AIMING AT 400 ppm KLU FOR EFPC
UP FROM 180 ppm REMEDIATION OBJECTIVE
PUBLIC WANTED IT RAISED

✓ DATA QUALITY?, H_2O RELEASE
✓ ACIDIFICATION?
✓ FISH UPTAKE
✓ pH data + Fish in each
✓ SPILL VOLATILIZATION

MERCURY ABATEMENT AT AN INDUSTRIAL FACILITY[1]

DISCHARGED AS MERCURIC NITRATE
350 SUMPS AT Y-12
SUMP WATER OFTEN SATURATED WITH ELEMENTAL MERCURY 50 ppb

MERCURY IN SOIL PRIMARILY ASSOCIATED WITH SULFUR

BIOAVAILABILITY STUDY
PH 2.5 THAN PH 6.5 - SIMULATE GUT
JUSTIFIED 30% BIOAVAILABILITY
30% FROM OUTLIER

Ralph R. Turner
Environmental Sciences Division
Oak Ridge National Laboratory[2]
Oak Ridge, TN 37831

Presentation at

Lunchtime Seminar Series
Frontier Geosciences, Inc
Seattle, Washington

March 22, 1995

ChemRisk Document No. 3053

$30 MILLION SPENT ON EFPC STUDIES

CHLORINE IN COOLING WATER WAS WORST TOXICANT

MERCURY COMES OUT OF WATER READILY IF IT IS IN ELEMENTAL FORM

TAKING CHLORINE OUT INCREASED FRACTION OF ELEMENTAL MERCURY (DECHLORINATED WITH BISULFIDE)

9201-2 BUILT OVER 600 GPM SPRING (OUTFALL 51) WHERE ELEMENTAL MERCURY WAS SPILLED

SEDIMENT MOVES ONLY SLIGHTLY SLOWER THAN WATER. ROCKY BOTTOM

UNEXPECTEDLY LOW Hg IN BIOTA

[1] Supported by the U.S. Department of Energy's Environmental Restoration Program.

[2] Oak Ridge National Laboratory is managed for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400.

CHLOR ALKALI PLANT ON HIWASSEE RIVER IS ONE OF THE LARGEST IN THE WORLD

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Outline

- Brief Overview of the environmental legacy of mercury use at a nuclear weapons plant
- Approach to, and results of, characterization of continuing aquatic releases
- Past and current corrective measures and their effectiveness
- Innovative research and development
- Prognosis on further abatement and some thoughts on process

Aerial Photo of Y-12 Looking West
(89-1151)

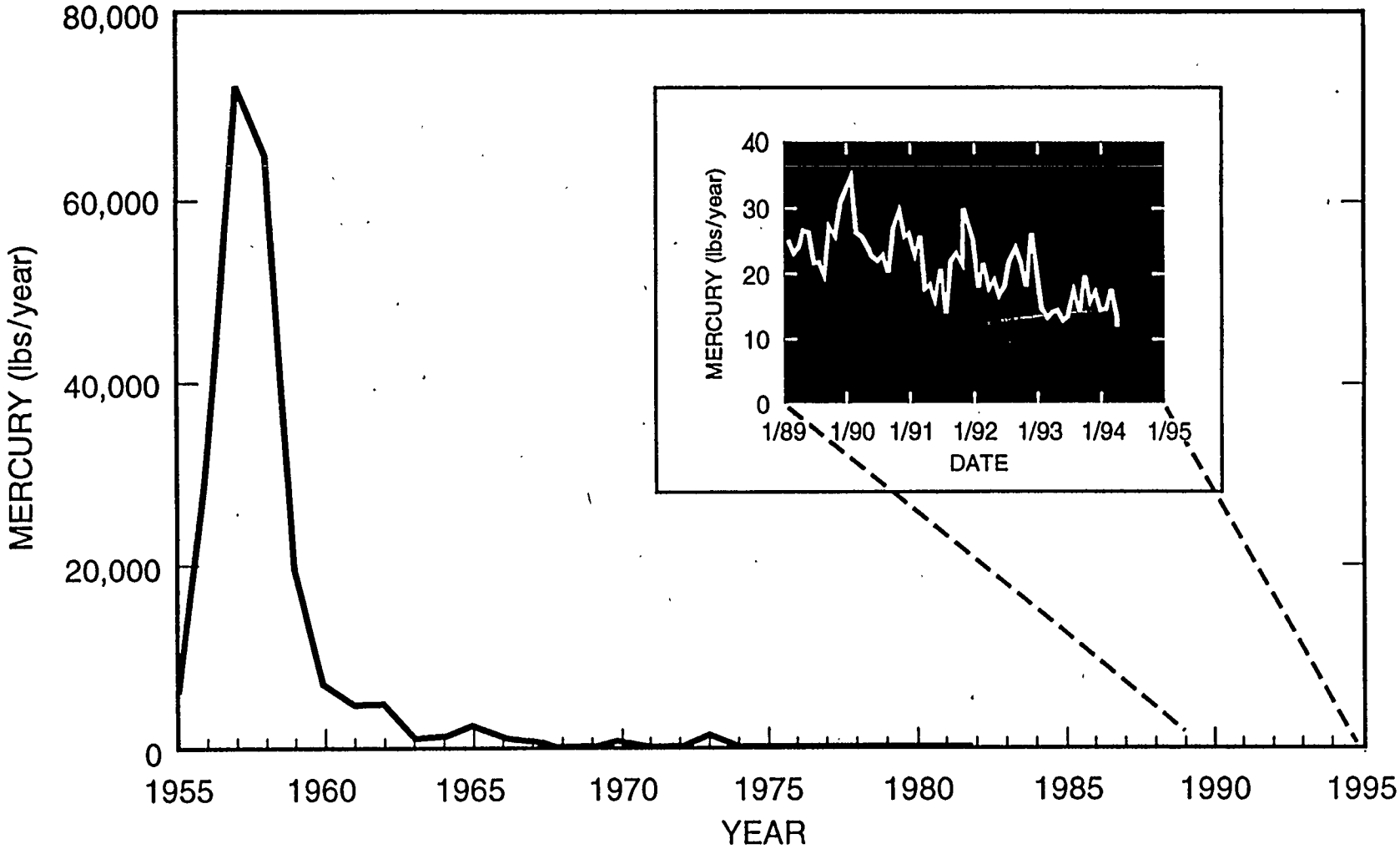
Mass Balance of Mercury at the Y-12 Plant

Environmental media	Mercury (lbs)	Percent of Inventory[a]
Lost to air (1950-1963)	51,000	0.21
Lost to creek (1950-1993)	240,000	1.0
Lost to soil/rock under facility	428,000	1.8
Lost to headwater pond sediments	15,000	0.063
Not accounted for[b] NEVER GOT THERE?	1,300,000	5.4
Total	2,034,000	8.5

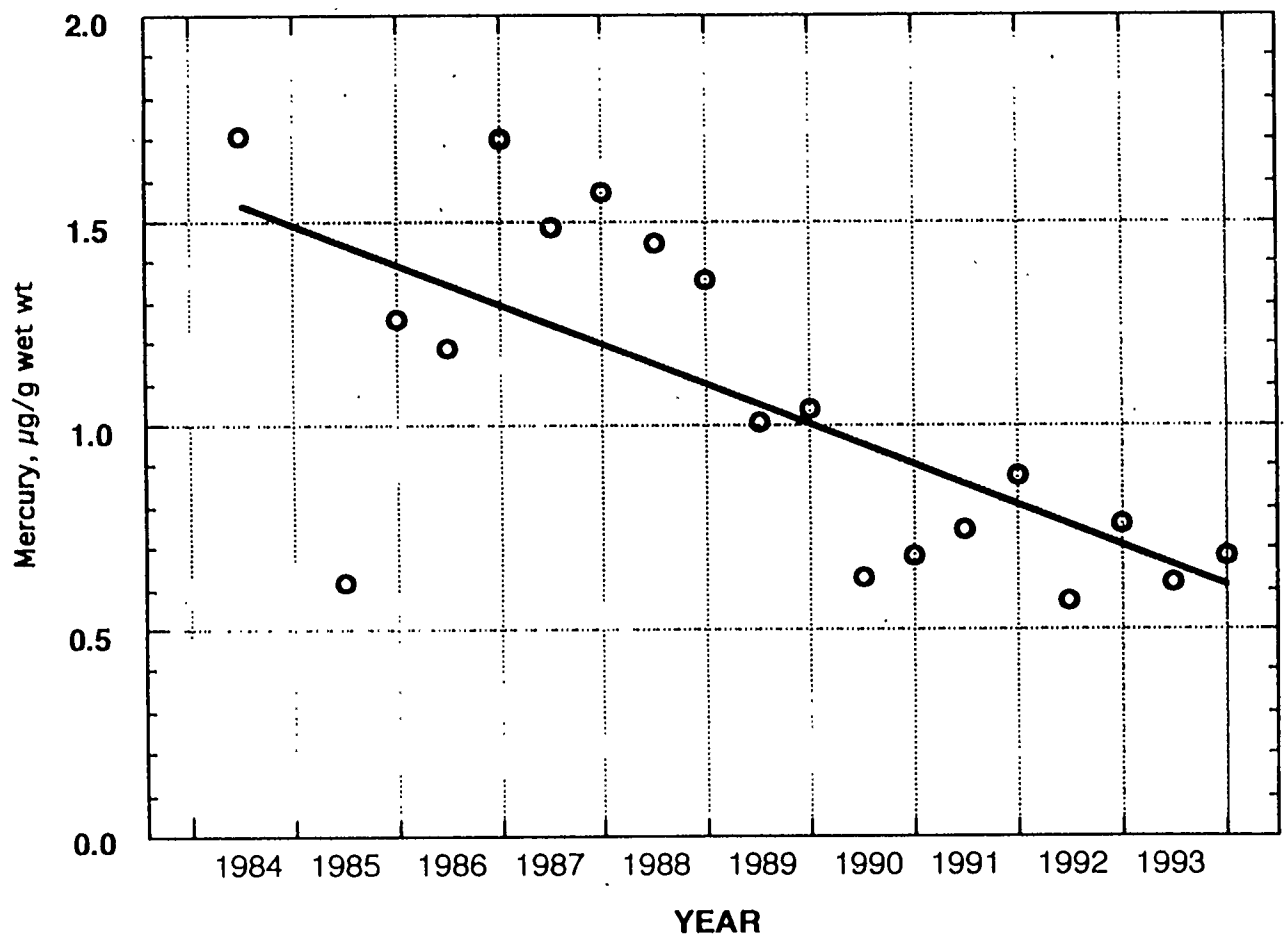
SMALL % COMPARED TO OTHER INDUSTRIES

[a] Total inventory charged to facility by GSA = 24,000,000 lbs.
[b] Charged inventory minus accounted for inventory plus amounts lost or spilled.

ORNL-DWG 94M-1424



Mercury in redbreast sunfish vs time, East Fork Poplar Creek at Y-12



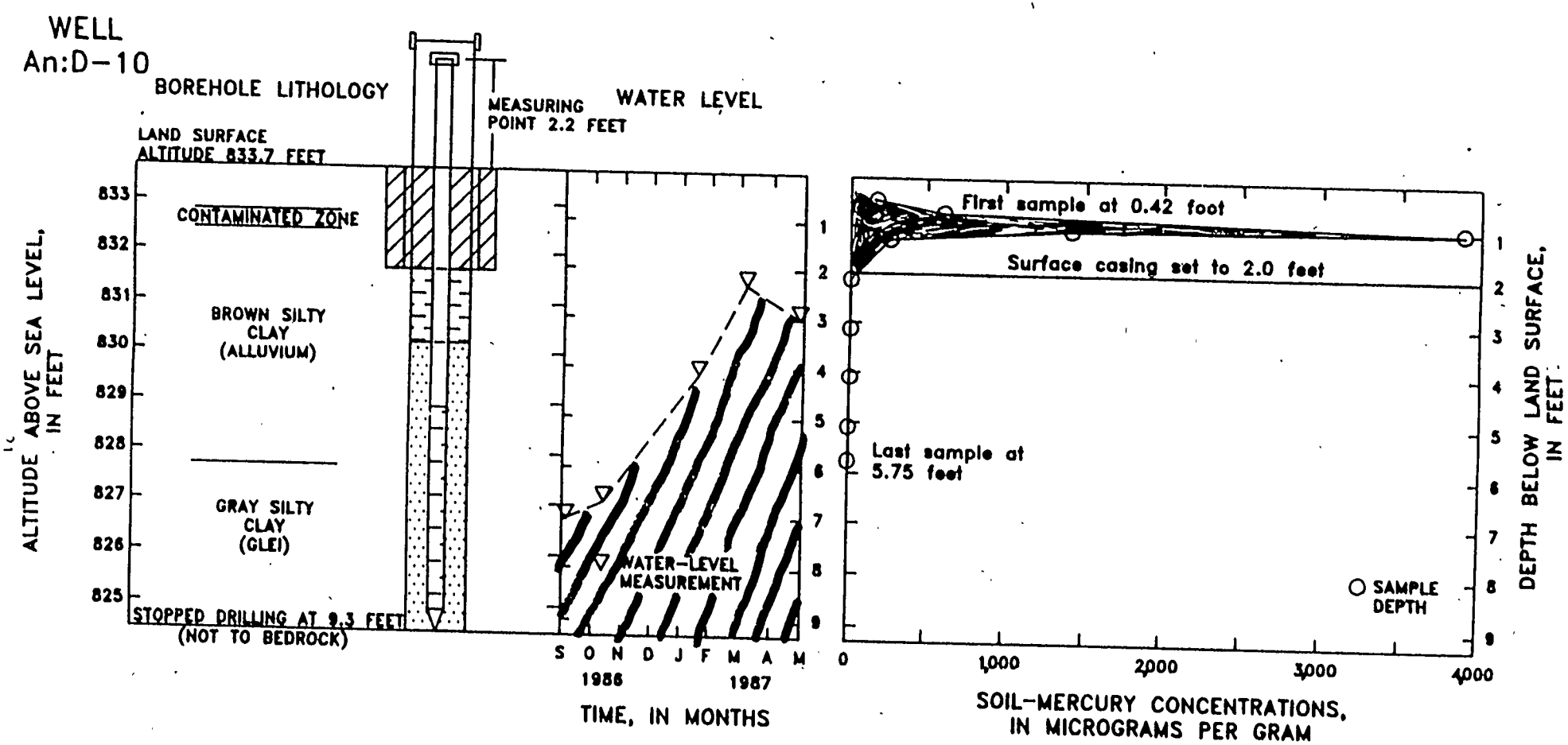
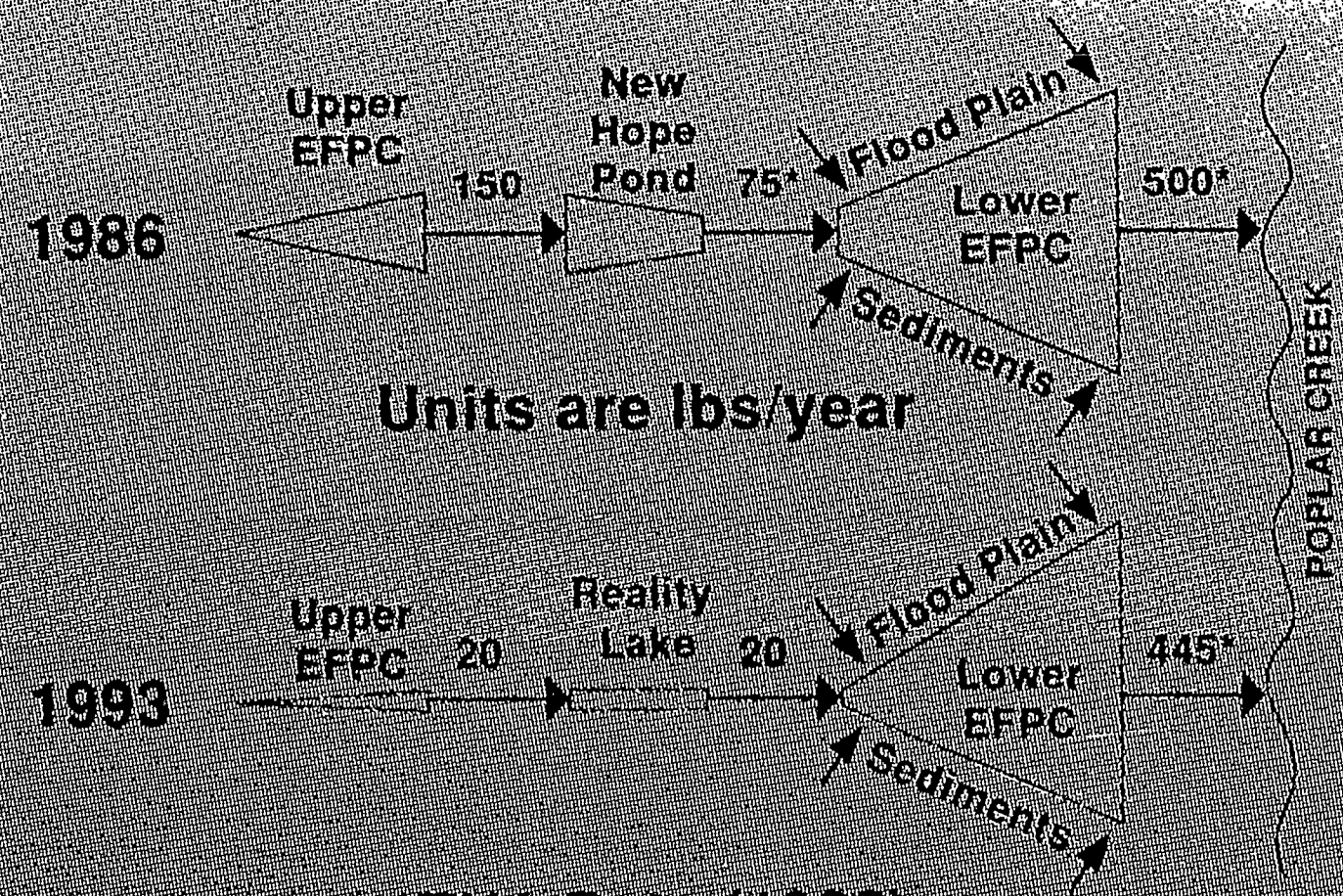


Figure 11.--Construction, lithology, soil-mercury concentrations, and water levels at site 2 well An:D-10.

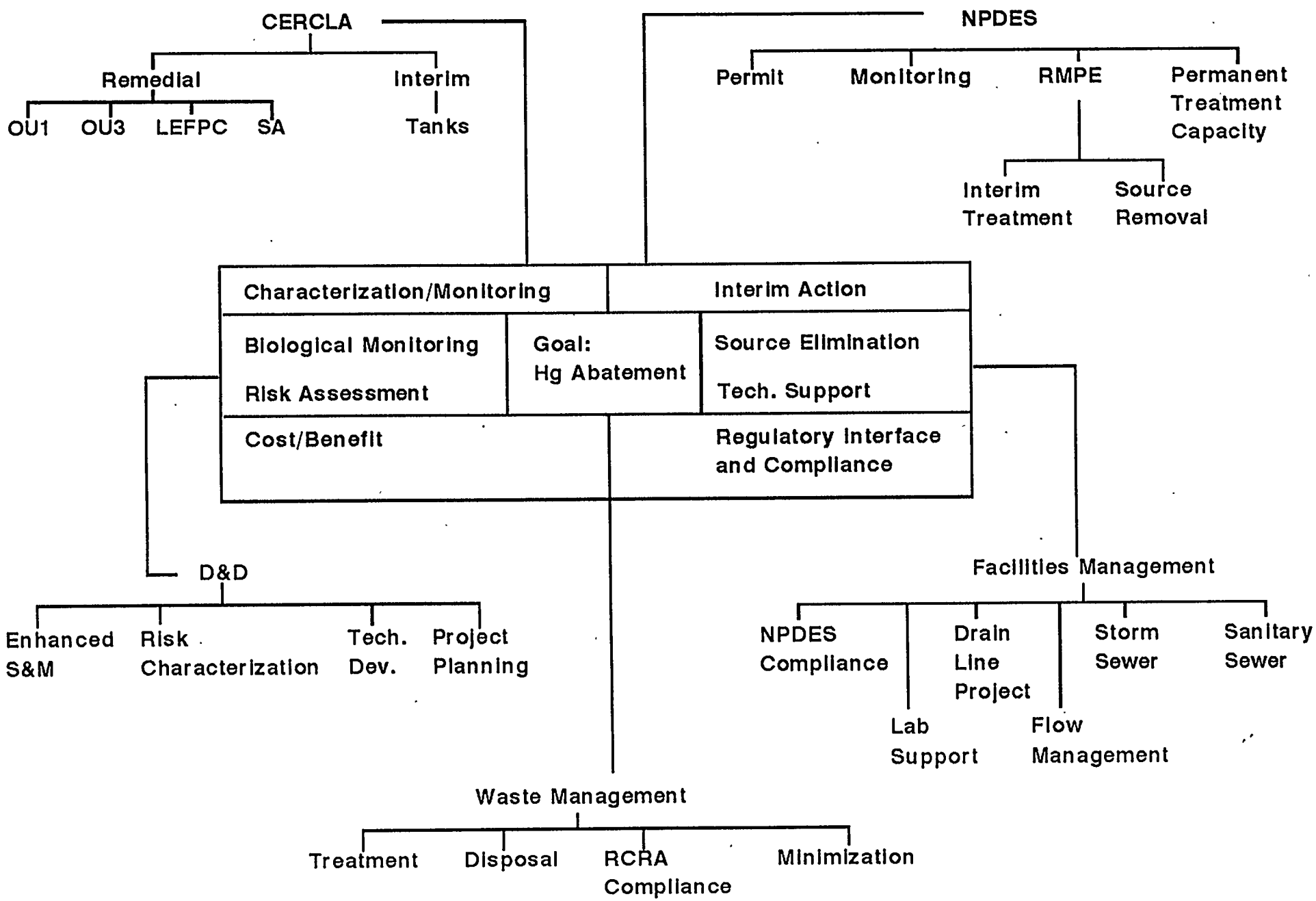
C-1

ORNL-DWG 94M-1017

Resuspension of creek sediments and flood plain soils contribute more than 85% of the total EFPC watershed Export of Mercury



MERCURY STRATEGY



RMPE

Reduction of Mercury in Plant Effluents

RMPE Strategies

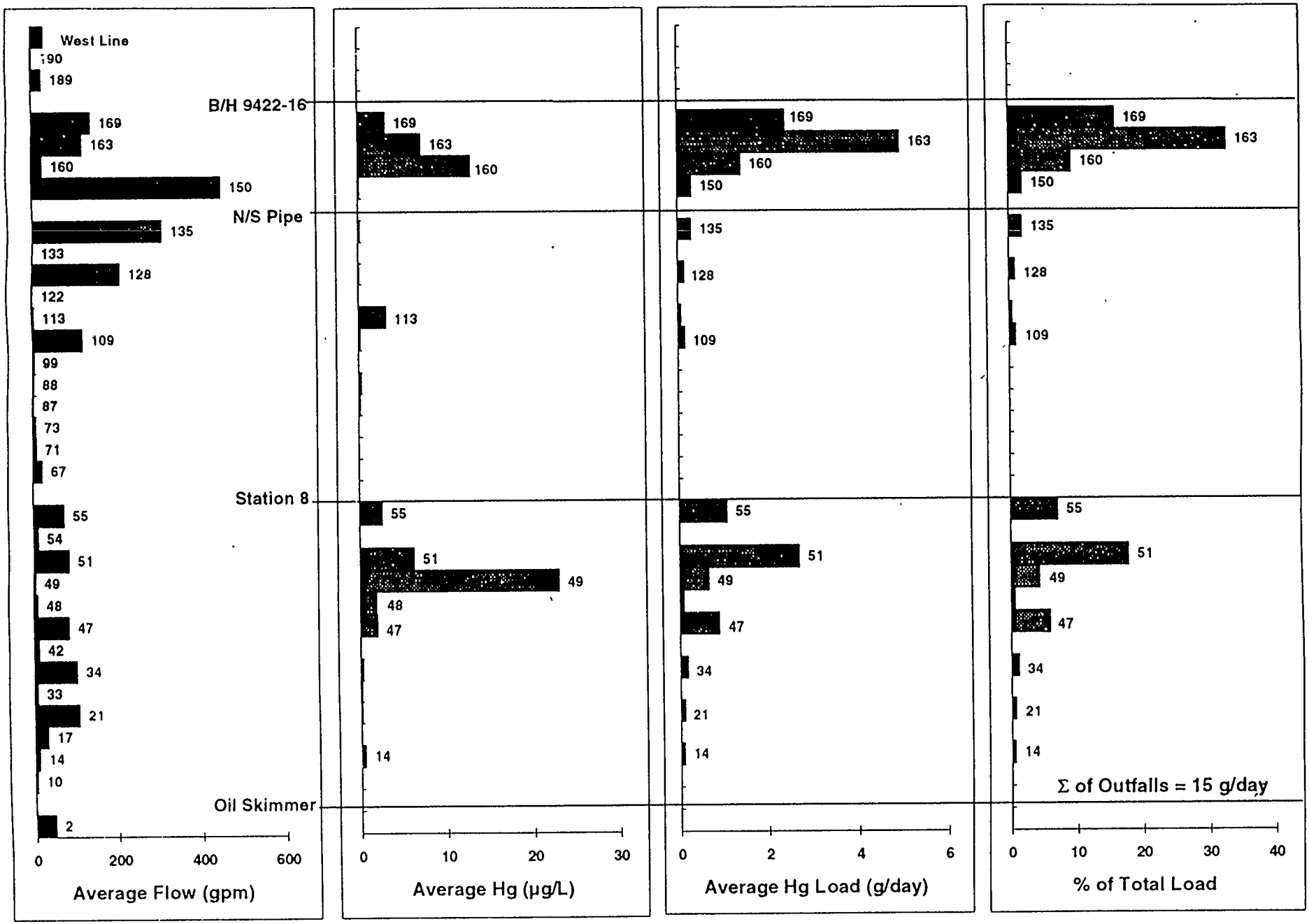
- Identify and prioritize of Hg sources
- Eliminate Hg sources which are obvious and can be removed in a cost effective manner
- Contain Hg sources which cannot be easily removed (e.g., reroute clean water away from contaminated conduits)
- Capture and treat effluents which cannot otherwise be eliminated or avoided
- Investigate / support *innovative* strategies to extract Hg from, or immobilize Hg within, building structures and the subsurface

Characterization of Sources

Photo of Outfall 49 Behind 9201-2
(304639)

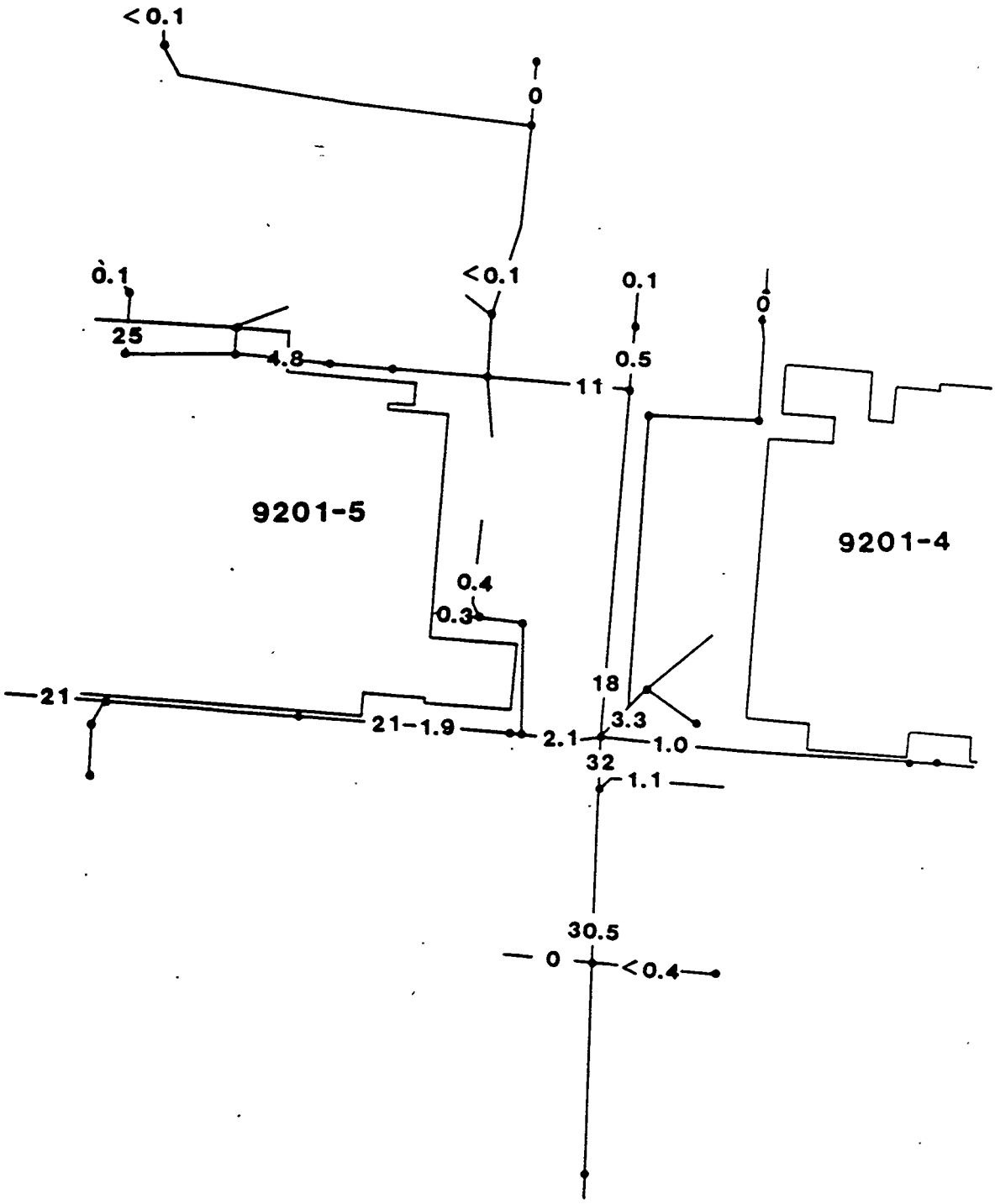
Mercury in Outfalls
Upper East Fork Poplar Creek

FROM HEADWATER TO EDGE OF Y-12



ORNL-DWG 85-1642

Hg LOADING (g/d)
DECEMBER 1, 7-8, 1983



WEST OF 9201-4

Photo of Storm Drain With Mercury
(276151)

Photo of Pipe Drilled/Plugged for RMPE Sampling
(311147)

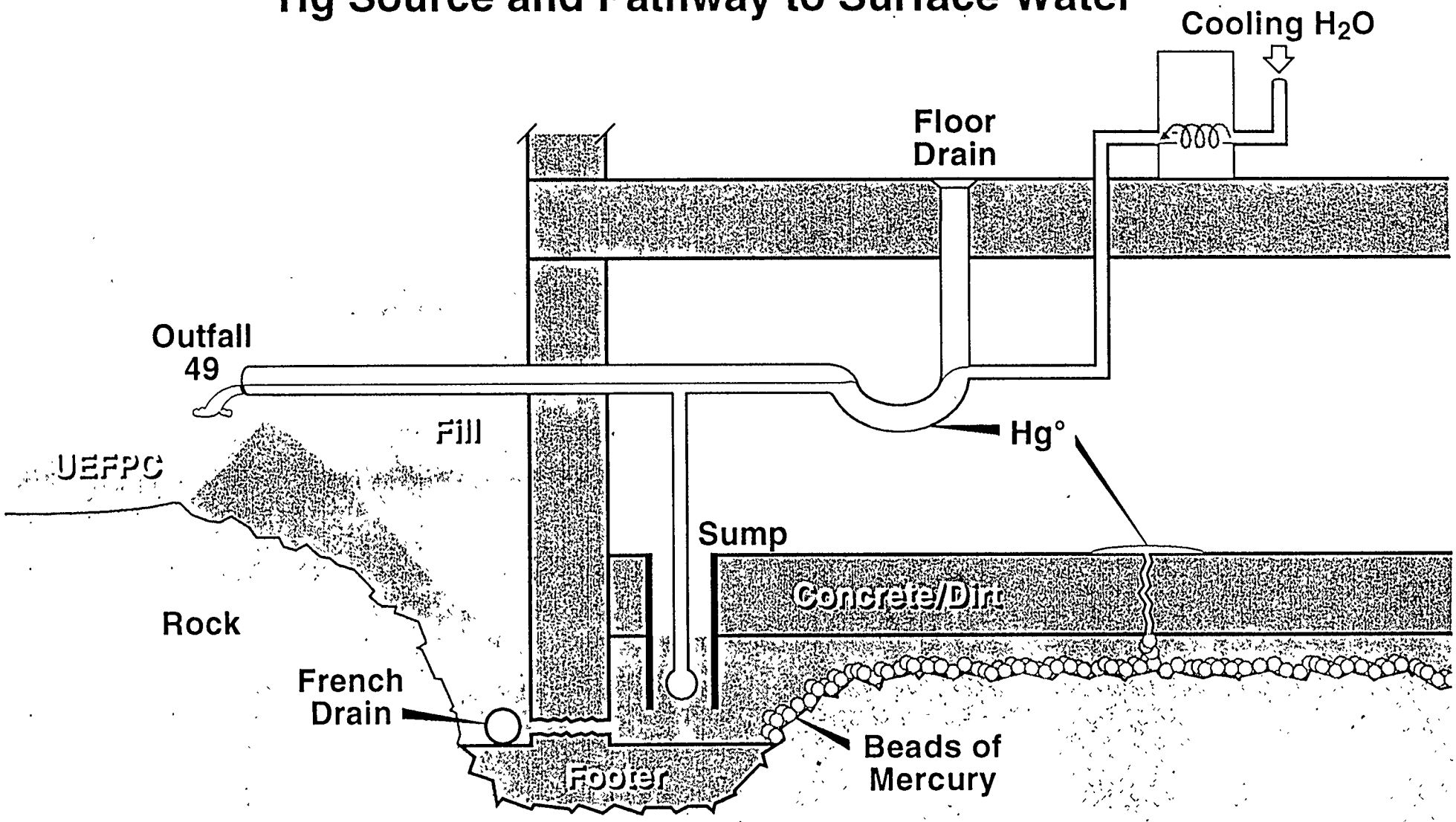
Photo of Rusted Out Pipe (side view) in 9201-2
(305652)

Photo of Rusted Out Pipe (top view) in 9201-2
(305651)

Photo of Sump in 9201-2
(311170)

ORNL DWG 93M-1457

Foundation and Equipment Drains Provide Hg Source and Pathway to Surface Water



Corrective Actions

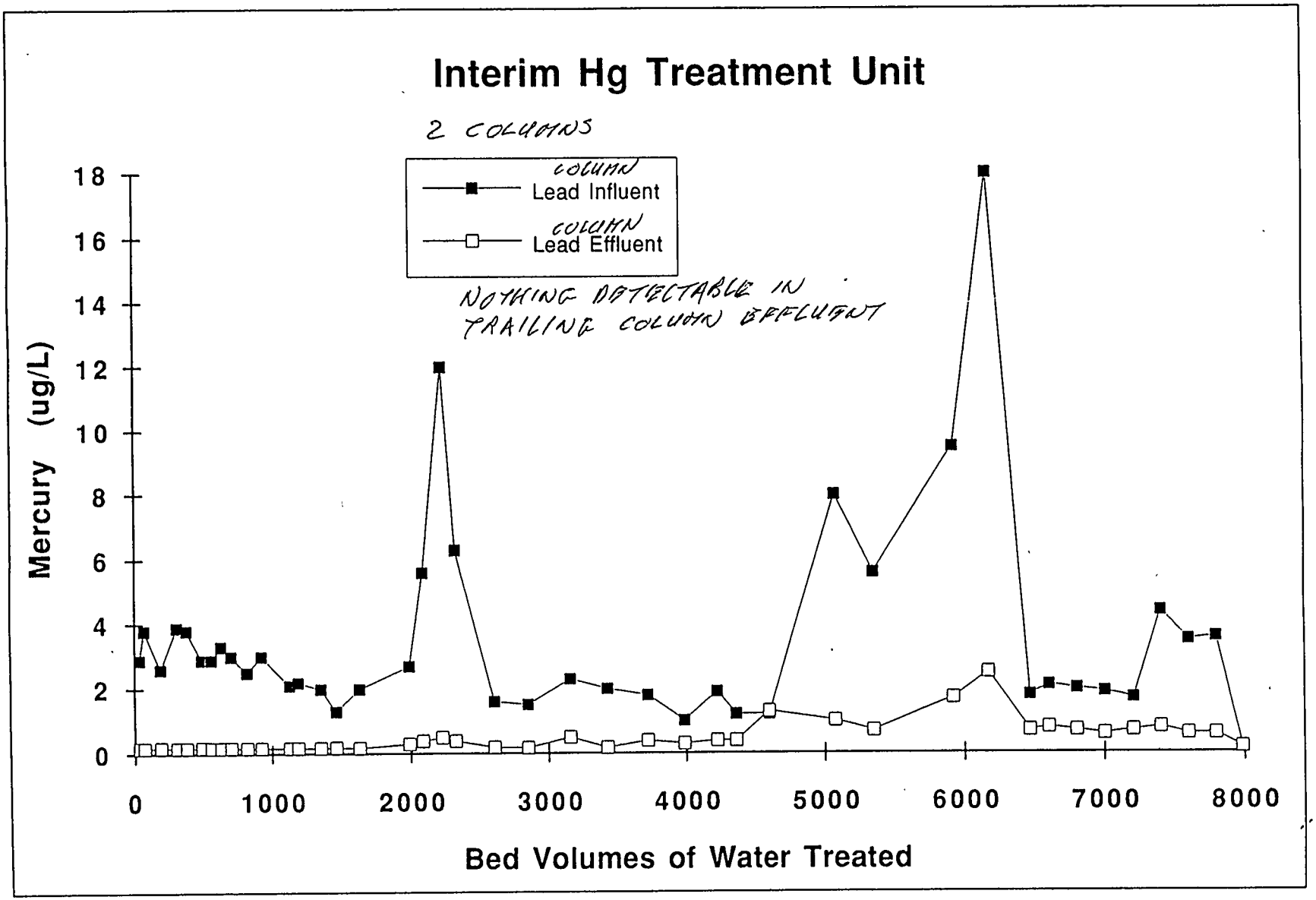
Photo of Pipe Reroute (Trunkline) in 9201-2
(311157)

Photo of Pipe Reroute (Floor Drain) in 9201-2
(311158)

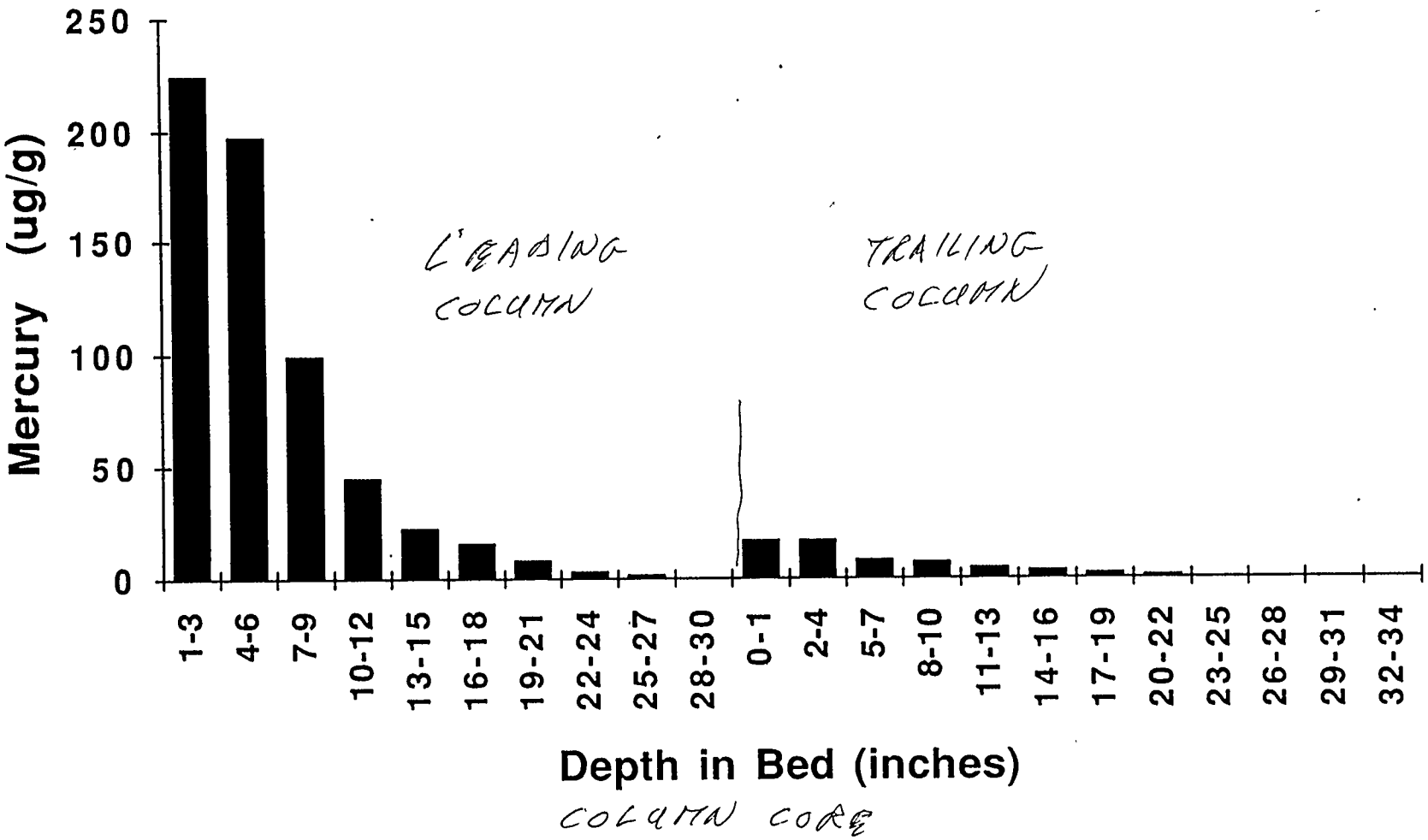
Photo of Pipe Reroute (Roof Drain) in 9201-2
(311151)

Photo of Sump O-12 in 9201-2
(303355)

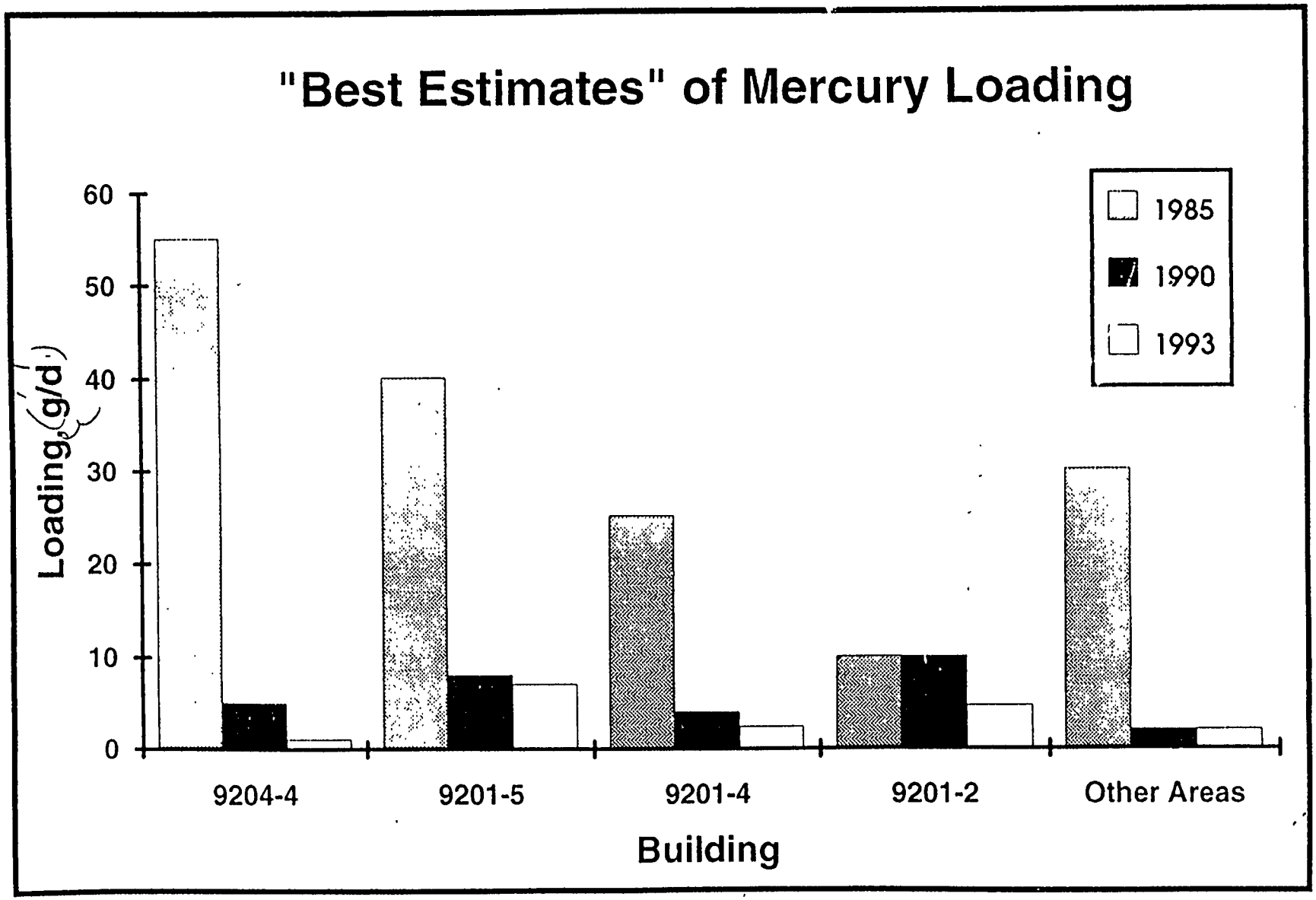
Photo of Interim Hg Treatment Unit in 9201-2
(311159)


Interim Hg Treatment Unit
2 COLUMNS
COLUMN
Lead Influent
COLUMN
Lead Effluent
NOTHING DETECTABLE IN
TRAILING COLUMN EFFLUENT
Mercury (ug/L)
0
2
4
6
8
10
12
14
16
18
0
1000
2000
3000
4000
5000
6000
7000
8000
Bed Volumes of Water Treated

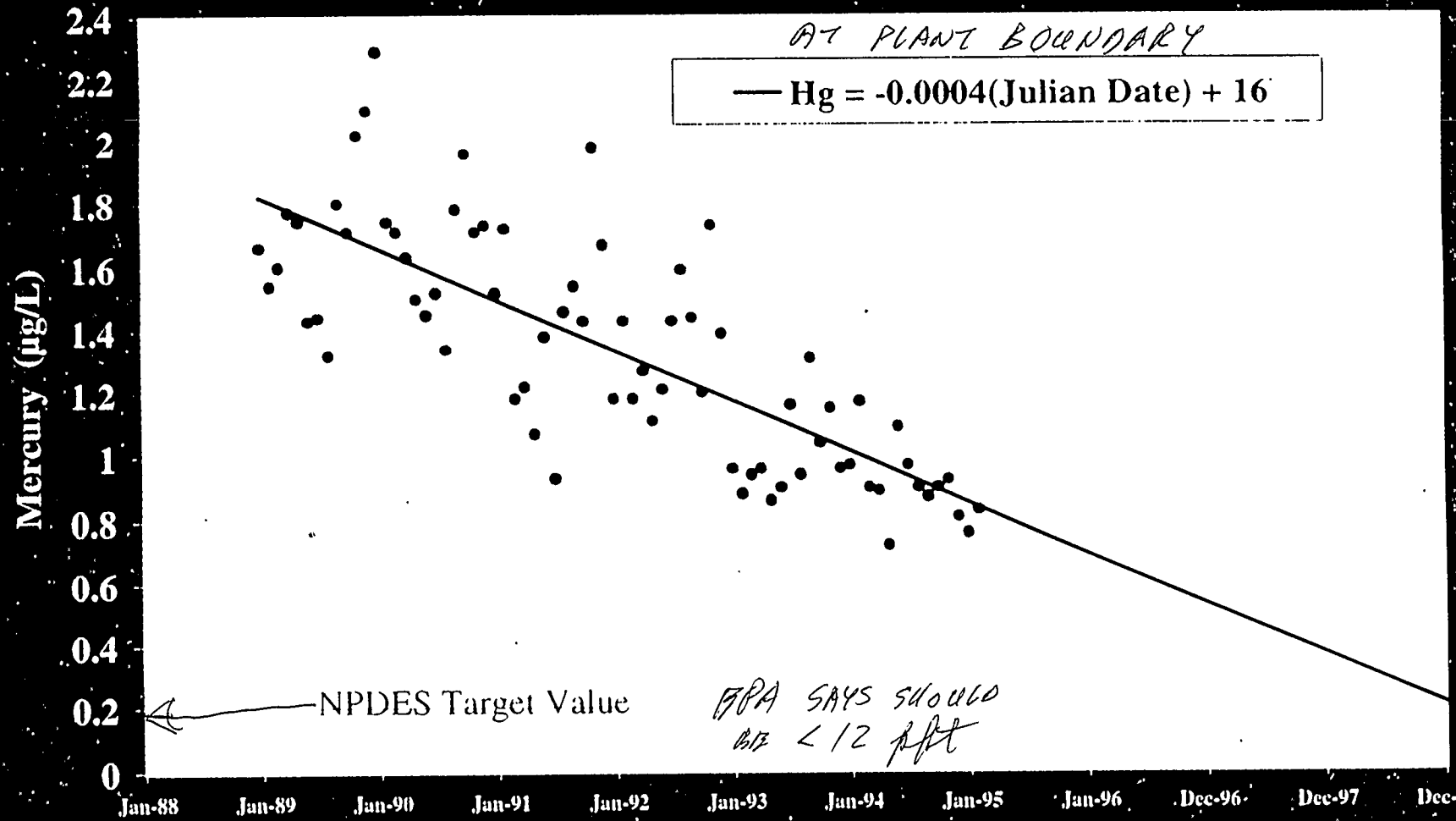
GAC After 9000 Column Bed Volumes



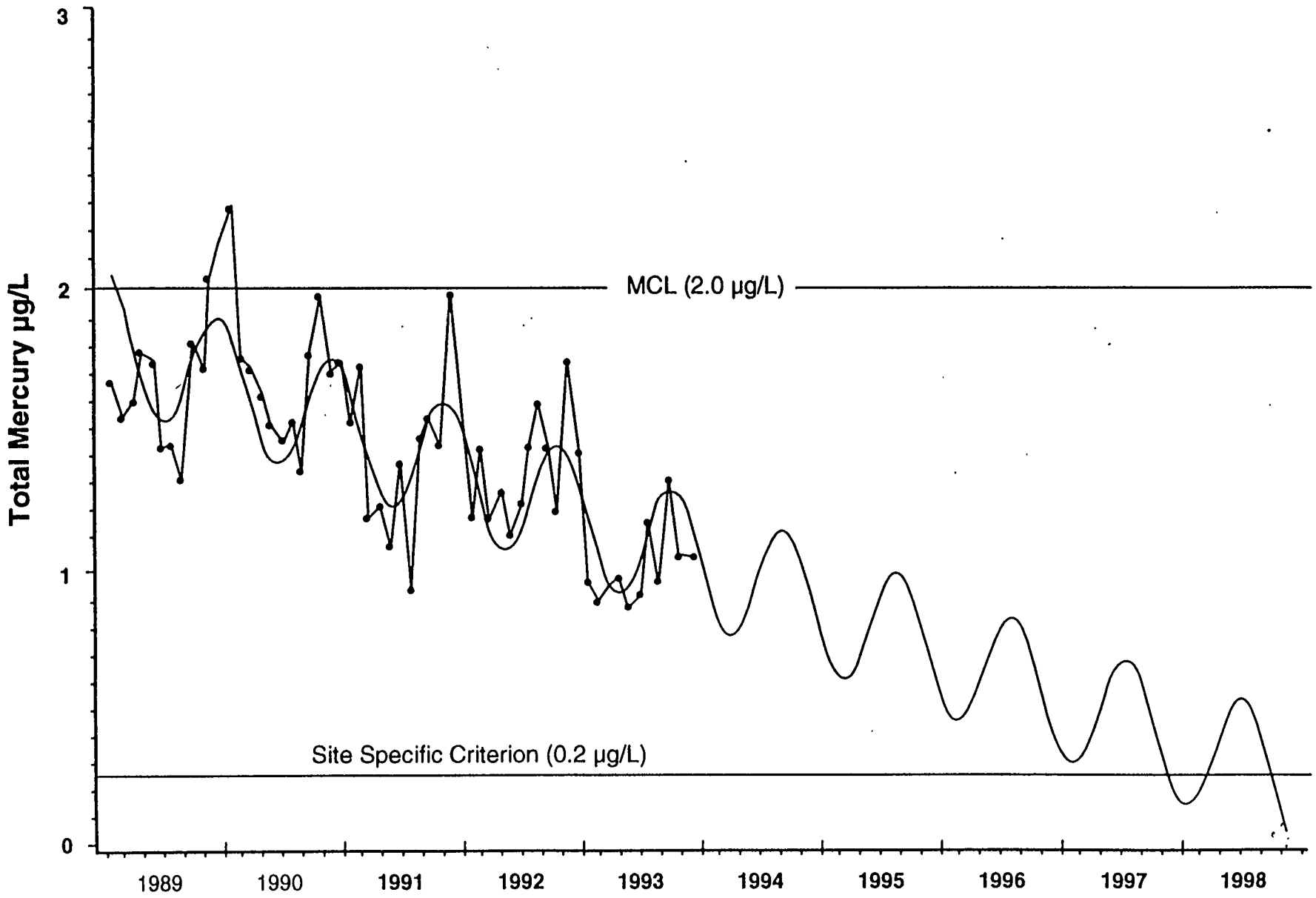
Effectiveness of Remedies

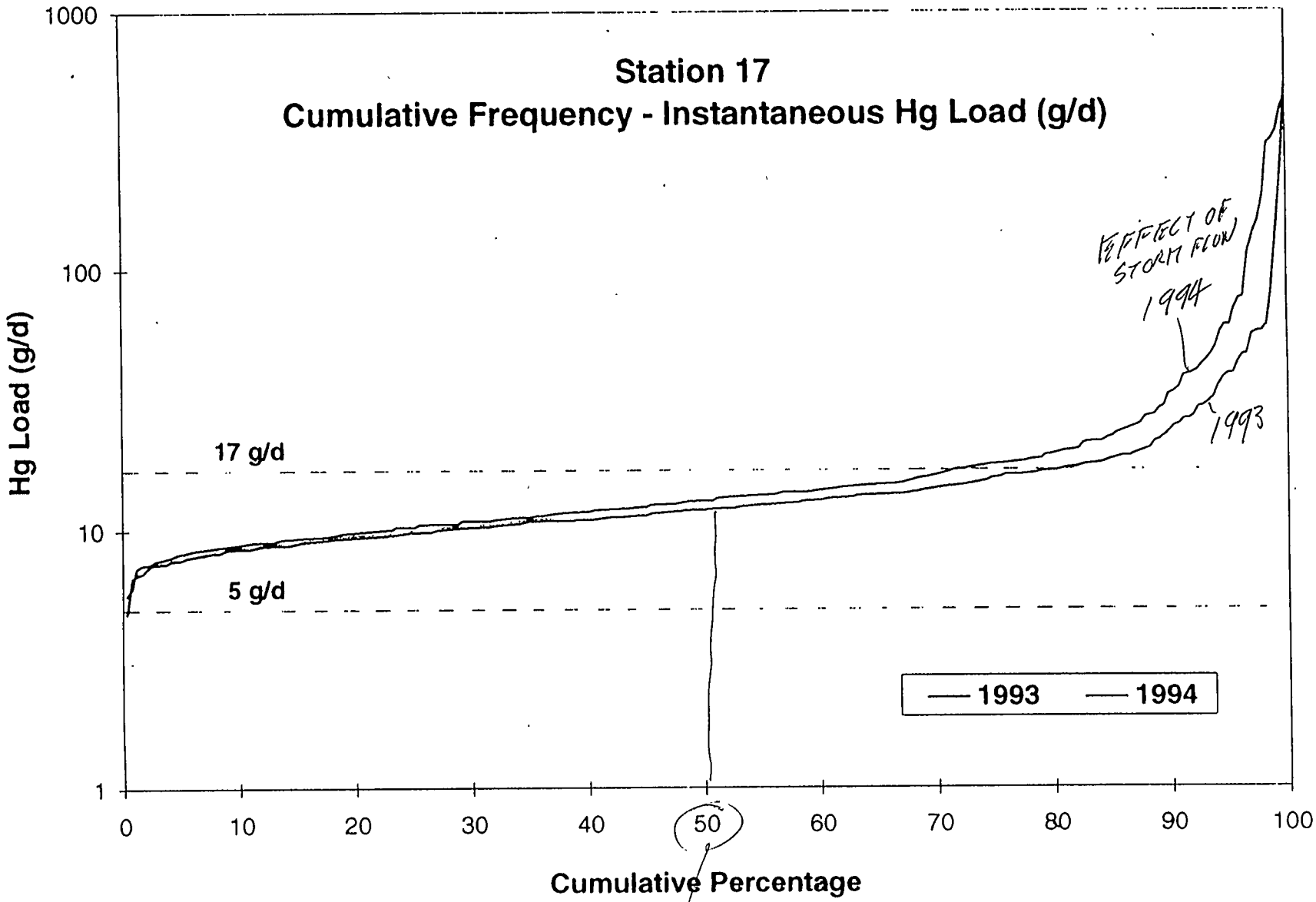

"Best Estimates" of Mercury Loading
Loading (g/d)
60
50
40
30
20
10
0
1985
1990
1993
9204-4
9201-5
9201-4
9201-2
Other Areas
Building

Monthly Average Hg Concentration at Station 17



ORNL-DWG 94M-1018



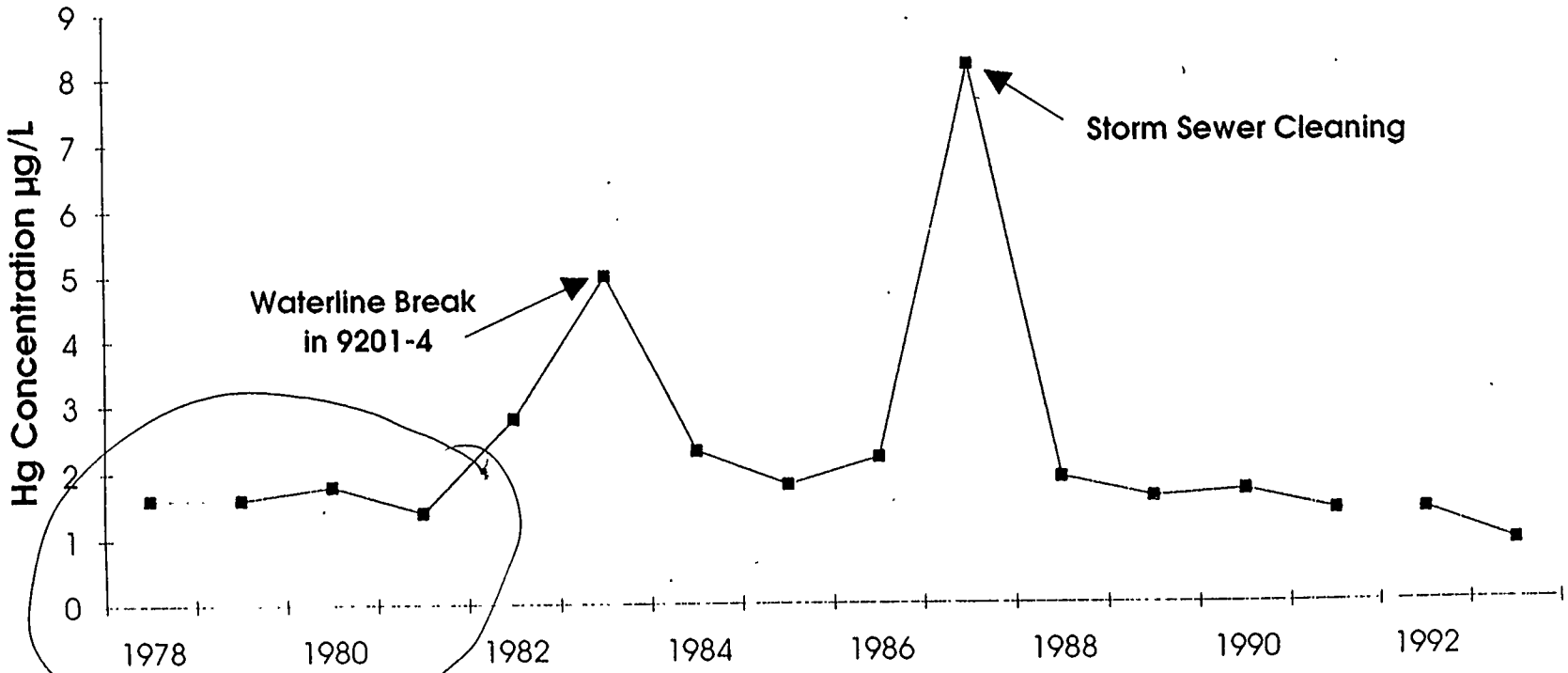


50% OF THE TIME, LOADING < ~10 gm/day

YEARLY MEAN

Mercury Concentrations in Upper EFPC
1978 - 1993

GRAB SAMPLES ARE THE BEST, TURNER SAYS



TURNER SAYS HE DOESN'T TRUST DATA AT THIS TIME

Reductions in Hg Loading to Upper East Fork Poplar Creek
Hypothetically Achievable
Within Five Years (NPDES Permit Period)

Major Hg Sources[1]		Present Loading (grams/day)	Expected Change (grams/day)[2]	Percent Change	Schedule
Outfalls 47+48		1.0	-0.5	50	12/98
Outfall 49	Sumps	0.02	-0.02	100	7/94
	Pipes	2.2	-2.2	100	7/94
Outfall 51		2.6	0	0	NA[3]
Outfall 55	Sumps	0.1	-0.1	100	7/94
	Pipes	0.9	-0.45	50	10/95
Outfall 113		0.15	-0.08	50	12/98
9201-4[4]	Sumps	2.2	-2.2	100	5/97
	Pipes	0.2	-0.1	50	7/96
9201-5[5]	Sumps	3.0	-3.0	100	3/96
	Pipes	4.0	-3.0	75	12/95
9204-4[6]	Pipes	0.5	-0.5	100	11/96
	Sumps	0.5	-0.25	50	5/97
HgTU (9201-2)[7]		0	+0.05	NA	7/94
HgTF (CPCF)[8]		0	+0.16	NA	5/97
TOTALS		17	-12	71	12/98

Net Loading of 5 g/d @ 6 mgd = Instream Concentration @ Station 17 of 0.22 μg/L.
Net Loading Above N-S Pipe = 2 g/d.
Net Loading of 2 g/d @ 2 mgd = Instream Concentration @ N-S Pipe of 0.26 μg/L.
Net Loading of 2 g/d @ 4 mgd = Instream Concentration @ N-S Pipe of 0.13 μg/L.

---

[1] Hg Loading $\geq$ 1.0 g/d or Concentration $\geq$ 2.0 μg/L.

[2] Due to capture and treatment, pipe reroutes or other corrective measures.

[3] Source characterization and plan for corrective action complete by 12/98.

[4] Feeds Outfalls 150, 160 and 163.

[5] Feeds Outfalls 163, 169 and 179.

[6] Feeds Outfalls 179 and 189.

[7] Assumes 5gpm @ $\leq$ 2 μg/L.

[8] Assumes 15 gpm @ $\leq$ 2 μg/L.

Innovative R & D

- Bioreduction / biosorption
- Air stripping
- Rapid field analysis of Hg in water and solids
- In situ immobilization of Hg in the subsurface

Innovative R & D

Bioreduction / Biosorption

Air Stripping of Hg from Water

Ralph R. Turner

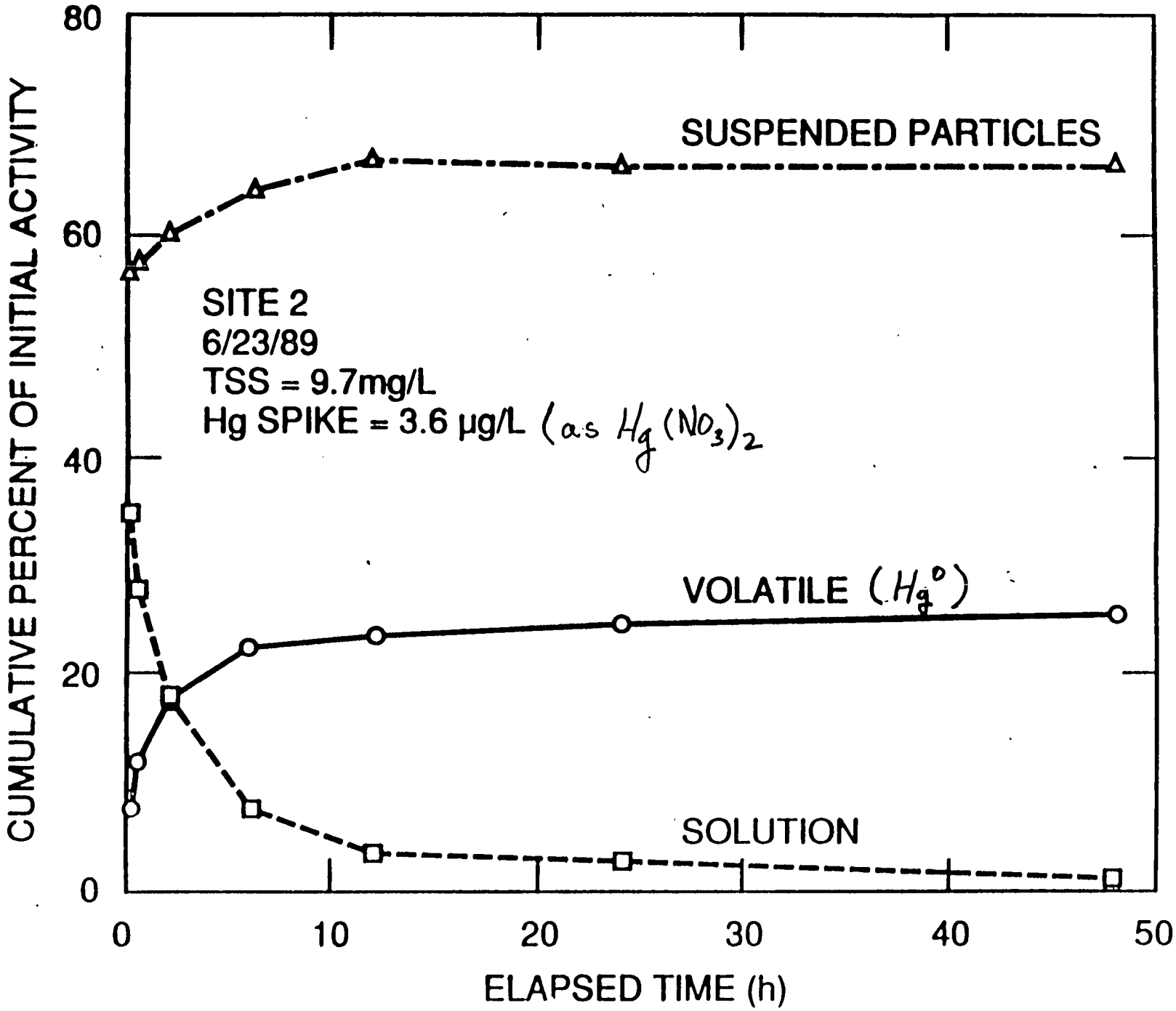
Advantages

- Simple proven technology for VOC
- Capture of Hg from air phase more cost effective than capture of Hg from water

Disadvantages (Challenges)

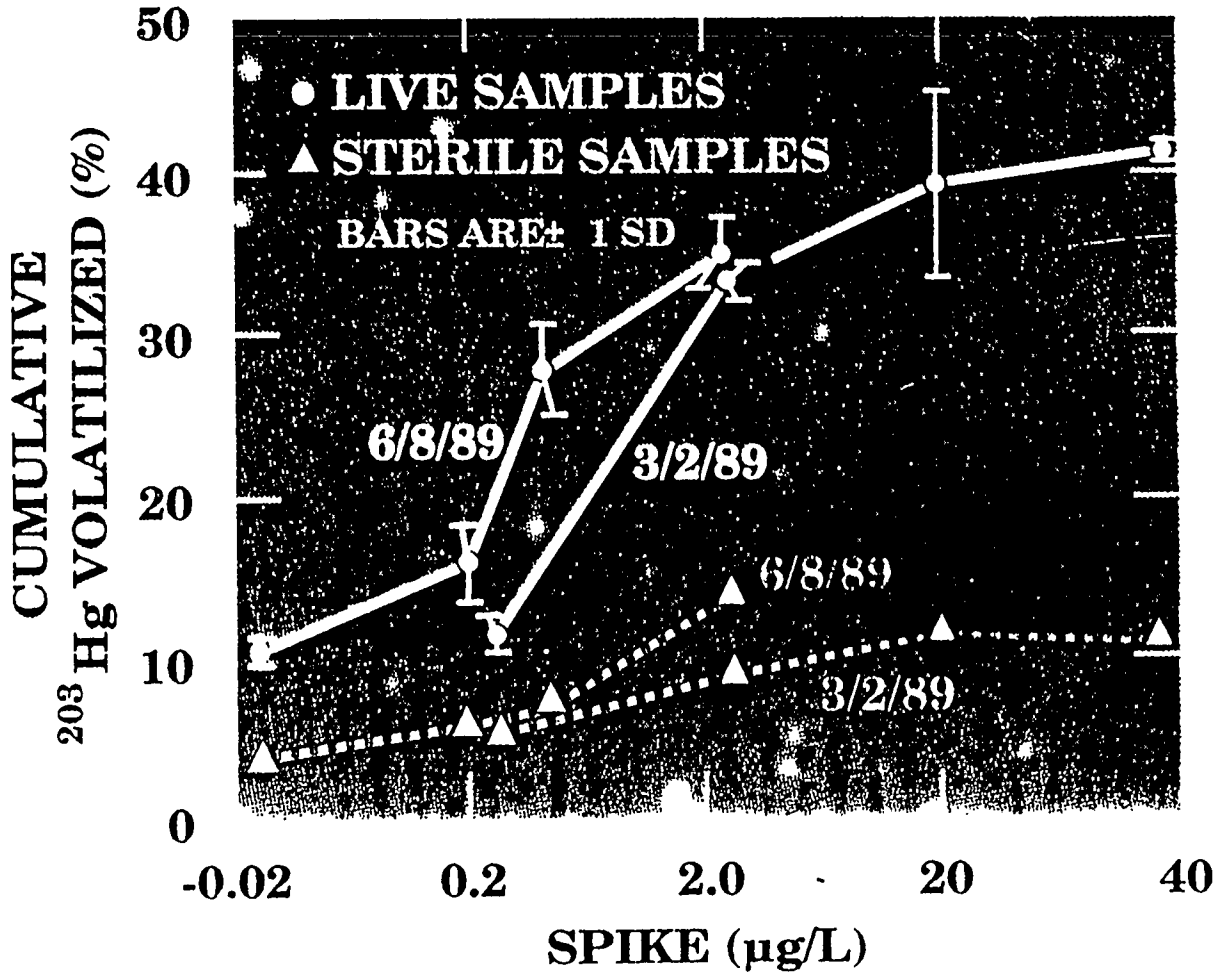
- Hg must be in the volatile elemental state for effective stripping
- Most Hg is not elemental

ORNL-DWG 89M-14079



ORNL DWG 90MC-11214

Reduction/Volatilization of Mercury is Dependent on [Hg] and is Mediated Significantly by Microorganism



ORNL-DWG 90MC-11214A

merA Genes Which Encode Mercuric Reductase are More Abundant in the Microbial Communities of New Hope Pond Than in Those of the Clinch River

Location	Sampling Date	Abundance of Sequences Homologous To Tn21 + Tn501 (ng target DNA/µg community DNA)
New Hope Pond	Oct 1988	18.1 ± 4.1
Clinch River	Oct 1988	0.25 ± 0.023
New Hope Pond	June 1989	0.51 ± 0.069
Clinch River	June 1989	0.029 ± 0.001

Observations

- Elimination of chlorine from outfalls has increased the fraction of Hg which is elemental
- Hg in building sump waters is up to 50% elemental
- Hg in Outfall 51 (springflow at 9201-2) is 30 to 50% elemental
- Henry's Constant for elemental Hg is highly favorable for air stripping
- Strong bioreduction potential present

Planned Tasks for FY95

- Purchase pilot-scale (10 gpm) air stripper with carbon treatment system for offgas and bag filter unit for aqueous effluent
- Test unit at Outfall 51 over extended period and at variable flows and temperatures
- Encourage biofouling with Hg-resistant microorganisms (Hg reducers)

Innovative R & D

Field Analysis of Mercury

Advantages of a Field Method

- Improve selection of samples for formal laboratory analysis
- Guide field cleanup activities
- Rapidly track surface water Hg sources
- Direct push screen groundwater sampling to track plumes
- Define boundaries of soil / sediment contamination
- Detect breakthrough of Hg in sorbent columns

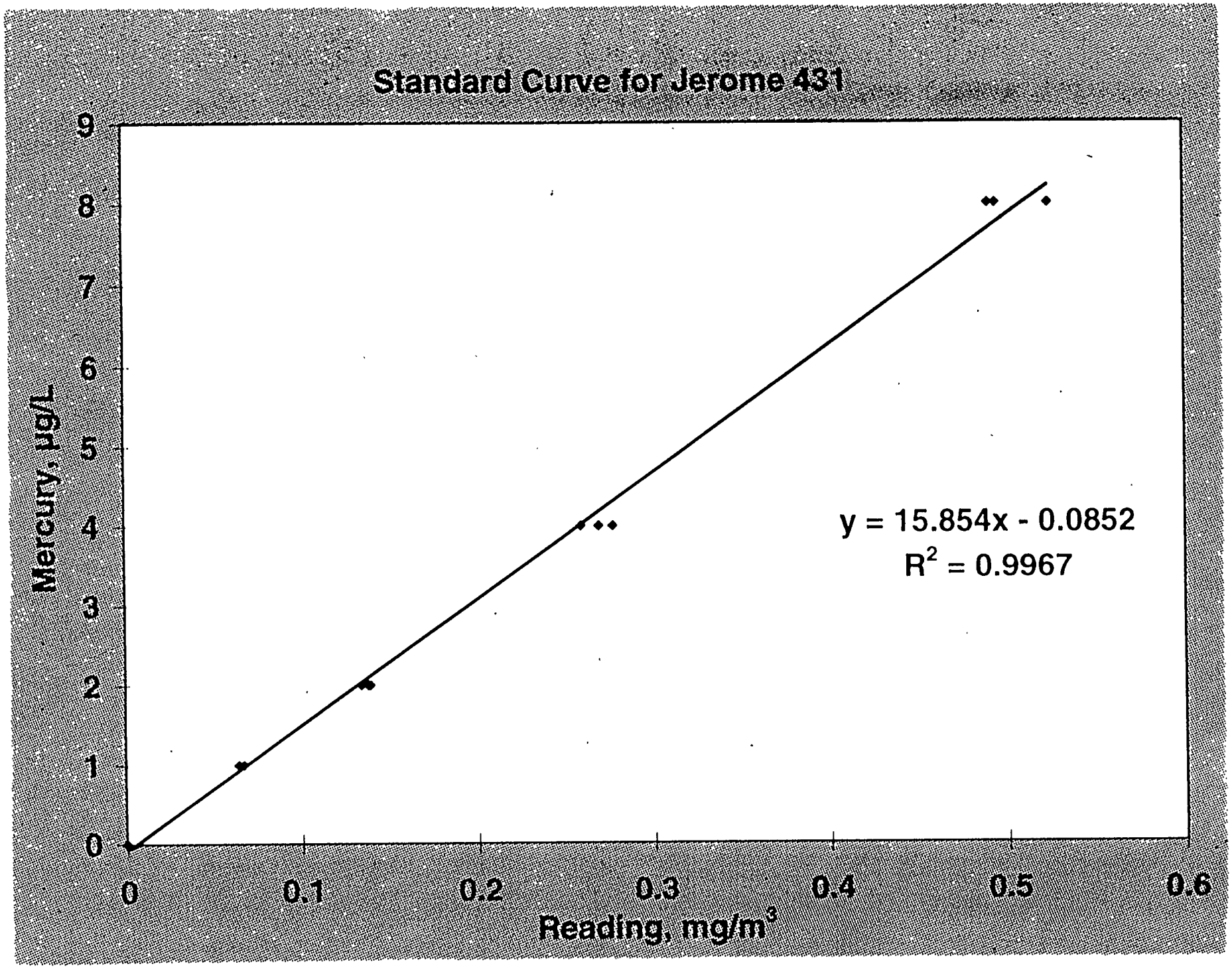
Approach

- Use commercially-available analyzer designed for air measurements of Hg°
- Adapt / test analyzer for headspace application using Henry's Law
- Treat samples to convert mercury to Hg°

Photo of Field Hg Analyzer Operation (Injecting Reductant)
(4805-94)

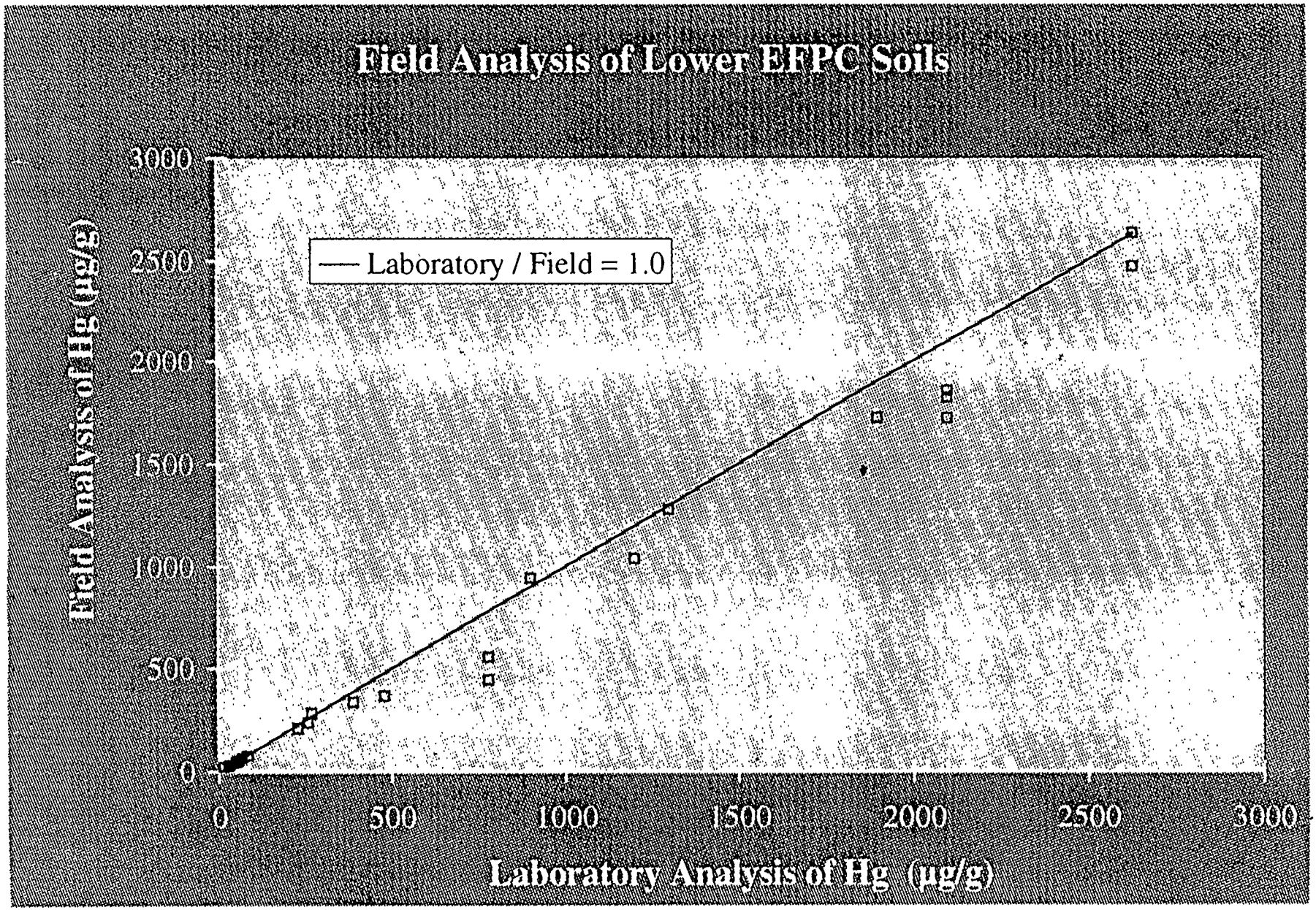
Photo of Field Hg Analyzer Operation (Shaking Sample)
(4807-94)

Photo of Field Hg Analyzer Operation (Taking Reading)
(4808-94)


Standard Curve for Jerome 431
Mercury, µg/L
0
1
2
3
4
5
6
7
8
9
0
0.1
0.2
0.3
0.4
0.5
0.6
Reading, mg/m3
y = 15.854x - 0.0852
R2 = 0.9967

EXTRACT MERCURY FROM SOIL WITH AQUA REGIA

TEST OF NEW FIELD SAMPLING METHOD USING JEROME MONITOR

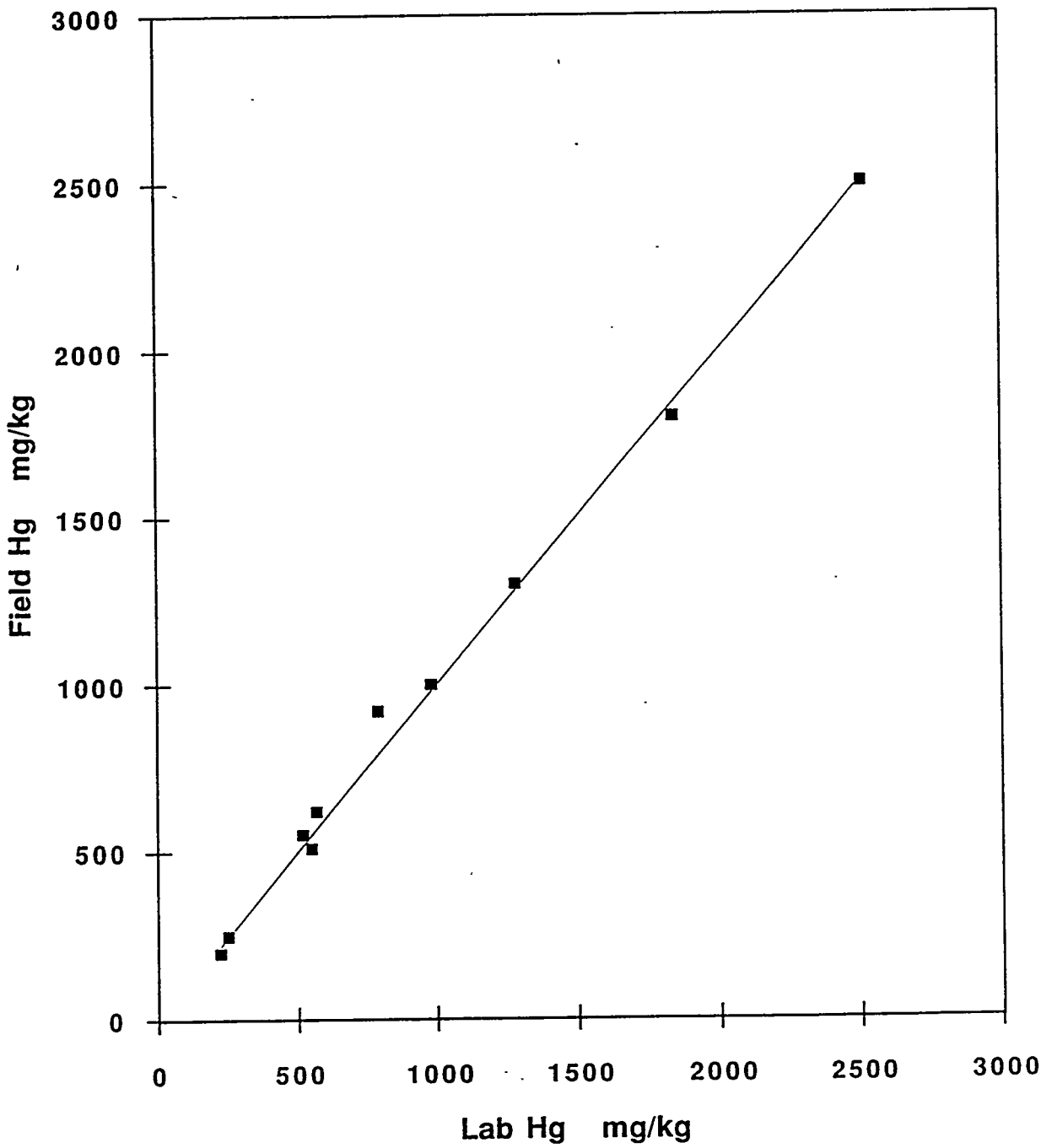


Innovative R & D

In situ Immobilization of Hg°

TEST OF NEW FIELD SAMPLING METHOD

EFPC Soil Analyses-March 1995



Batch Soil Test Results

(Solution/solid= 3 - 6, treat time = 20 d)

Soil Type	Pre Treat Hg (µg/L)	Additive	Post Treat Hg (µg/L)
Red clay	1.7	None	11
"	5.2	FeS_2	47
"	9.7	FeS_2	28
"	8.9	ZnS/0.1g	9.6
"	6.0	ZnS/0.2g	1.2
"	8.0	Thio-Red	5.7
Weathered shale	2.1	None	1.2
"	0.7	FeS_2	23
"	1.2	ZnS/0.1g	<0.13
"	0.1	ZnS/0.2g	<0.14
"	3.2	ZnS/0.2g	<0.13
"	0.5	Thio-Red	1.2

REDUCTION TO ELEMENTAL Hg?

ORNL DWG 92MC-8386

$$Hg + Ca(OH)_2 = Ag + CaO$$

Alchemical Translation:

Quicksilver + Lime = Silver + Quicklime

Summary

- Source elimination and containment strategies have been effective (> 75 % reduction since 1985)
- Current source treatment and additional source elimination / containment projects expected to achieve another 75 % reduction by 1998
- Innovative water treatment not attempted to date - NPDES permit disincentive
- Early results from in situ immobilization studies are promising
- Inexpensive and fast field screening technique for Hg in water and soil has been developed

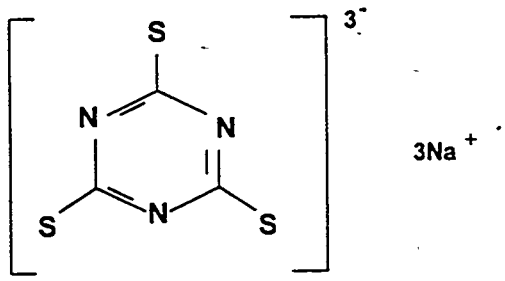
Fine Chemicals Division

Degussa

Degussa Corporation

Data Sheet

TMT 15



Chemical formula:	$C_3N_3Na_3S_3$
Chemical name:	TriMercapto-s-Triazine, trisodium salt
Synonyms:	1,3,5-Triazine-2,4,6-(1H,3H,5H)-trithione, trisodium salt
	Trithiocyanuric acid, trisodium salt
CAS No:	17766-26-6
Appearance:	Pale yellow liquid
Molecular Weight:	243.22
Density (68°F):	1.12 g/cm³ [9.35 lbs./gal]
Boiling point:	101°C [214°F]
Melting point:	-3°C [26-27°F]
pH:	12.5 approx.
HMIS:	
	Health 0
	Flammability 0
	Reactivity 0
	Personal Protection B

The active ingredient is listed on the TSCA inventory

Specification: **Assay ≥ 15%**

08-93

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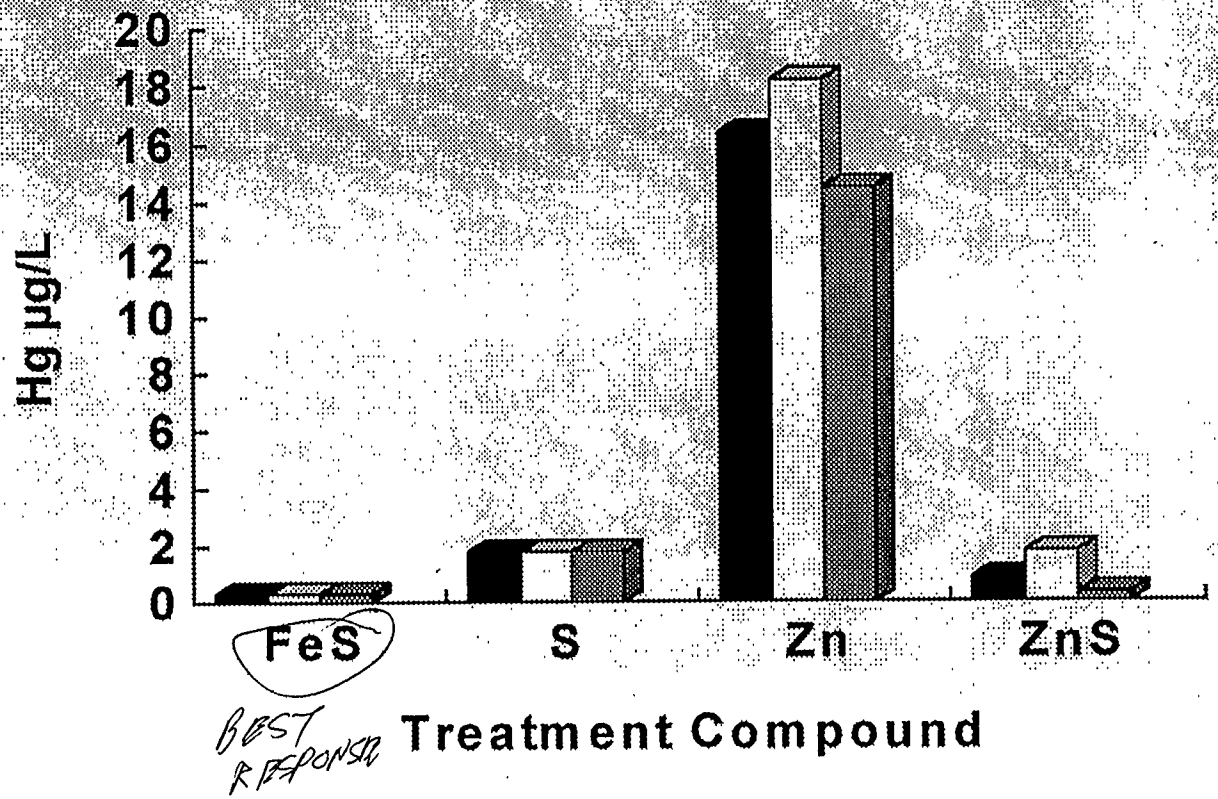
In situ Treatment of Hg° in Sand



BEST RESPONSE

ELEMENTAL MERCURY SATURATION LEVEL IN WATER ~60 ppb

MERCURY IMMOBILIZATION AGENTS

Candidate Materials

	Reaction
Zinc metal	Amalg
Zinc sulfide (sphalerite)	Redox
Elemental sulfur	Redox
Iron sulfide (pyrite, pyrrhotite)	Sorption
Sodium thiocarbonate (Thio-Red)	Ppt
Sodium trithiolcyanurate (TMT-15)	Ppt

REACTION OF ELEMENTAL MERCURY AND SULFUR TO FORM MERCURIC SULFIDE

Half Reaction	E_H	ΔG
$Hg(l) = Hg^{2+} + 2e^-$	-0.85	+164.7
$S(s) + 2e^- = S^{2-}$	-0.44	+85.8
$Hg(l) + S(s) = Hg^{2+} + S^{2-}$	-1.29	+250.5

Oxidation reduction reaction not thermodynamically favorable

However mercuric sulfide precipitation reaction very thermodynamically favorable

$Hg^{2+} + S^{2-} = HgS(s) \quad \Delta G = -296.9$

Add redox and precipitation reactions to yield overall reaction

$Hg(l) + S(s) = HgS(s)$

$\Delta G = +250.5 + -296.9 = -46.4$

Overall reaction proceeds spontaneously

Goal

Identify compound(s) capable of reacting with Hg° in the subsurface to reduce solubility

Desirable Properties of an Immobilizing Agent

Effective (reactive) with all forms of mercury

Non-toxic

No nuisance (e.g., odor, material handling problems)

No, or insignificant, release of other contaminants

Cheap/abundant

Capable of being injected or infused

Product non-degradable (stable)

Photo of Mercury Beads in Soil
(224100)

Rationale

- Spills and leaks of Hg° have migrated into foundation drainage systems
- Access to the Hg for cleanup is very limited or non-existent, and its exact location is difficult to identify
- Shallow groundwater dissolves some of this Hg and enters sumps where it is pumped into the storm sewer system
- Capture and treatment of sump water is not ideal permanent solution