Speciation of Mercury in Hg-contaminated Soils from Oak Ridge TN

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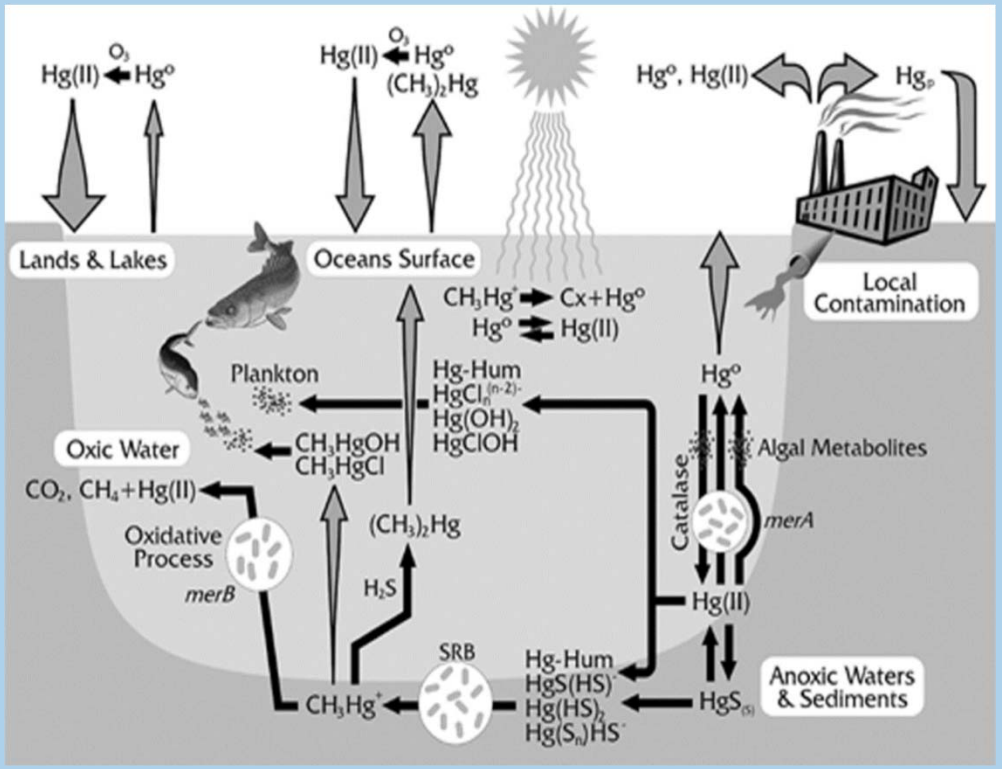
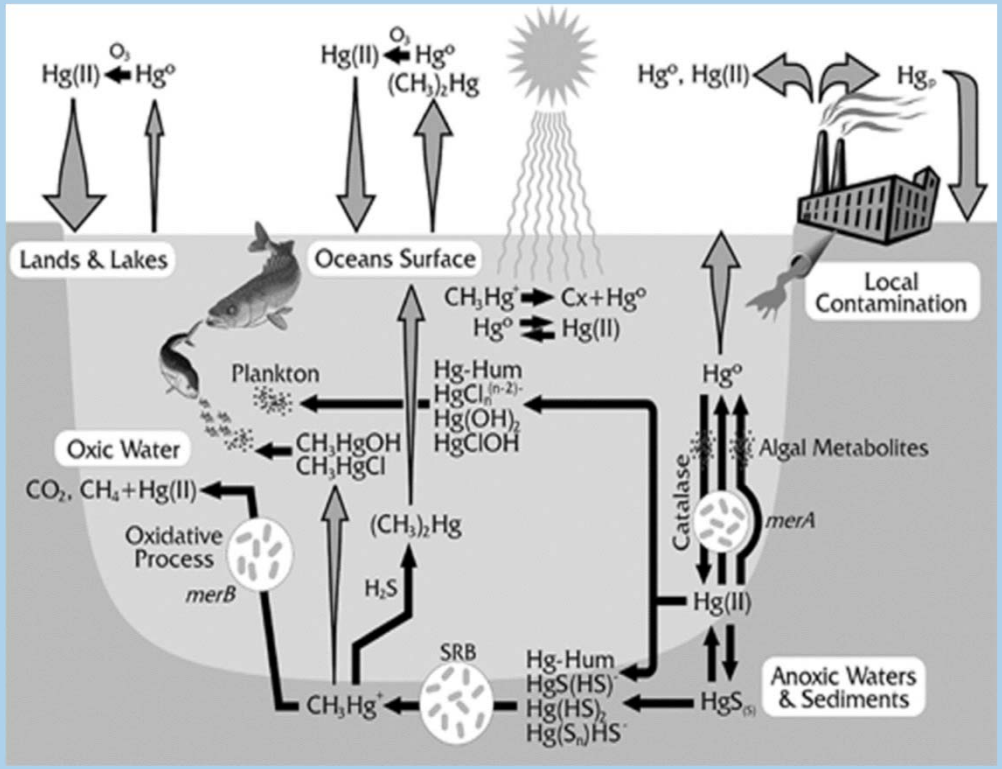
Mercury

- Released into the atmosphere from natural sources, such as volcanic eruptions and ocean emissions, as well as from anthropogenic sources.
- Distributed throughout the environment in various inorganic and organic forms, including elemental (Hg^0), mercurous (Hg_2^+), mercuric (Hg^{2+}) and alkylated compounds (methylmercury and ethylmercury).
- Strong neurotoxin impacting the central and peripheral nervous system. Organomercury species (methylmercury) bioaccumulate in many different environments.



Mercury

- Mercury exists in the environment in different forms: *elemental (Hg^0), mercurous (Hg_2^{2+}), mercuric (Hg^{2+}), and alkylated mercury compounds (CH_3Hg^+).*
- HgO and $HgCl_2$ are relatively soluble Hg species in water, with solubilities of 0.051 g/L at 25 °C and 69 g/L at 20 °C, respectively.
- Mineral cinnabar (HgS) is the most insoluble (4.65×10^{-25} g/L at 25 °C) form.
- (CH_3HgCl) is considered lipid soluble due to its lower solubility in water (0.10 g /L at 21 °C).



Legacy Hg Contamination in Oak Ridge, TN

- In 1960's, elemental Hg was used at Y-12 National Security Facility to separate Li isotopes for manufacturing components of nuclear weapons.
- It is estimated that 350 tons of Hg was released to environment.
- Hg distributed through run-off by the East Fork Poplar Creek (EFPC) which ran through the Y-12 complex, flowing into the surrounding community and terminating at the Clinch River.

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History of mercury use and environmental contamination at the Oak Ridge Y-12 Plant

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Mercury discharges from an industrial plant have created a legacy contamination problem exhibiting complex and at times counter-intuitive patterns in Hg cycling.

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ABSTRACT

Between 1950 and 1963 approximately 11 million kilograms of mercury (Hg) were used at the Oak Ridge Y-12 National Security Complex (Y-12 NSC) for lithium isotope separation processes. About 3% of the Hg was lost to the air, soil and rock under facilities, and East Fork Poplar Creek (EFPC) which originates in the plant site. Smaller amounts of Hg were used at other Oak Ridge facilities with similar results. Although the primary Hg discharges from Y-12 NSC stopped in 1963, small amounts of Hg continue to be released into the creek from point sources and diffuse contaminated soil and groundwater sources within Y-12 NSC. Mercury concentration in EFPC has decreased 85% from ~2000 ng/L in the 1980s. In general, methylmercury concentrations in water and in fish have not declined in response to improvements in water quality and exhibit trends of increasing concentration in some cases.

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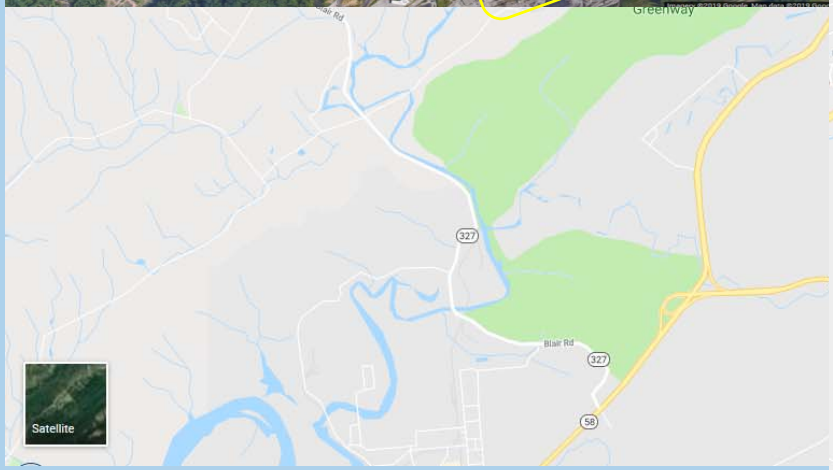
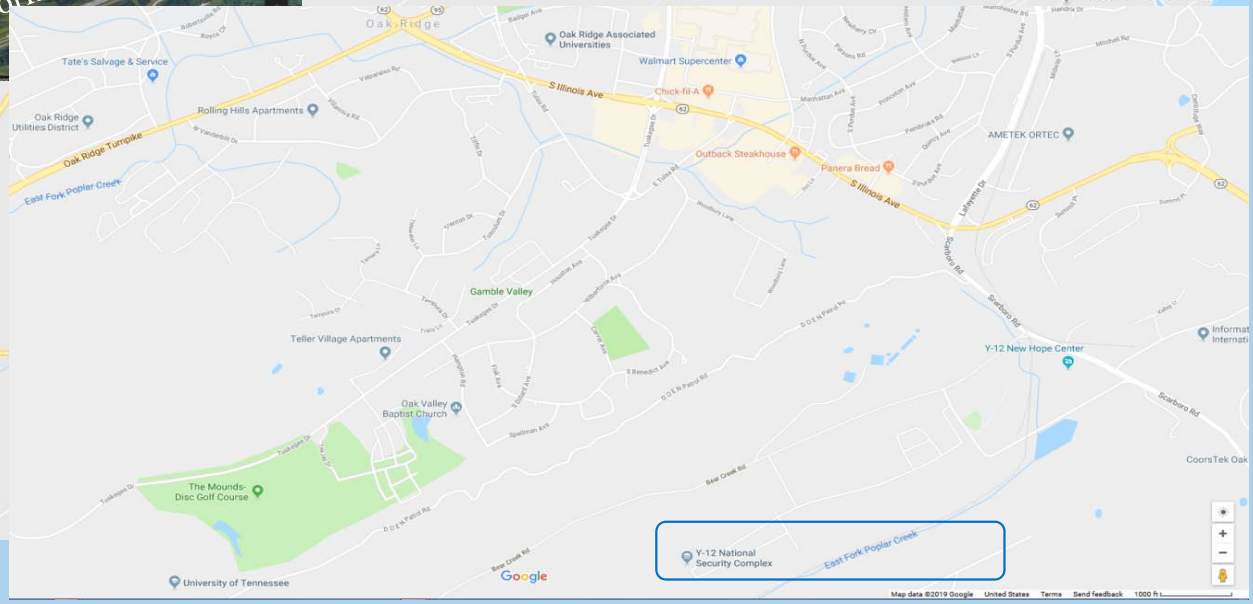
Legacy Hg Contamination in Oak Ridge, TN





Statement of Problem

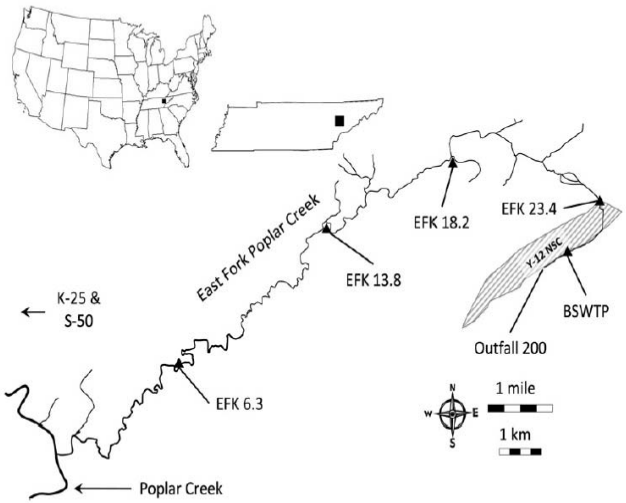


Fig. 2. The Y-12 National Security Complex and East Fork Poplar Creek. The former K-25 and S-50 plants are farther to the west, rescaling to include them obscures more relevant features of East Fork Poplar Creek. BSWTP = Big Springs Water Treatment Plant.

Through remedial actions over the last 25 years, Hg concentrations and fluxes have been reduced, but Hg levels in water at the Y-12 Complex boundary continue to exceed both the regulatory limit (51 ng/L) and the remediation goal (200 µg/L) (Brooks and Southworth 2011). Commensurate reductions in the fish tissue concentrations (to achieve the EPA criteria of 0.3 µg/g) have not been observed (Peterson et al. 2011).

Validation digestion/extraction of Hg and heavy metals from soils

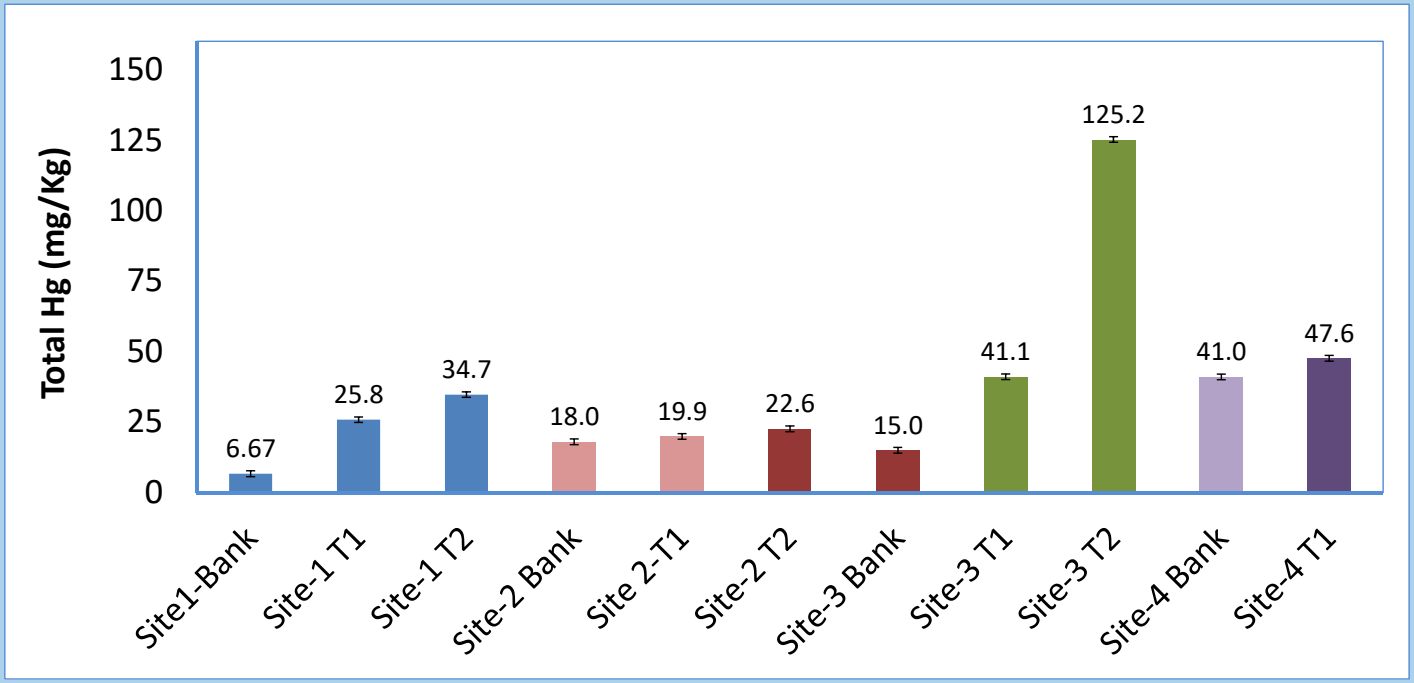
		Hg(µg/g)	Mn (µg/g)	Fe (µg/g)	Al (µg/g)
SRM 2781	Domestic Sludge	3.9 (3.68)	695 (na)	23005 (2.8%*)	9363 (1.6%*)
SRM 2711	Montana Soil II	6.1 (6.25)	396 (638)	2.24 (2.88%)	1.68 (6.53%)
SRM 2710	Montana Soil I	36.0 (32.6)	0.843 (1.01%)	3.92 (3.38%)	2.49 (6.44%)
ERM 580	Estuarine sediment	120 (132)	250 (na)	4300 (na)	2340 (na)

		As(µg/g)	Pb (µg/g)	Cu (µg/g)	Zn (µg/g)
SRM 2781	Domestic Sludge	12.4 (7.81)	169 (200.8)	548 (627.8)	1163 (1272)
SRM 2711	Montana Soil II	97.6 (105)	949 (1162)	96.9 (114)	326 (350.4)
SRM 2710	Montana Soil I	757 (626)	5699 (5532)	3180 (2950)	8452 (6952)
ERM 580	Estuarine sediment	13.9 (na)	24.3 (na)	57.3 (na)	381 (na)

Values in parenthesis are certified or indicative* values

Total Hg results from Oak Ridge soil samples

- Total Hg analysis were made by acid digestion of the soils. About 0.1-0.2 g soil samples (n=3) were digested on a Graphite Digestion Block at 160 ^{o}C in 5 mL HNO_3 and 1 mL HF.
- Montana soil (SRM 2710) from NIST, (Gaithersburg, MD) was used for verification of total mercury analysis.



Bank soils had relatively lower Hg than top soils in all sampling sites

Sequential Extraction of Hg from top soils

Soluble Hg fraction (F1)

DI water

Cation exchangeable Hg (F2)

0.1 $Mg(NO_3)_2$, pH 7.5

Carbonate associated Hg fraction (F3)

1 M NaAc, pH 5

Reducible oxide associated Hg fraction (F4)

0.1M NH_2OH HCl in 0.01 M HCl pH 2

Organic matter associated Hg fraction (F5)

0.1 HNO_3-30% H_2O_2-$AcNH_4$ Digest at 80 °C 2h

Amorphous iron-oxide associated Hg fraction (F6)

0.25M NH_2OH HCl 0.25 M HCl 50 °C 1h

Crystalline Fe-oxide associated fraction (F7)

0.04M NH_2OH 25% HAc Digest at 100 °C 3h

Residual Hg fraction (F8)

4M HNO_3 digest at 80 °C 16h

Insoluble fraction

HNO_3 /HF

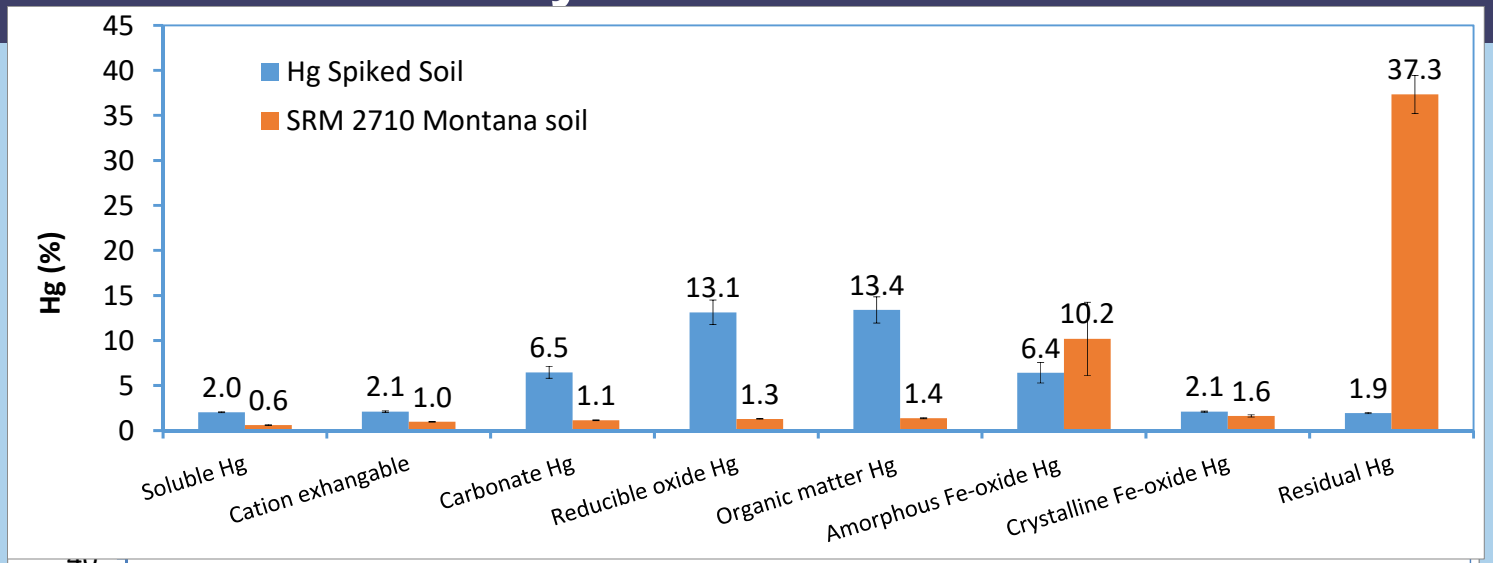
The supernatants were collected and stored in ~5% HNO_3 (and 0.2% HCl for Hg)

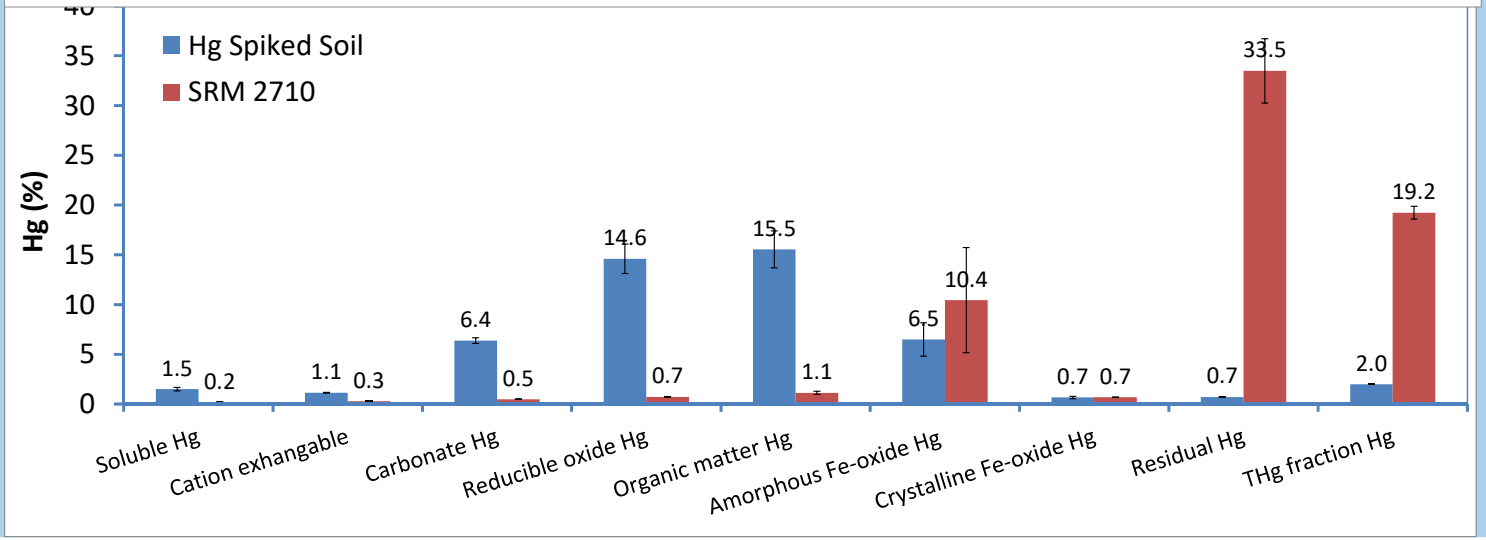
Diluted samples were analyzed by ICP-MS

Hg distribution in freshly contaminated soils

- Hg free soil/sediment Sample (10 g) was contaminated with 50 µg/g ^{200}Hg Incubated for 3 months at room temperature in the laboratory. Freshly contaminated soils

- SRM 2710 serves as control. Soil with persistent Hg contamination





Mn-Al-Fe fractions from SRM 2710

	Hg(%)	Mn (µg/g)	Fe (µg/g)	Al (µg/g)
Water Soluble	0.20	252	0.0	5.2
Cation exhangeable	0.33	844	0.0	4.0
Carbonate associated	0.39	336	81.9	66.2
Reducible oxide associated	0.44	1000	692	33.6
Organic matter associated	0.46	804	87.3	421
Amorphous Fe-oxide associated	3.47	2360	6762	3865
Crystalline Fe-oxide associated	0.55	1358	4389	1870
Residual	12.7	529	11295	21637
Total digestion	**34.0 (32.6)**	**8314 (1.01%)**	**35266 (3.38%)**	**19514 (6.44%)**
	As (µg/g)	**Pb (µg/g)**	**Cu (µg/)**	**Zn (µg/g)**
Water Soluble	3.17	2.6	60.1	29.6
Cation exhangeable	1.66	63.9	128	131
Carbonate associated	58.2	1648	895	74.2
Reducible oxide associated	92.6	135	119	38.0
Organic matter associated	2.06	824	942	108
Amorphous Fe-oxide associated	368	1230	476	306
Crystalline Fe-oxide associated	82.1	79.1	101	191
Residual	65.0	173	137	151
Total digestion	**914 (626)**	**5404 (5532)**	**3055 (2950)**	**7903 (6952)**

As-Pb-Cu-Zn fractions from SRM 2710

	As (µg/g)	Pb (µg/g)	Cu (µg/)	Zn (µg/g)
Water Soluble	3.17	2.6	60.1	29.6
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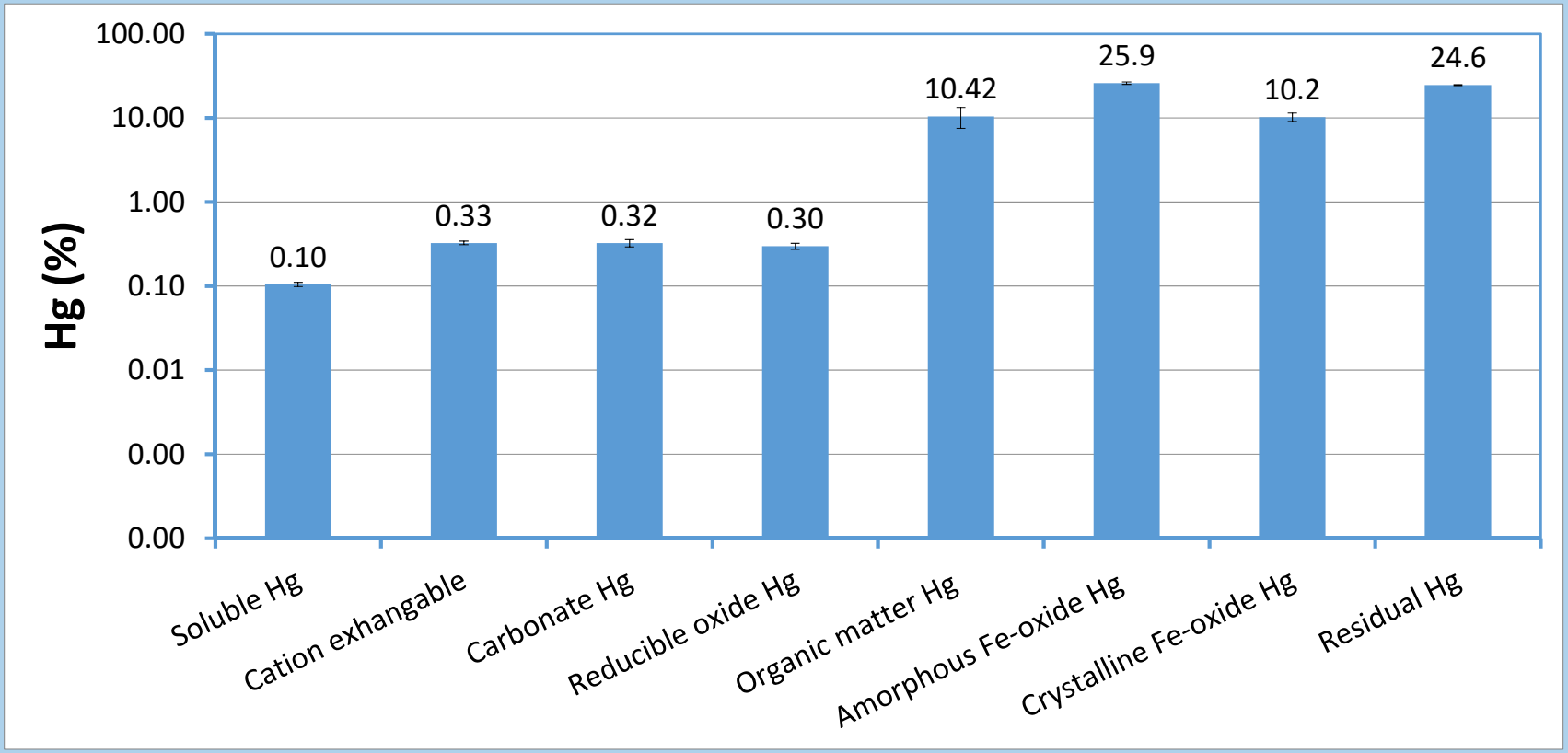
Hg distribution in in top soils from Oak Ridge TN



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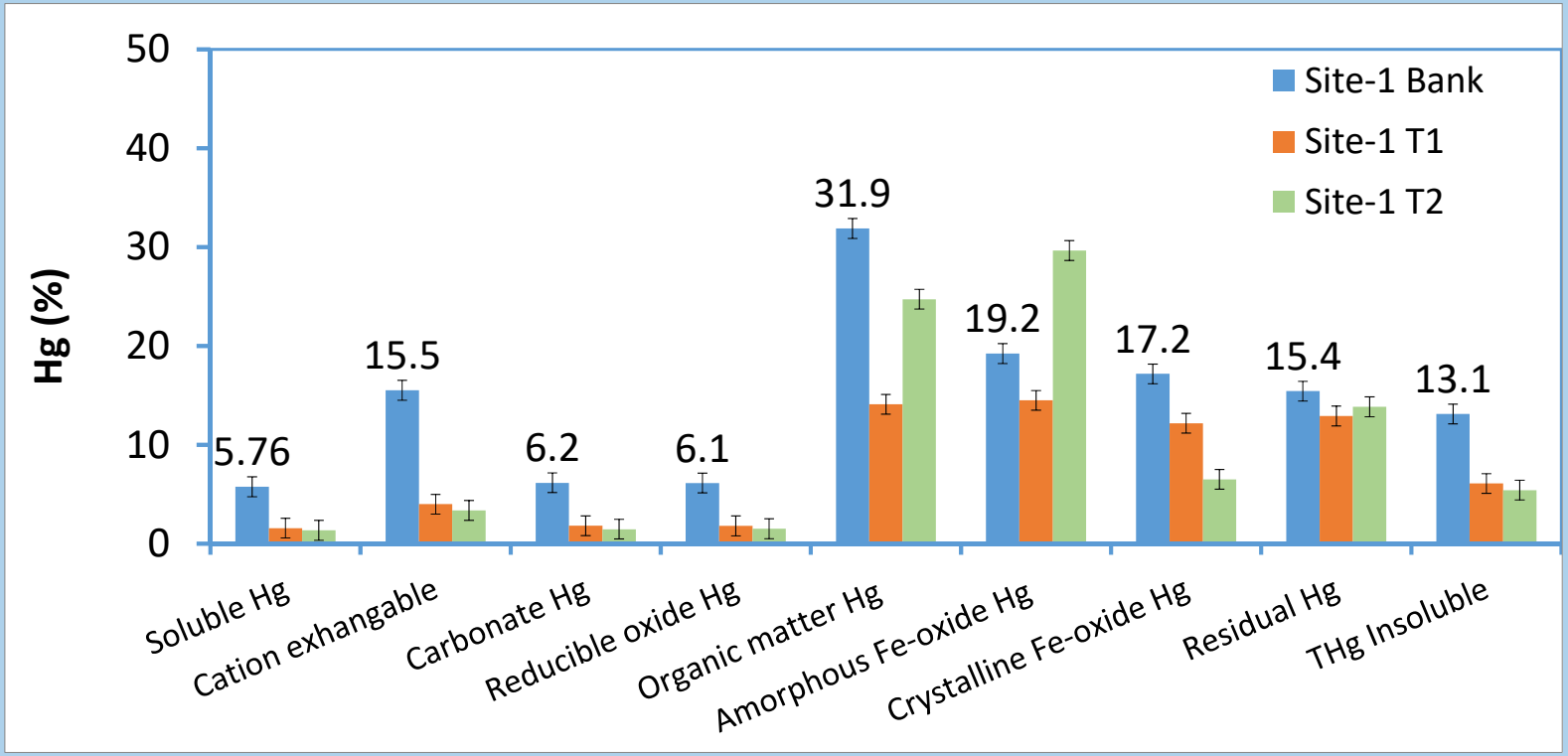

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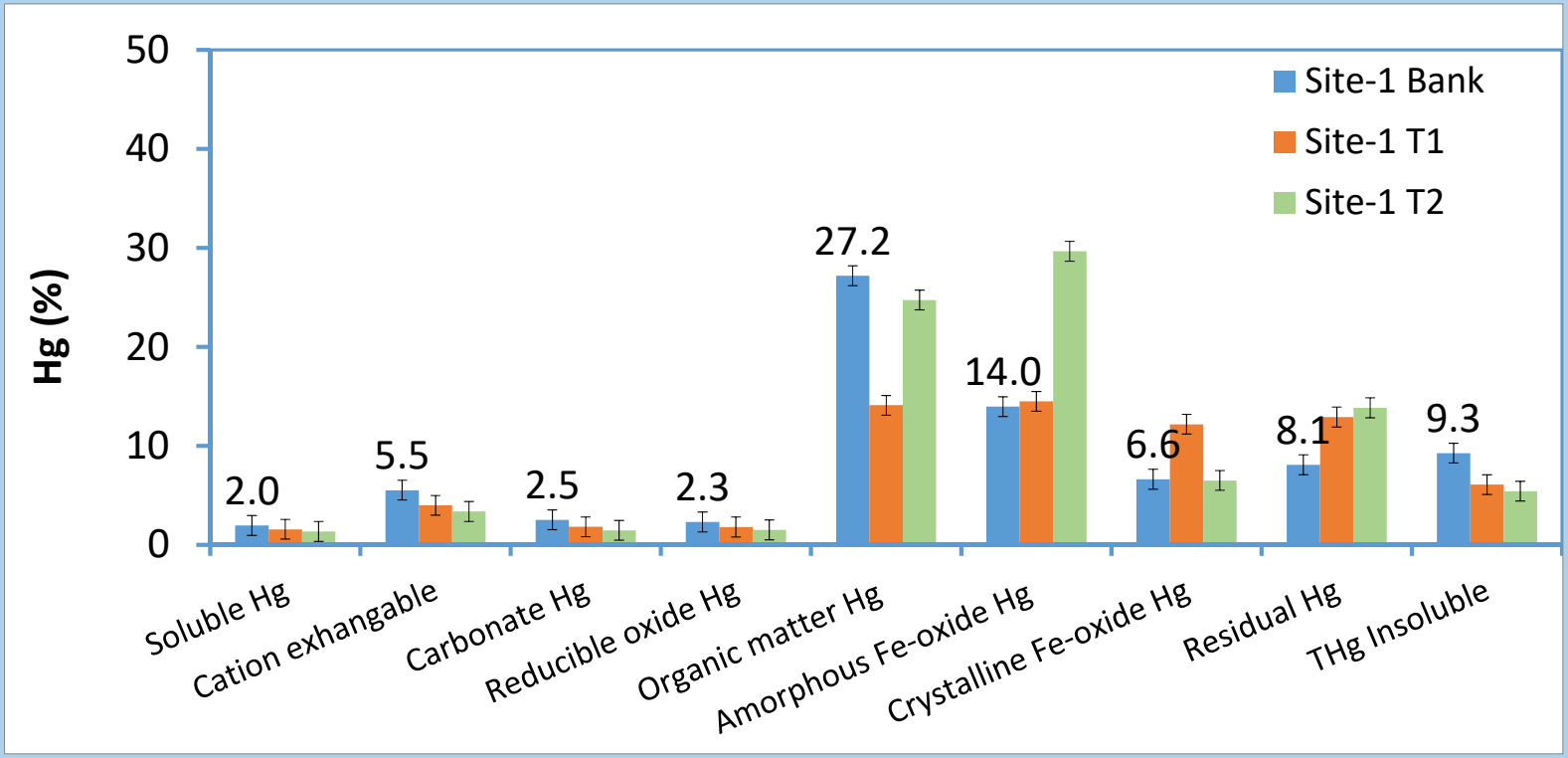

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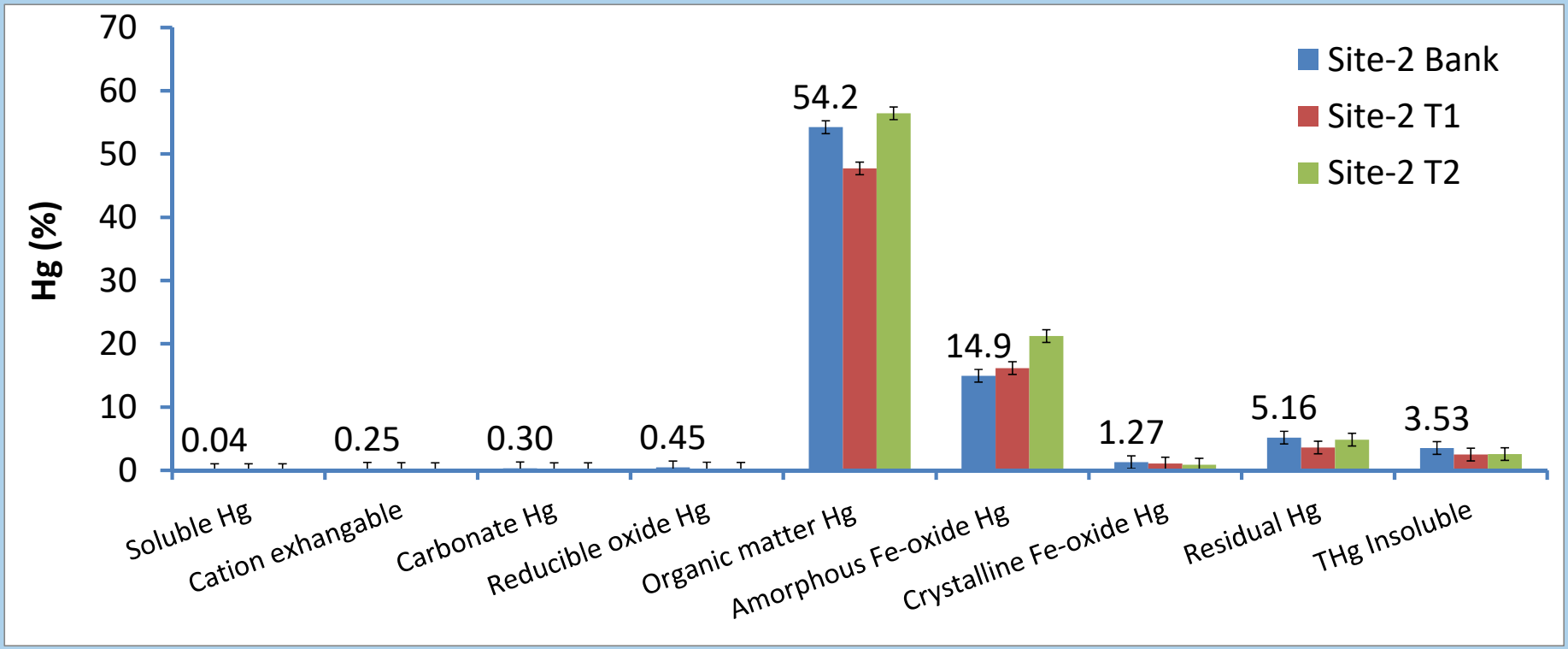

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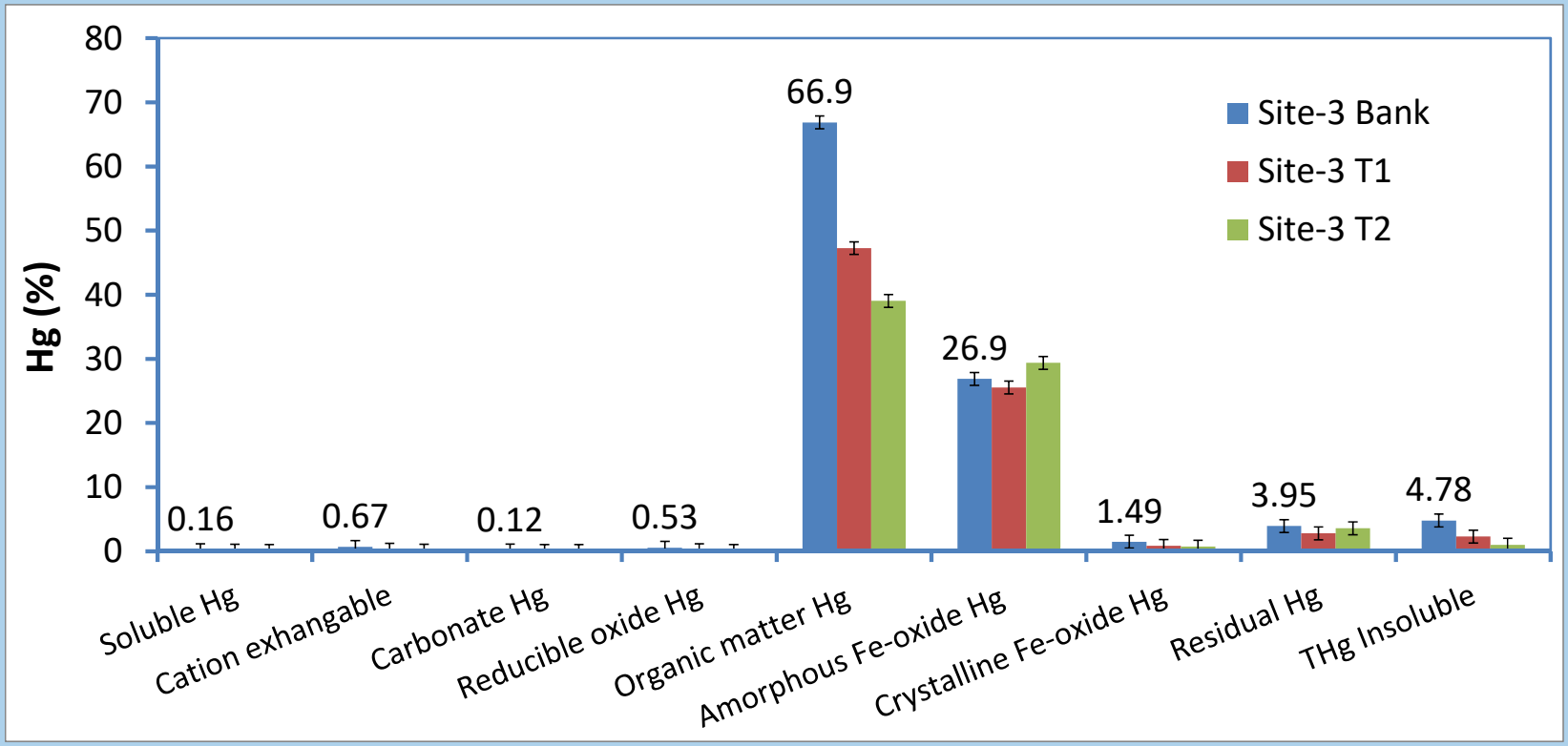

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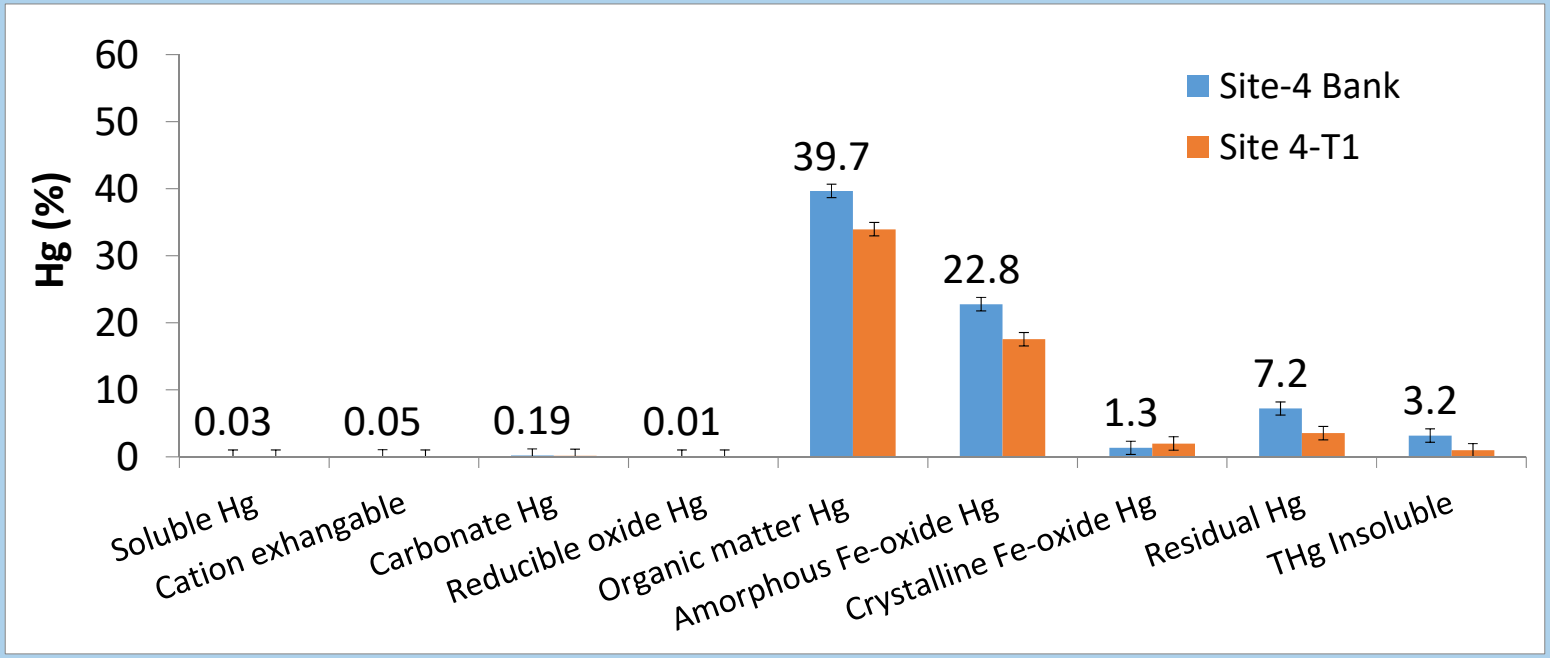

Mn-Al-Fe fractions from Oak Ridge Soils - ORNL site top soil

	Hg(%)	Mn (µg/g)	Fe (µg/g)	Al (µg/g)
Water Soluble	0.10	0	0	1.2
Cation exchangeable	0.33	17	2.0	0.2
Carbonate associated	0.32	162	15.5	6.9
Reducible oxide associated	0.30	745	114	1.1
Organic matter associated	10.4	133	0	27.8
Amorphous Fe-oxide associated	25.9	103	3711	1286
Crystalline Fe-oxide associated	10.2	22	2026	918
Residual	24.6	32	6893	8205

	As (µg/g)	Pb (µg/g)	Cu (µg/g)	Zn (µg/g)
Water Soluble	0.04	0.0	0.2	0.0
Cation exchangeable	0.54	0.0	0.3	0.5
Carbonate associated	0.91	1.5	34.4	58.1
Reducible oxide associated	1.72	0.0	0.7	18.9
Organic matter associated	0.48	0.4	5.7	14.4
Amorphous Fe-oxide associated	3.46	26.8	21.4	109
Crystalline Fe-oxide associated	0.72	2.1	0.9	27.0
Residual	2.58	3.2	1.6	21.0

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