table names: Isolate-Data-Reference-Code - contains reference number and description of reference, Isolate-Data-References - contains numbers of references which belong to particular isolate information

Column	Description	Example
Reference_Code	number of reference	E
Reference	description of reference	Ravichandran, M. et al. (1998): Enhanced Dissolution of HgS by DOM, ES&T, 32, 3305
Ref_red_S	number of reference were particular information resulted from	
Ref_Elementals_CHONS_ash		E
Reference_SUVA		E
Reference_mol_wt		E
Ref_Isolate_Origin_info		A
Ref_acid_site_density		E
Ref_13C-NMR_Analysis		E

Mercury analyses

Table D 10. Mercury analysis data for batch and colloid experiments, tests and kinetics

Access table names: Hg-Analyis-Data-Tests, Hg-Analysis-Data-Batch, Hg-Analysis-data-colloids, Hg-Analysis-Data-Kinetics … comprises instrumental output, calculation of Hg(II) concentrations and instrument information

Column	Description	Example
Analysis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	pH3_1 pH3_2
Experiment_code	abbreviation for the main experiment	pH
Experiment_sub_code	abbreviation for the sub experiment	pH3
Analysis_date	date of analysis	02/02/06
Calibration_curve	equation for calibration, resulting by plotting instrument output versus standard concentration	y=4.21*x+17.58; R^2=0.9958
Instrument-Output_Peak_high	Instrument output = peak high	pH3_1 27.6 pH3_2 21.4
Hg_ngL_measured_conc	calculated measured Hg(II) concentration	pH3_1 2.4 ng/L pH3_2 0.9 ng/L
DF	Dilution factor = sample volume / total volume (dilution with reagent blank)	pH3_1 0.51 pH3_2 0.51
Hg_ngL_dil_corr	concentration for Hg(II) corrected for dilution	pH3_1 4.7 ng/L pH3_2 1.8 ng/L
Soil_input_g	soil input for batch experiment	pH3_1 0.26 g pH3_2 0.25 g
Hg_ngL_soil-input_corr	concentration for Hg(II) corrected for soil input	pH3_1 4.6 ng/L pH3_2 1.8 ng/L
Hg_ngL_final_conc	Final Hg(II) concentration for replicate	pH3_1 4.6 ng/L pH3_2 1.8 ng/L
Reaction_time_h:min:s	just for kinetics - reaction time = time after sample take off from over-head shaker	
pH-value	pH-value of filtrate	pH3_1 4.77 pH3_2 4.75
Device	instrument were analysis was performed	CVAFS - Millenium Merlin PSA 10.025 - Atomic Fluorescence System
Sample_preparation_Hg-Analysis	Sample preparation procedure for Hg(II) analysis	sampling after 24 h; immediately spun at 2800 rpm (Beckman CPR Centrifuge, afterwards filtration with 0.45 um filter, then BrCl-addition, dilution with Reagent Blank
Hg_Excel-File	Excel file with calculations for analysis run	Hg060202_Isolates content (WL), pH-Experiment (pH 3, 12).XLS
Hg_Instrument-File	Instrument file for Hg(II) analysis	ES060202.RES
Comments_Hg	Comments and notes	

Table D 11. Final data for mercury analyses (batch, colloid, test, and kinetic experiments)
Access table names: Hg-Final-Data-Batch, Hg-Final-Data-Colloids, Hg-Final-Data-Kinetics, Hg-Final-Data-Kinetics - comprises final Hg(II) concentrations for soil samples

Column	Description	Example
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH3_MCL107A
SampleID	identification of soil sample	MCL107A
Experiment_code	abbreviation for the main experiment	pH
Experiment_sub_code	abbreviation for the sub experiment	pH3
Analysis_date	date of analysis	02/02/06
Hg_ngL_sample	Hg(II) concentration of replicate "sample"	pH3_1 4.6 ng/L
Hg_ngL_duplicate	Hg(II) concentration of replicate "duplicate"	pH3_2 1.8 ng/L
Hg_ngL_Avg	average Hg(II) for sample calculated from replicates	pH3_MCL107A 3.2 ng/L
STD_Hg_ngL	SD between replicate Hg(II) concentrations	2.0
RSD_Hg	RSD between replicate Hg(II) concentrations	0.6
Hg_ngL_Avg_corr	corrected Hg(II) sample concentration for experiment blank	2.1 ng/L
Hg_ngL_Blank_for_corr_Hg	Hg(II) concentration for experiment blank	1.1 ng/L
Experiment_ID_Blank_for_ cor_Hg	identification of blank used for correction	pH3_Blank
Hg_increase_ngL	calculated Hg(II) increase = Hg(II) sample – Hg(II) background leaching	
base_for_increase_calc	Hg(II) concentration for increase calculation	
base_experimentID_for_ increase_calc	identification of base used for increase calculation (background leaching)	
Reaction_time_sample_h:min:s	reaction time for replicate "sample"	
Reaction_time_duplicate_h:min:s	reaction time for replicate "duplicate"	
Reaction_time_Avg_h:min:s	average reaction time calculated from replicate times	
pH_sample	pH-value from replicate "sample"	pH3_1 4.77
pH_duplicate	pH-value from replicate "duplicate"	pH3_2 4.75
pH_Avg	average pH calculated from replicates	pH3_MCL107A 4.76

DOC Analyses

Table D 12. DOC analysis data for batch and colloid experiments, tests and kinetics

Access table names: DOC-Analysis-Data-Batch, DOC-Analysis-Data-Colloids, DOC-Analysis-Data-Kinetics, and DOC-Analysis-Data-Tests … Analysis data comprises calculated concentrations for DOC and total nitrogen (TN) for sample replicates, information to experiments and instrument were analysis were ran

Column	Description	Example
Analysis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	replicates:pH3_1, pH3_2
Experiment_sub_code	abbreviation for the sub experiment	pH3
Analysis_date	date of analysis performance	01/31/06
Dilution_factor	Dilution factor = volume of filtered sample/ total volume (dilution with UPW)	pH3_1 2.0 pH3_2 1.9
DOC_ppm_ 1st_determ	DOC analysis of first 7 mL sample injection (total volume for DOC analysis 14 mL)	pH3_1 1.6 ppm pH3_2 1.5 ppm
DOC_ppm_ 2nd_determ	DOC analysis of second 7 mL sample injection	pH3_1 1.6 ppm pH3_2 1.5 ppm
Avg_DOC_ppm	average of 1st and 2nd determination per replicate	pH3_1 1.6 ppm pH3_2 1.5 ppm
SD_DOC	standard deviation (SD)	
RSD_DOC	relative standard deviation (RSD)	
RPD_DOC	relative percent error (RPD)	
UVA_254nm_cm-1	UV absorbance at 254 nm for replicates	pH3_1 0.03 cm^{-1}] pH3_2 0.03 cm^{-1}
SUVA_L*mg C-1*m-1	specific UV absorbance calculated by: $SUVA[L*mgC^{-1}*m^{-1}] = 100 * \frac{UVA[cm^{-1}]}{DOC[ppm]}$	pH3_1 2.3 L*mgC^{-1}*m^{-1} pH3_2 2.4 L*mgC^{-1}*m^{-1}
TN_ppm_ 1st_determ	total nitrogen (TN) first sample volume injection	TN 1st determination for pH3_1 TN 1st determination for pH3_2
TN_ppm_ 2nd_determ	total nitrogen (TN) second sample volume injection	TN 2nd determination for pH3_1 TN 2nd determination for pH3_2
Avg_TN_ppm	average of 1st and 2nd TN determination for one replicate	TN for pH3_1 [ppm], TN for pH3_2 [ppm]
STD_TN	standard deviation	
RSD_TN	relative standard deviation	
Original-File_DOC	instrument file from analysis run	OI20060323
Excel-File_DOC	Excel file with calculations	DOC060323.XLS
Excel-File_UVA	Excel file with UVA results for replicates	UV-data.XLS
Device	instrument (Shimadzu, O.I. Analytical 1010, O.I. Analytical 700)	O.I. Analytical 700
Experiment	brief description of experiment	pH experiment, pH 4
Comments_ DOC	comments and notes	

Table D 13. DOC final data for batch and colloid experiments, tests and kinetics

Access table names: DOC-Final-Data-Batch, DOC-Final-Data-Colloids, DOC-Final-Data-Kinetics, DOC-Final-Data-Tests … final DOC results for each soil sample calculated from sample replicates (sample, duplicate) and blank correction

Column	Description	Example
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH3_MCL107A
Experiment_sub_code	abbreviation for the sub experiment	pH3
Analysis_date	date of analysis	01/31/06
Blank_for_correction	identification of blank which was used for the corrections	pH3_Blank
Avg_DOC_ppm_sample	average (avg.) DOC calculated from analysis data for one sample replicate "sample"	pH3_1 1.6 ppm
Avg_DOC_ppm_duplicate	average DOC calculated from analysis data for second sample replicate "duplicate"	pH3_2 1.5 ppm
Avg_DOC_ppm	average DOC calculated from the two replicates for soil sample	Average DOC for sample MCL107A for experiment with pH 3 (pH3_MCL107A) 1.5 ppm
SD_Avg_DOC_ppm	SD between replicates	0.04
DOC_corr	Blank corrected DOC content = Avg_DOC_ppm – DOC_value_for_correction	corrected DOC for pH3_MCL07A 1.4 pm
DOC_value_for_correction	Blank value for correction (DOC for blank in sub experiment)	DOC from pH3_Blank 0.2 ppm
UVA_254nm_cm-1_sample UVA_254nm_cm-1_duplicate	average UVA calculated from analysis data for replicates "sample", "duplicate"	pH3_1 0.03 cm^{-1} pH3_2 0.04 cm^{-1}
Avg_UVA_cm-1	avg. UVA from replicates	pH3_MCL107A 0.03 cm^{-1}
SD_Avg_UVA	SD between replicates	0.003
UVA_corr_com-1	blank corrected UV absorbance	pH3_MCL107A 0.04 cm^{-1}
UVA_cm-1_value_for_corr	UVA for blank in sub experiment	pH 4_blank 0.003 cm^{-1}
SUVA_L*mgC-1*m-1_sample SUVA_L*mgC-1*m-1_duplicate	SUVA calculated for replicates "sample", "duplicate"	pH3_1 3.4 $L*mgC^{-1}*m^{-1}$ pH3_2 3.5 $L*mgC^{-1}*m^{-1}$
Avg_L*mgC-1*m-1_SUVA	avg. SUVA from replicates	pH3_MCL107A 3.5
SUVA_L*mgC-1*m-1_calc	average SUVA for soil sample calculated from corrected UVA and DOC values from replicates	pH3_MCL107A 3.8 $L*mgC^{-1}*m^{-T}$
TN_ppm_sample TN_ppm_duplicate	TN for replicates "sample", "duplicate"	TN for pH3_1 [ppm] TN for pH3_2 [ppm]
TN_ppm_Avg_samples	avg. TN calculated from replicates	TN for pH3_MCL107A [ppm]
STD TN	SD between replicates	
TN_ppm_Avg_corr	blank corrected TN content	TN corrected for pH3_MCL107A
Blank_value_for_corr_TN	TN for blank in sub experiment	TN for pH3_Blank [ppm]
Comments_DOC	Comments and notes	

Fluorescence analyses

Table D 14. Fluorescence analyis data

Access table name: Fluorescence-Analysis-Data

Column	Description	Example
SAS ID	identification in lab database (USGS, Boulder)	Elke
Analyis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	pH3_1 pH3_2
Dilution factor	dilution factor = sample volume / total volume (dilution with UPW)	1
pH_adjusted	adjusted pH after neutralization	6.68
Analysis_date	date of analysis	03/30/06
Blank Subtracted file name	instrument file name after intern subtraction of blank values (UPW)	pH31s
UV Absorbance file name (csv)	exported UVA file name	pH31uv
Corrected EEM file name	File name after inner filter correction	pH3_1c
FI (fluoresence index)	calculated FI with MATLAB	1.095
EEM Figure scale	Scale (resolution) for MATLAB figure	4
Comments	comments and notes	
Performance	analysis and calculation performed by	Jennifer Schnackel, Kenna Butler, USGS, Boulder

Table D 15. Fluorescence final data

Access table name: Fluorescence-Final-Data

Column	Description	Example
Analysis_date	date of analysis	03/30/06
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH3_MCL107A
FI_sample FI_duplicate	FI for replicates “sample”, “duplicate”	FI for pH3_1 1.095 FI for pH3_1 1.095
FI_average	average FI calculated from replicates	pH3_MCL107A FI 1.095
FI_SD	SD between replicates	0
FI_RSD	RSD between replicates	0

Ion Chromatography (IC) analyis

Table D 16. IC analysis data

Access table name: IC-Analysis-Data - comprises calculated data for replicates

Column	Description	Example
Analysis_date	date of analysis	03/28/06
Analysis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	IC_1 IC_2
Experiment_code	abbreviation for the main experiment	IC
Experiment_sub_code	abbreviation for the sub experiment	IC
Cl_ueqL (NO3_ueqL, SO4_ueqL)	chloride (nitrate, sulfate) concentration [µeq/L] for replicates	Cl^- for IC_1 1.51 µeq/L Cl^- for IC_2 4.36 µeq/L
Cl_mgL (NO3_mgL, SO4_mgL)	chloride chloride (nitrate, sulfate) concentration in [mg/L] for replicates	Cl^- for IC_1 0.05 mg/L Cl^- for IC_2 0.15 mg/L
Performance	analysis and calculation performed by	J. Schnackel, K. Butler, USGS
Device	instrument were analyses were performed	Dionex DX-120 Ion Chromatograph

Table D 17. IC conversion factors and detection limit

Access table names: IC-Conversion-Factors, IC-DetectionLimit - comprises conversion factors for µeq/L to mg/L conversion and MDL for IC

Column	Description	Example
Analysis_date	date of analysis	03/28/06
Cl_CF_IC NO3_CF_IC SO4_CF_IC	conversion factors for chloride, nitrate and sulfate calculation from µeq/L into mg/L	CF for chloride 0.03 → mg/L = µeq/(1000*CF)
Description_Conversion_Factor_IC	description of CF calculation	CF=formula weight*charge; conc_mgL=conc_ueqL/1000/CF
Cl_ueqL (NO3_ueqL, SO4_ueqL)	detection limit for chloride (nitrate, sulfate) [µeq/L]	MDL chloride 0.8 µeq/L
Cl_mgL (NO3_mgL, SO4_mgL)	detection limit for chloride (nitrate, sulfate) [mg/L]	MDL chloride 0.03 mg/L

Table D 18. Final data IC

Access table name: IC-Final-Data - comprises final concentrations for chloride, nitrate and sulfate for samples and blank corrected results

Column	Description	Example
Analysis_date	date of analysis	03/28/06
🗗 Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	IC_MCL107A
Sample_ID	sample identification	MCL107A
Experiment_code	abbreviation for main experiment	IC
🗗 Experiment_sub_code	abbreviation for sub experiment	IC
Cl_ueqL_sample (Cl_ueqL_duplicate (corresponding for NO3, SO4)	concentrations for replicates [µeq/L]	Cl^- for IC_1 1.51 µeq/L Cl^- for IC_2 4.36 µeq/L
Cl_mgL_DLrepl_sample Cl_mgL_DLrepl_duplicate (corresponding for NO3, SO4)	concentrations for replicates [mg/L] with replacement of values < MDL by 0.3*MDL	Cl^- for IC_1 0.05 mg/L Cl^- for IC_1 0.15 mg/
Cl_mgL_Avg (corresponding for NO3, SO4)	average concentration of replicates [mg/L], MDL replaced	0.1 mg/L
Cl_mgL_Blank_corr (corresponding for NO3, SO4)	concentration corrected for experiment blank	0.1 mg/L
Blank_for_correction	identification of blank used for correction	IC_Blank

ICP-AES Analysis

Table D 19. ICP-AES upper and minimum detection limit

Access table name: ICP-AES-DetectionLimit - contains calculated minimum detection limit (MDL) (standard deviation above the blanks multiplied with the t-statistic at 95 %) for each run and all emission wavelength's, ICP-AES-Upper-DetectionLimit - contains upper detection limit (UDL) given by the highest standard concentration

Column	Description	Example
🗗 Analysis_date	date of analysis	03/21/06
Al1_ugL	MDL: calculated by the standard deviation above the blanks multiplied with the t-statistic at 95 %, → here: for the first emission line for Al UDL: highest standard concentration, here → highest concentration for Al standard	MDL 4.46 µg/L UDL 20,000 µg/L
Al2_ugL	MDL→ for the 2nd emission line for Al UDL → highest concentration for Al standard	MDL 2.33 µg/L UDL 20,000 µg/L
corresponding for 1st and 2nd emission line for: B, Ba, Ca, Cu, Fe, K (axial, radial), Li, Mg, Mn, Na (line 1,2 and 3), Ni, S, Si, Sr, V, Zn		

Table D 20. ICP-AES emission wavelengths

Access table name: ICP-AES-Wavelength - contains emission wavelength used for ICP-AES detection

Column	Description	Example
Analysis_date	date of analysis	03/21/06
Al1	emission wavelength for 1st Al line [nm	349.401 nm
Al2	emission wavelength for 2nd Al line [nm]	396,153 nm
corresponding for 1st and 2nd emission line for: B, Ba, Ca, Cu, Fe, K (axial, radial), Li, Mg, Mn, Na (line 1,2 and 3), Ni, S, Si, Sr, V, Zn		

Table D 21. Wavelength's used for analysis and interpretation of experiment results

Access table name: ICP-AES-Wavelength-for-Calculation - contains wavelength used for further interpretation and analyses of experimental results

Column	Description	Example
Analysis_date	date of analysis	03/21/06
Al	identification of most sensitive line, with in the range of detected sample concentration [nm] → for Al	Al2
B	identification of most sensitive line, with in the range of detected sample concentration [nm] → for B	B2
corresponding for Ba, Ca, Cu, Fe, K (axial, radial), Li, Mg, Mn, Na (line 1,2 and 3), Ni, S, Si, Sr, V, Zn		

Table D 22. ICP-AES analysis data

Access table name: ICP-AES-Analysis-data - contains calculated ICP-AES data for replicates dilution corrected for al wavelength

Column	Description	Example
Analysis_code	identification of replicates belonging to particular sub experiment during analysis and data processing	pH3_1 pH3_2
Experiment_code	abbreviation of main experiment	pH
Experiment_sub_code	abbreviation for the sub experiment	pH3
Analysis_date	date of analysis	03/21/06
Al1_ugL_1st_determ	calculated element concentration [µg/L] for first emission line, 1st determination of replicates → Al	pH3_1 … 81.94 µg/L pH3_2 … 57.77 µg/L
Al1_ugL_2nd_determ	calculated element concentration [µg/L] for first emission line, 2nd determination of replicates → Al	pH3_1 … 79.39 µg/L pH3_2 … 44.86 µg/L
Al2_ugL_1st_determ	calculated element concentration [µg/L] for second emission line, 1st determination of replicates → Al	pH3_1 … 56.17 µg/L pH3_2 … 41.69 µg/L
Al2_ugL_2nd_determ	calculated element concentration [µg/L] for second emission line, 2nd determination of replicates → Al	pH3_1 … 52.39 µg/L pH3_2 … 42.26 µg/L
corresponding for 1st and 2nd emission line for: B, Ba, Ca, Cu, Fe, K (axial, radial), Li, Mg, Mn, Na (line 1,2 and 3), Ni, S, Si, Sr, V, Zn		
Device	instrument were analyses were performed	ICP-AES, Perkin Elmer Optima 3300DV
Comments_ICP	comments and notes	

Table D 23. ICP data for replicates

*Access table names: ICP-AES-Data-Replicates - data restricted for most sensitive emission line, within the detected range of samples, ICP-AES-Data-Replicates-DL-replaced – restricted data with replacement of values < MDL by 0.3*MDL*

Column	Description	Example
Analysis_date	date of analysis	03/21/06
Analysis_Code	identification of replicates belonging to particular sub experiment during analysis and data processing	
Al_ugL_1st_determ	calculated element concentration [µg/L] for most sensitive emission line within detected range of sample, first determination of replicates → Al	pH3_1 … 56.17 µg/L pH3_2 … 41.69 µg/L
Al_ugL_2nd_determ	calculated element concentration [µg/L] for most sensitive emission line within detected range of sample, second determination of replicates → Al	pH3_1 … 52.39 µg/L pH3_2 … 42.26 µg/L
Al_ugL_Avg_replicates	average between replicates [µg/L]	pH3_1 … 54.28 µg/L pH3_2 … 42.11 µg/L
RSD_Al	RSD between replicates	pH3_1 … 0.05 pH3_2 … 0.01
corresponding for: B, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Ni, S, Si, Sr, V, Zn		

Table D 24. ICP-AES final data

Access table name: ICP-AES-Final-Data-Blank-corr - contains final data for samples with correction for experiment blank

Column	Description	Example
Analysis_date	date of analysis	03/21/06
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH3_MCL107A
Experiment_ID_Blank_for_corr_ICP_results	identification of experiment blank used for the correction	pH3_Blank
Al_ugL_Avg_replicates_sample	element concentration for replicate “sample”[µg/L]	pH3_1 54.28 µg/L
Al_ugL_Avg_replicates_duplicate	element concentration for replicate “duplicate” [µg/L]	pH3_2 42.11 µg/L
Al_ugL_Avg	average calculated from replicates	48.20 µg/L
Al_ugL_Avg_corr	average corrected for experiment blank	38.58 µg/L
corresponding for: B, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Ni, S, Si, Sr, V, Zn		
Comments_ICP_Samples		

UVA analysis and pH-values

Table D 25: pH-values for all experiments

Access table name: pH-all-Experiments – contains pH-values of all experiments measured immediately after filtration of first 10 mL leaching sample

Column	Description	Example
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	pH
Experiment_sub_code	abbreviation for the sub experiment	pH3
pH-value	measured pH-value for replicates	pH3_1 4.77 pH3_2 4.75
Analysis_date	date of analysis	02/02/2006
experimental_conditions	brief description of experimental conditions (pH, ionic strength)	pH =3, I = 0.1 M
Excel-File_pH	file were pH-values can be found	Hg060202_Isolates content (WL), pH-Experiment (pH 3, 12).XLS

Table D 26. UVA data

Access table names: UVA-Analysis-Data – contains measured UV absorbance for replicates, UVA-Data-Nitrate-corrected – contains corrected values for Ca sample to recalculate nitrate interference

Column	Description	Example
Analysis_Code	identification of replicates belonging to particular sub experiment during analysis and data processing	Ca_1 Ca_2
Analysis_date	date of analysis	03/18/06
UVA_254nm_cm-1	measured UV absorbance at 254 nm for replicates	Ca_1 0.04 cm^{-1} Ca_2 0.04 cm^{-1}
UVA_280nm_cm-1	measured UV absorbance at 280 nm for replicates	Ca_1 0.03 cm^{-1} Ca_2 0.03 cm^{-1}
Instrument-File_UVA	instrument file name for UVA run	CA031406.SD
Comments_UVA, performance	comments, performance and notes	Ryan Davis, UC student, USGS, Boulder
UVA_254nm_NO3_corrected	UVA corrected for Ca_Blank to recalculate interference of nitrate at UV absorbance	Ca_1 0.04 cm^{-1} Ca_2 0.04 cm^{-1}
Blank_for_NO3_corr	identification of blank used for correction	Ca_Blank
UVA_value_for_NO3_correction	UVA for correction blank	Ca_Blank 0.004 cm^{-1}

TOC and THg analysis

Table D 27. TOC and THg data

Access table name: TOC-THg-Final-Data – contains THg and TOC concentrations for samples

Column	Description	Example
Sample_ID	sample identification	MCL107A
Experiment_code	abbreviation for the main experiment	THg_TOC
TOC_%	total organic carbon content [%]	1.1 %
THg_ugG	total mercury content [µg/G]	4.3 µg/G
THg_STD	SD for THg	0.4 µg/G
Performance_THg	performance of THg analysis	Jarrod D. Gasper, USGS Boulder, CO, USA
Performance_TOC	performance of TOC analysis	Huffman Analysis Laboratories, Golden, CO, US

Background leaching results

Table D 28. Background leaching

Access table name: Hg-DOC-UVA-Background-Leaching - presents average blank corrected values for DOC, UVA, SUVA and Hg(II)

Column	Description	Example
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	MCL107A_avg_basic_leach
DOC_Avg_ppm	avg. DOC calculated from blank corrected replicates of four separate background leaching experiments	1.3 ppm
DOC_Avg_SD	SD between replicates of all four experiments	0.1 ppm
DOC_Avg_RSD	RSD between replicates of all four experiments	0.1
UVA_254nm_Avg	avg. UVA calculated from blank corrected replicates of four separate background leaching experiments	0.04 cm^{-1}
UVA_254nm_Avg_SD	SD	0.01 cm^{-1}
UVA_254nm_Avg_RSD	RSD	0.1
SUVA_calc	calculated SUVA from blank corrected results	3.5 [$L*mgC^{-1}*m^{-1}$]
Hg_Avg_ngL	avg. Hg(II) concentration calculated from blank corrected replicates of five separate background leaching experiments	13.0 ng/L
Hg_Avg_SD	SD between replicates of five experiments	1.9 ng/L
Hg_Avg_RSD	RSD between replicates of all four experiments	0.2
Comments	comments and notes	corrected with Hg(II) Blank_avg_basic_leach

Average data for DOM and isolate experiment

Table D 29. Average results for DOM experiment

Access table name: Average-DOM-Experiment - contains calculated average values for Hg(II), UVA, DOC and SUVA for the two runs of isolate and DOM experiments

Column	Description	Example
Sample_ID	identification of soil sample	MCL107A
Experiment_sub_code	abbreviation for the sub experiment	F1FA_0
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	F1FA_MCL107A
Hg_ngL_1st_run	Hg(II) concentration from first run	23.8 ng/L
Hg_ngL_2nd_run	Hg(II) concentration from second run	19.7 ng/L
Hg_ngL_Avg	average between runs	2.7 ng/L
STD_Hg_ngL	SD between runs	2.9 ng/L
Avg_Hg_ngL_corr	average corrected for experiment blank	17.4 ng/L
Net_Hg_increase_ngL	calculated Hg(II) increase as difference of Hg(II) concentration for sample and average Hg(II) concentration from background leaching	4.4 ng/L
UVA_254nm_cm-1_1st_run DOC_ppm_1st_run SUVA_L*mgC-1*m-1_1st_run	UVA (DOC, SUVA)from first run	UVA 0.07 cm^{-1}
UVA_254nm_cm-1_2nd_run DOC_ppm_2nd_run SUVA_L*mgC-1*m-1_2nd_run	UVA (DOC, SUVA)concentration from second run	UVA 0.08 cm^{-1}
UVA_254nm_cm-1_avg DOC_ppm_Avg SUVA_L*mgC-1*m-1_avg	average between runs	UVA 0.08 cm^{-1}

Table D 30. Average results for isolate experiment

Access table name: Average-Isolate-Experiment - contains calculated average values for Hg(II), UVA, DOC and SUVA for the two runs of isolate and DOM experiments

Column	Description	Example
Sample_ID	identification of soil sample	MCL107A
Experiment_sub_code	abbreviation for the sub experiment	Isolates_WLHPoA
Experiment_ID	identification of samples belonging to a sub experiment after processing of final data	Avg_WLHPoA/MCL107A
Hg_ngL_1st_run_blankcorr	Hg(II) concentration from first run, blank corrected	29.0 ng/L
Hg_ngL_2nd_run_ run_blankcorr	Hg(II) concentration from second run, blank corrected	30.4 ng/L
Hg_ngL_ Avg_blankcorr	average between runs, blank corrected	29.7 ng/L
STD_Hg_ngL	SD between runs	1.0 ng/L
Net_Hg_increase_ngL	calculated Hg(II) increase as difference of Hg(II) concentration for sample and average Hg(II) concentration from background leaching	16.7 ng/L
UVA_254nm_cm-1_1st_run DOC_ppm_1st_run SUVA_L*mgC-1*m-1_1st_run	UVA (DOC, SUVA)from first run	UVA 0.15 cm^{-1}
UVA_254nm_cm-1_2nd_run DOC_ppm_2nd_run SUVA_L*mgC-1*m-1_2nd_run	UVA (DOC, SUVA)concentration from second run	UVA 0.16 cm^{-1}
UVA_254nm_cm-1_avg DOC_ppm_Avg SUVA_L*mgC-1*m-1_avg	average between runs	UVA 0.16 cm^{-1}

Sequential extraction data

Table D 31. Sequential extraction data

Access table name: Sequential-Extraction-Final-Data – contains mercury content in various fractions depending on solubility with different chemicals for replicates and soil samples

Column	Description	Example
Sample_ID	sample identification	MCL107A
Experiment_code	abbreviation for the main experiment	SeqExtract
Hg_%_F1_sample	mercury content in particular fraction as % of total mercury → Hg for replicate "sample" in fraction 1	0.2 %
Hg_%_F1_duplicate	mercury content in particular fraction as % of total mercury → Hg for replicate "duplicate" in fraction 1	0.2 %
Hg_%_F1_avg	average mercury content of replicates → form fraction 1	0.2%
Hg_%_F1_SD	SD between replicates	0.01
Performance_SeqExtraction	performance of sequential extraction	Jarrod D. Gasper

Table D 32. Sequential extraction fractions

Access table name: Sequential-Extraction-Fractions – contains description of all five fractions and THg - extract, mercury fraction, and typical extracted mercury form

Column	Description	Example
Experiment_code	abbreviation for the main experiment	SeqExtract
Performance_information	information about performance - extract and mercury fraction	Extract
F1 to F5, THg	fraction 1	Ultrapure water (i.e. extract for fraction 1 is UPW)

XRD analysis

Table D 33. XRD data

Access table names: XRD-Analysis-Data – contains weight % of detected minerals in soil samples, XRD-Mineral-Overview – contains an overview about minerals – class and formula

Column	Description	Example
Analysis_date	date of analysis	12/06/05
Experiment_code	abbreviation for the main experiment	XRD
Sample_ID	identification of sample	MCL107A
intermediate_Microline_feldspar	detected minerals and content in weight %	0 wt %
corresponding for other minerals		
Device	instrument were analysis was performed	Siemens D5000 Diffractometer, Cu K-alpha radiation, Software for data processing RockJock
Performance_XRD	XRD performed by	Zan Frederick, Dennis Eberl, USGS Boulder, CO, USA
mineral_name	name of mineral	intermediate Microline feldspar
formula	chemical formula for mineral	$AlSi_3O_8$
mineral class	class to which mineral occurs	feldspar

Particle size analysis

Table D 34. Final data for particle size analysis

Access table name: Sieve-Analysis-Final-Data – contains the percentages of each size fraction for the soil samples

Column	Description	Example
Experiment_code	abbreviation for the main experiment	
Sample_ID	sample identification	Starr
Analysis_date	date of analysis	11/26/05
%_particle_size_fraction > 710 µm	soil sample: percentage in particular particle size fraction for	11..5 %
%_particle_size_fraction 355 - 710 µm		53.4 %
%_particle_size_fraction 250 - 355 µm		13.4 %
%_particle_size_fraction 125 - 250		12.0 %
%_particle_size_fraction 74 - 125 µm		4.3 %
%_particle_size_fraction < 74 µm		5.3 %

Table D 35. Particle size analysis raw data

Access table names: Sieve-analysis-raw-data – contains sieve weights and calculated percentage of particle size fraction, Sieve-Analysis-Soil-Input-and-RPD – contains soil input and comparison to sum of net weight of al fractions

Column	Description	Example
Analysis_date	date of analysis	11/14/06
Sample_ID	sample identification	Starr
Mesh_size_um	mesh size of sieve	710 µm
Size_fraction_um	size fraction in µm	> 710 µm
Empty_weight_sieve_g	empty weight sieve [g]	432.0
Weight_plus_sieved_material_g	weight sieve plus sample [g]	434.3
Net_weight_in_fraction_g	net weight = weight sample plus sieve[g]– empty sieve weight [g]	2.3 g
Percentage_size_fraction_%	percentage of size fraction calculated by sum of weights of all fractions	11.5 %
total_soil_input_g	soil input for sieve analysis [g]	20.00 g
sum_net_weights_g	sum of net weights of all sieve fractions for one soil sample [g]	20.05 g
RRD_%	RPD calculated between soil input and sum of net weight	0.27 %

Table D 36. Corresponding size fractions to USDA and mineralochemical fractions

Access table name: Sieve-Analysis-Size-Fractions - contains corresponding size fractions to official size classifications, e.g. USDA

Column	Description	Example
Size_fraction_um	size fraction in µm	> 710 µm
Corresponding_USDA_fractions	corresponding fraction in USDA classification	gravel > 1000 µm + coarse sand (1000 – 500 µm)
Corresponding_mineralochemical_fractions	corresponding mineralochemical used classification	gravel and coarse sands (> 100µm)
Reference_fractions	reference of classification systems	Jackson, M. L. (1956): Soil Chemical Analysis - advanced Course. 2nd Edition, 11th printing. Published by the author, Madison, Wisconsin, 991 p.

Pipette tests

Table D 37. Results for pipette testing

Access table name: Results-Pipette-Tests – contains results from pipette tests were definite volume of UPW was pipetted onto balance an weight noted

Column	Description	Example
Experiment_code	abbreviation for the main experiment	PipetteTest
Analysis_date	date of analysis	03/24/06
pipette_type	pipette type, manufacturer	Fisherbrand ® Finnpipette® 200-1000 µL
definite_pipette_volume_uL	definite pipette volume for pipetting on to balance [µL]	350 µL
pipetting_step_1_g to pipetting_step_10_g	resulting weight for pipetted volume [g](procedure was repeated 10 times)	0.3504 g (step 1)to 0.3519 g (step 10)
Average_pipette_volume	average of weight of pipetted volume	0.3511 g
SD_pipette_volume	SD of weight of pipetted volume	0.0004 g
RSD_pipette_volume	RSD of weight of pipetted volume	0.001

Appendix E – Literature database

(EndNote database which can be found on CD attached to this thesis with mercury related literature: paper, master and doctoral thesis', reports and web pages)

Appendix F – Instrument and data files

(digital original data from instruments and calculations - mercury, UVA, and DOC attached on CD)