Metals Matrix Metadata Mistakes Modify Monitoring Management

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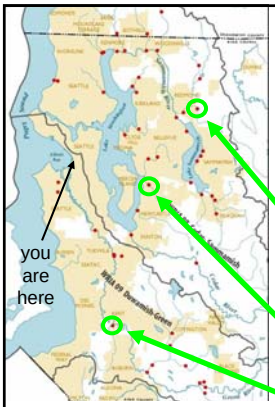
DISCLAIMER

The opinions expressed in this technical presentation are those of the authors and do not necessarily reflect the views of the US EPA, or King County.

how are sailing and data analysis similar?

this is a tale of how decisions that are supposed to be based on data, were inaccurate due to inattention to proper content and delivery quality features, and what was the impact to cost, efficiency, and process due to this poor attention to quality

you constantly find new and different ways to screw up, even when you are very, very careful



King County long-term stream monitoring program collects data from ~40 streams county-wide

data is also submitted to Washington Department of Ecology for the 303(d) Water Quality limited list

sometimes listings are incorrect

- ***why does this happen?***
- ***what is the cost of inappropriate listings***
- ***does anyone really care?***
- ***how do we minimize the probability that it will happen again?***

303(d) listed Waterbodies in Washington State, Based on the 1996 *303(d) List*

Waterbody Segment Number	Waterbody Name	Parameters Exceeding Standards
WA-08-1095	BEAR-EVANS CREEKS	Dissolved Oxygen, Fecal Coliform, Mercury
WA-09-1022	HILL (MILL) CREEK	Dissolved Oxygen, Temperature, Ammonia-N, Cadmium, Fecal Coliform, Zinc, Chromium.
WA-08-1130	MAY CREEK	Fecal Coliform, Temperature, Copper, Lead, Zinc

data in…

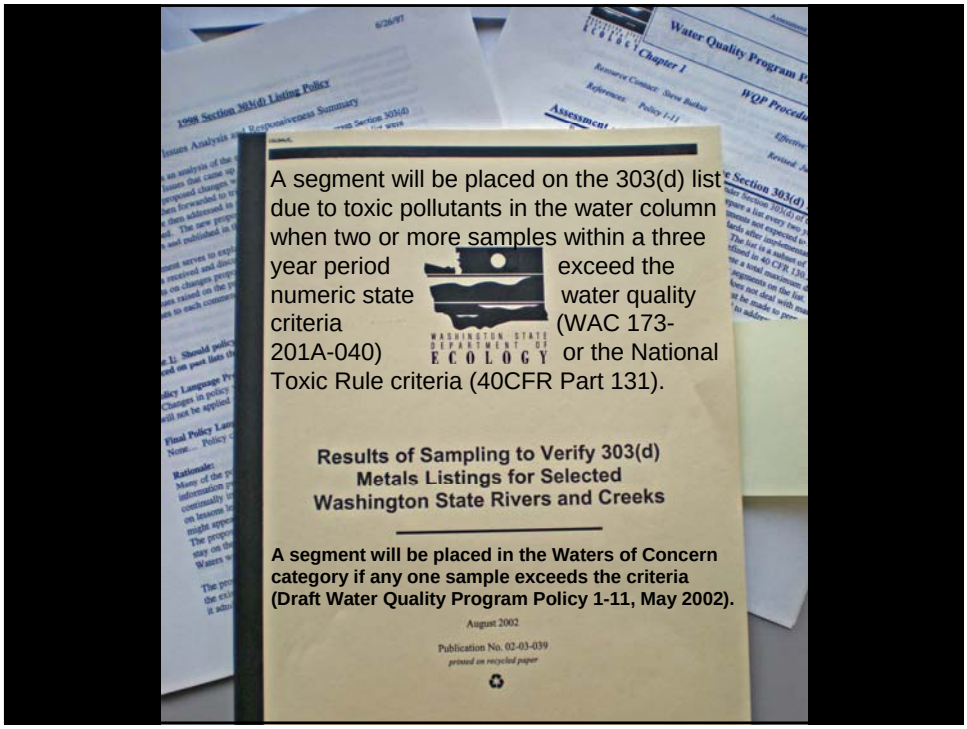
Collectdate	Matrix	Qual	Copper, Total, ICP	Units
9/3/98	SE FRSHWTRSED		6.86	mg/Kg
9/2/98	SE FRSHWTRSED		3.36	mg/Kg
8/30/99	SE FRSHWTRSED		8.48	mg/Kg
9/7/99	SE FRSHWTRSED	E	4.08	mg/Kg
7/27/00	SE FRSHWTRSED	E	5.72	mg/Kg
7/27/00	SE FRSHWTRSED	E	2.84	mg/Kg
7/25/00	SE FRSHWTRSED	E	2.35	mg/Kg
7/26/01	SE FRSHWTRSED		6.35	mg/Kg
7/30/01	SE FRSHWTRSED		3.15	mg/Kg

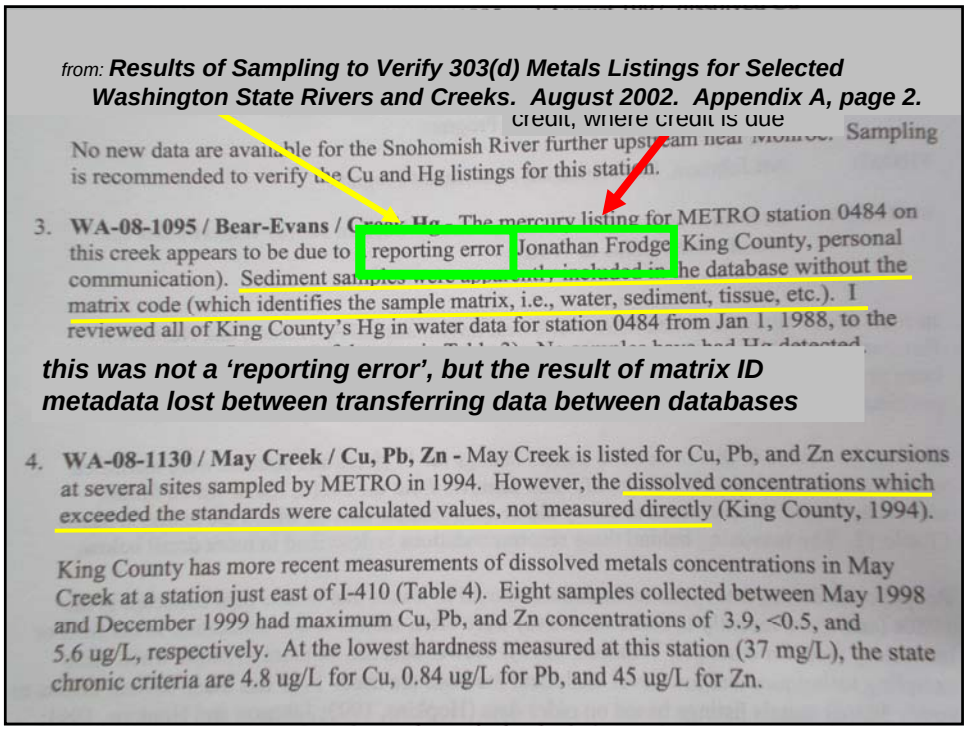
Copper, Total, ICP
6.86
3.36
8.48
4.08
5.72
2.84
2.35
6.35
3.15

the RAMIS database which ran on the soon to retire VAX computer, would put units, metadata and quantification into separate columns….

…garbage out,

and onto the 303(d) list as water column data you go!





from: ***Results of Sampling to Verify 303(d) Metals Listings for Selected Washington State Rivers and Creeks. August 2002. Appendix A, page 2.***

credit, where credit is due

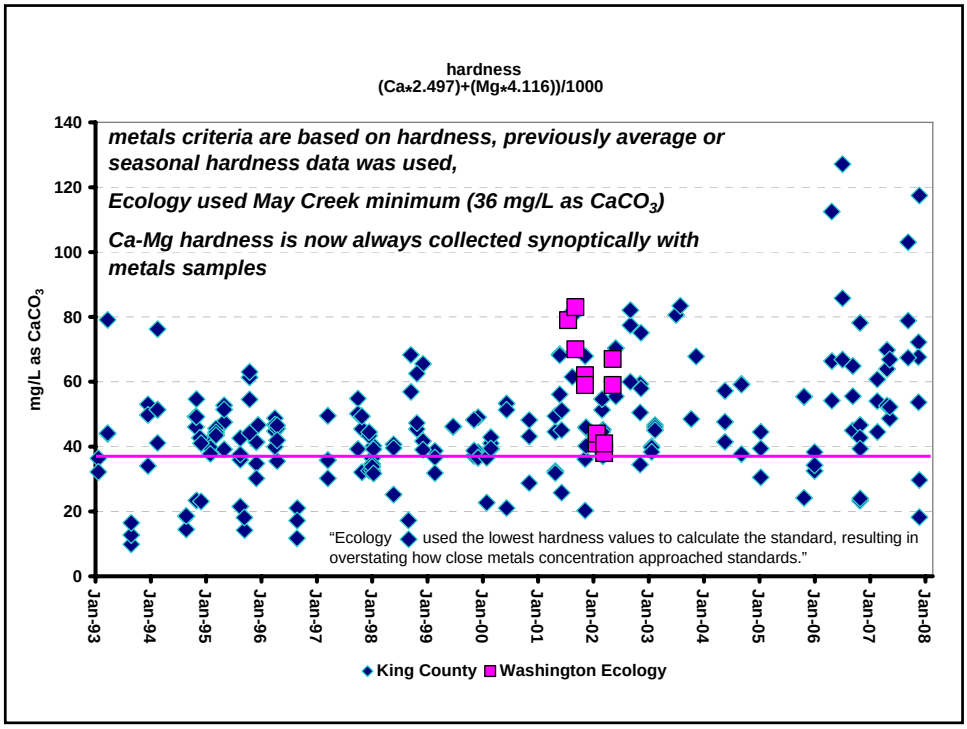
No new data are available for the Snohomish River further upstream near Monroe. Sampling is recommended to verify the Cu and Hg listings for this station.

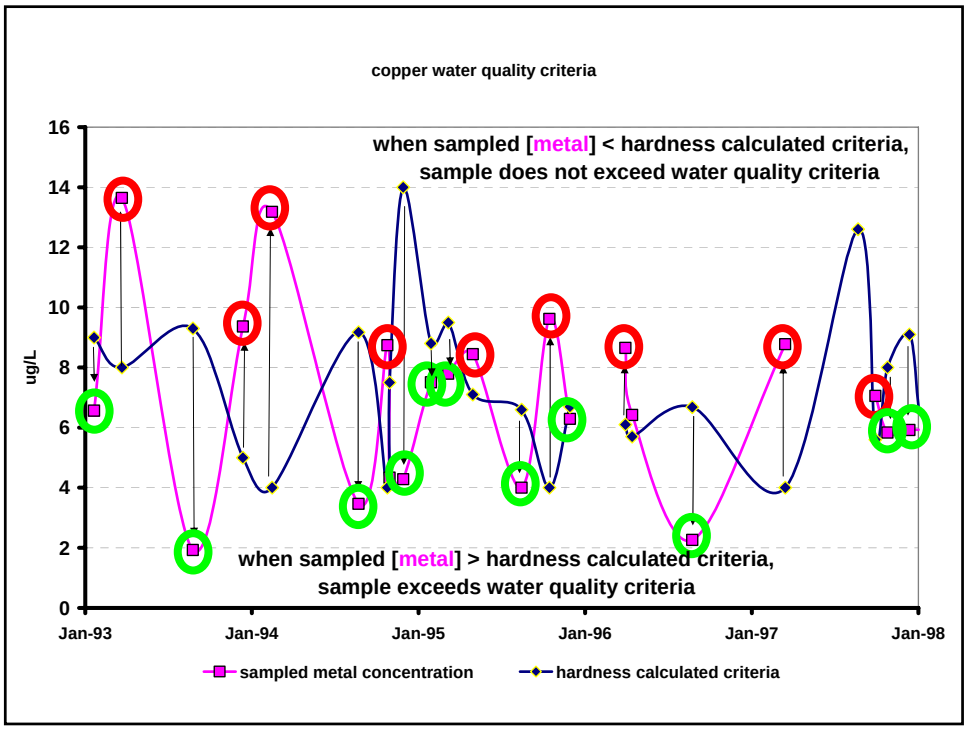
3. **WA-08-1095 / Bear-Evans / Green Hg** - The mercury listing for METRO station 0484 on this creek appears to be due to reporting error Jonathan Frodge King County, personal communication). Sediment samples were apparently included in the database without the matrix code (which identifies the sample matrix, i.e., water, sediment, tissue, etc.). I reviewed all of King County's Hg in water data for station 0484 from Jan 1, 1988, to the

this was not a 'reporting error', but the result of matrix ID metadata lost between transferring data between databases

4. **WA-08-1130 / May Creek / Cu, Pb, Zn -** May Creek is listed for Cu, Pb, and Zn excursions at several sites sampled by METRO in 1994. However, the dissolved concentrations which exceeded the standards were calculated values, not measured directly (King County, 1994).

King County has more recent measurements of dissolved metals concentrations in May Creek at a station just east of I-410 (Table 4). Eight samples collected between May 1998 and December 1999 had maximum Cu, Pb, and Zn concentrations of 3.9, <0.5, and 5.6 ug/L, respectively. At the lowest hardness measured at this station (37 mg/L), the state chronic criteria are 4.8 ug/L for Cu, 0.84 ug/L for Pb, and 45 ug/L for Zn.


hardness
(Ca*2.497)+(Mg*4.116))/1000
metals criteria are based on hardness, previously average or seasonal hardness data was used,
Ecology used May Creek minimum (36 mg/L as CaCO3)
Ca-Mg hardness is now always collected synoptically with metals samples
mg/L as CaCO3
"Ecology used the lowest hardness values to calculate the standard, resulting in overstating how close metals concentration approached standards."
King County
Washington Ecology


copper water quality criteria
when sampled [metal] < hardness calculated criteria, sample does not exceed water quality criteria
when sampled [metal] > hardness calculated criteria, sample exceeds water quality criteria
ug/L
sampled metal concentration
hardness calculated criteria

– *to graph if metals meet or exceed chronic water quality criteria*

> zero exceeds acute criteria, < zero does not exceed acute criteria

criteria from WAC 173-201A

Cu acute criteria = ((0.96)(EXP(0.9422*(LN(hardness))-1.464)))

*change from total to **dissolved** metals occurred in the 1997 WQ Std update*

Collectdate	hardness	Qual	Copper, Total, ICP	Cu acute	acute diff	Cu chronic	chronic diff
01/20/93	36	<RDL	9.00	6.56	2.44	4.78	4.22
03/22/93	79	<RDL	8.00	13.64	-5.64	9.29	-1.29
08/25/93	10		9.30	1.92	7.38	1.57	7.73
12/13/93	53	<RDL	5.00	9.36	-4.36	6.60	-1.60
02/15/94	76	<MDL	**4.00**	13.18	-9.18	9.00	-5.00
08/24/94	18		9.17	3.46	5.71	2.68	6.49
10/26/94	49	<MDL	**4.00**	8.74	-4.74	6.20	-2.20
10/31/94	23	<RDL	7.50	4.33	3.17	3.28	4.22
11/30/94	23	<RDL	14.00	4.28	9.72	3.25	10.75
01/30/95	42	<RDL	8.80	7.50	1.30	5.40	3.40

(sampled [metal] µg/L) – (hardness calculated acute criteria) = acute value

– *to graph if metals meet or exceed chronic water quality criteria*

> zero exceeds chronic criteria, < zero does not exceed chronic criteria

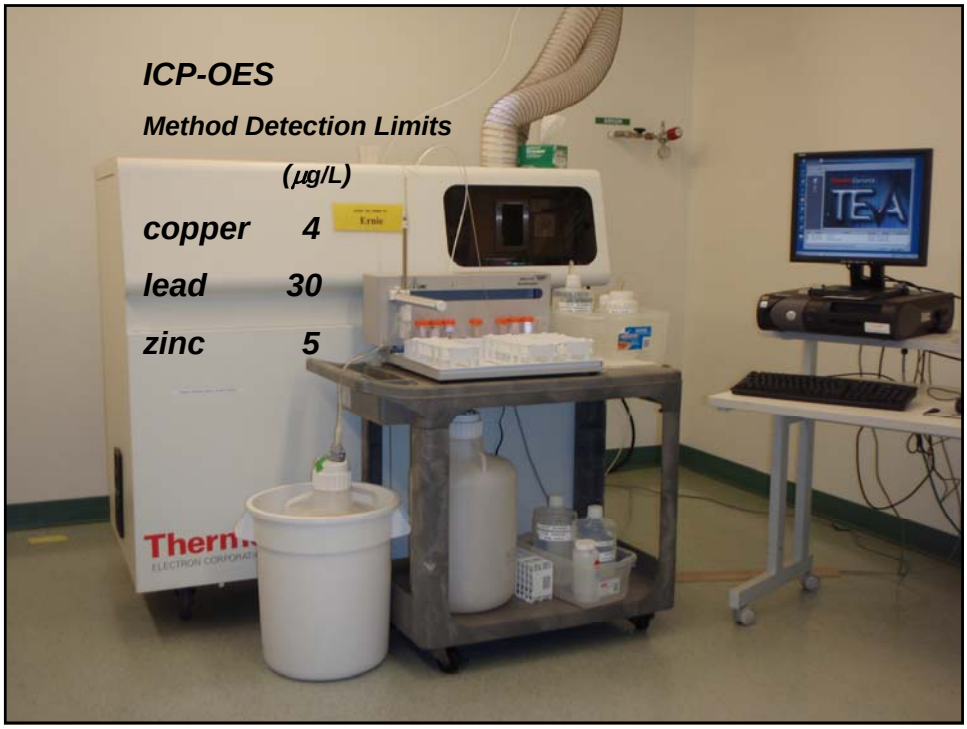
criteria from WAC 173-201A

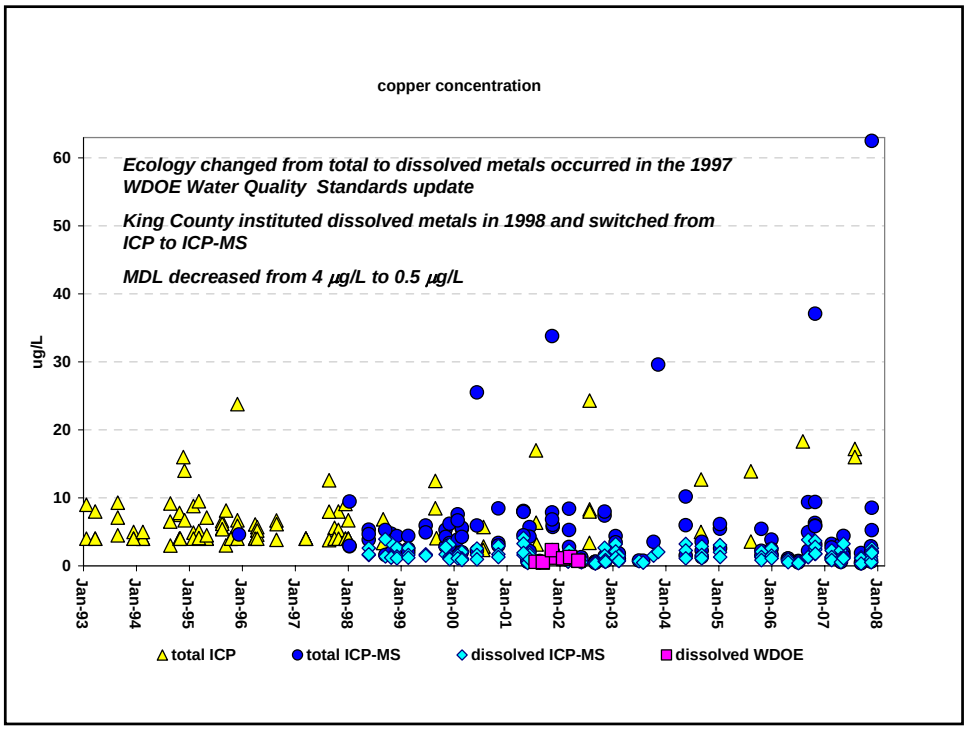
Cu chronic criteria = ((0.96)(EXP(0.8545*(LN(hardness))-1.464)))

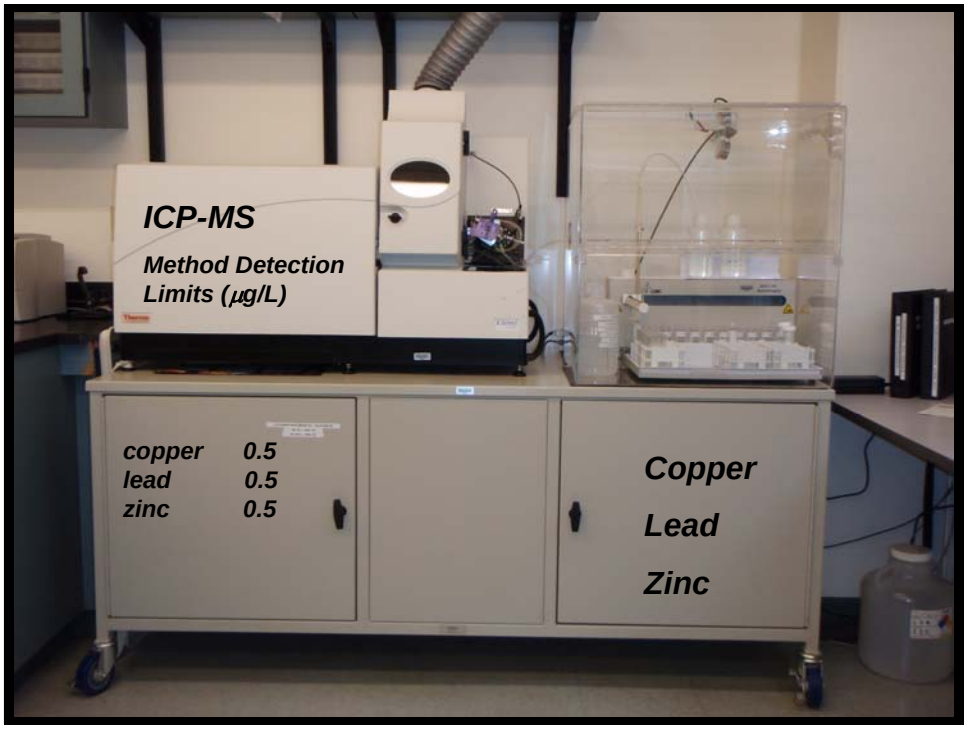
*change from total to **dissolved** metals occurred in the 1997 WQ Std update*

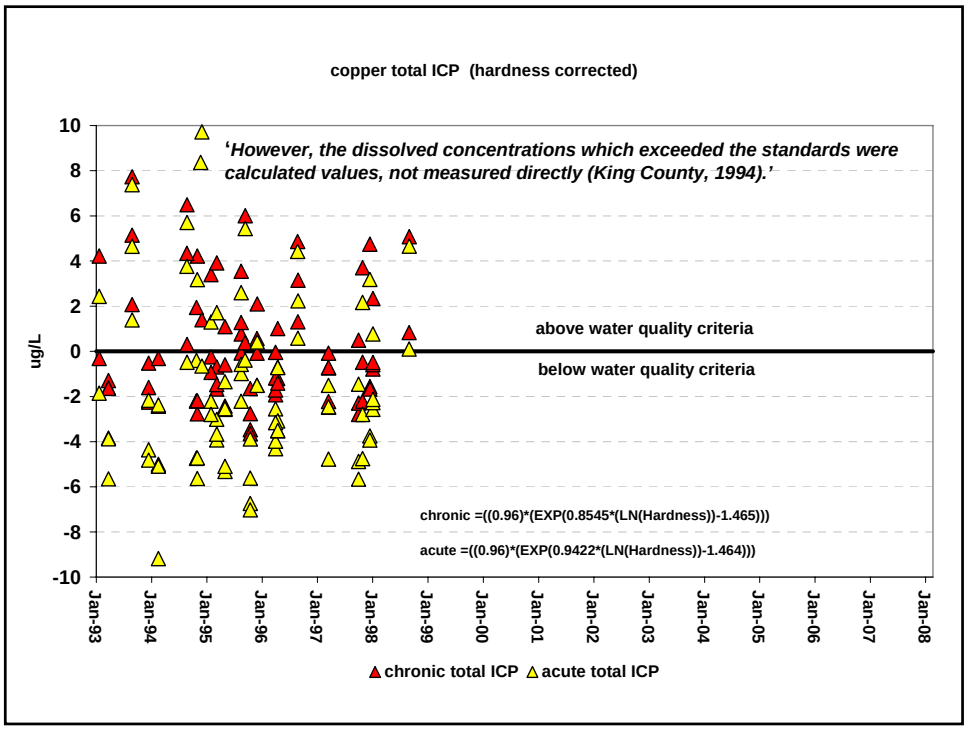
Collectdate	hardness	Qual	Copper, Total, ICP	Cu acute	acute diff	Cu chronic	chronic diff
01/20/93	36	<RDL	9.00	6.56	2.44	4.78	4.22
03/22/93	79	<RDL	8.00	13.64	-5.64	9.29	-1.29
08/25/93	10		9.30	1.92	7.38	1.57	7.73
12/13/93	53	<RDL	5.00	9.36	-4.36	6.60	-1.60
02/15/94	76	<MDL	**4.00**	13.18	-9.18	9.00	-5.00
08/24/94	18		9.17	3.46	5.71	2.68	6.49
10/26/94	49	<MDL	**4.00**	8.74	-4.74	6.20	-2.20
10/31/94	23	<RDL	7.50	4.33	3.17	3.28	4.22
11/30/94	23	<RDL	14.00	4.28	9.72	3.25	10.75
01/30/95	42	<RDL	8.80	7.50	1.30	5.40	3.40

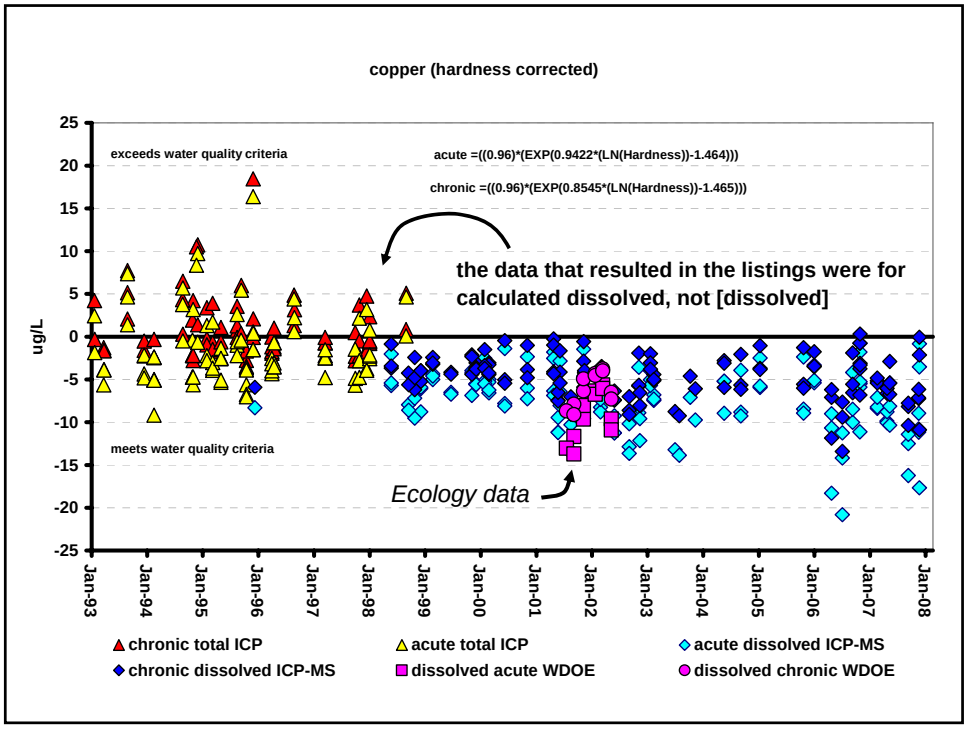
(sampled [metal] µg/L) – (hardness calculated chronic criteria) = chronic value

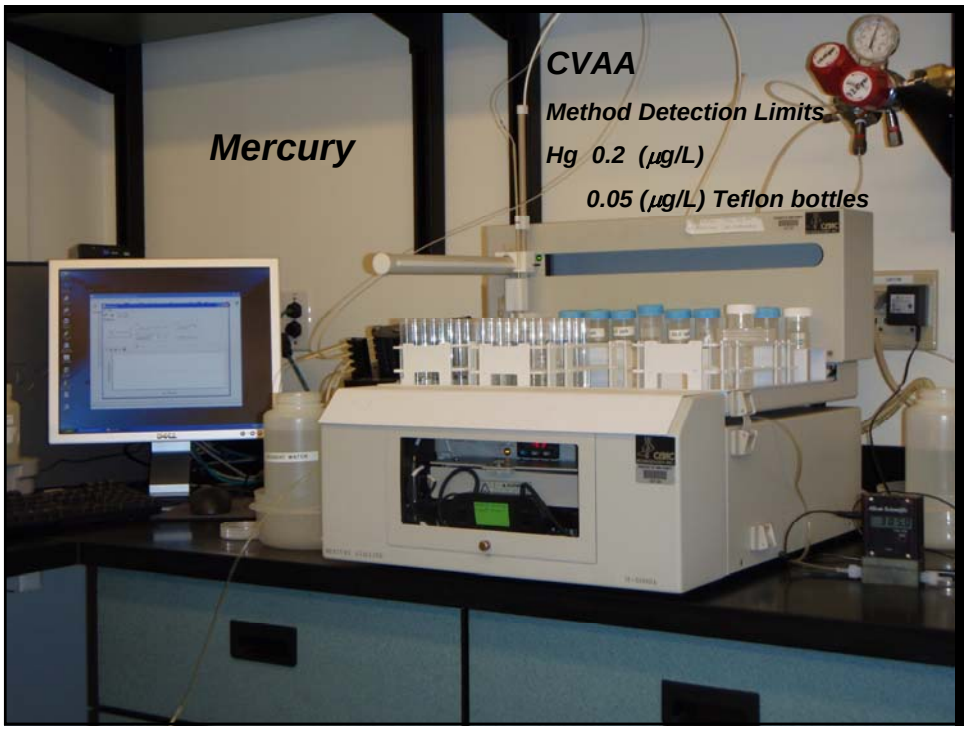

ICP-OES
Method Detection Limits
(µg/L)
copper 4
lead 30
zinc 5
TEVA

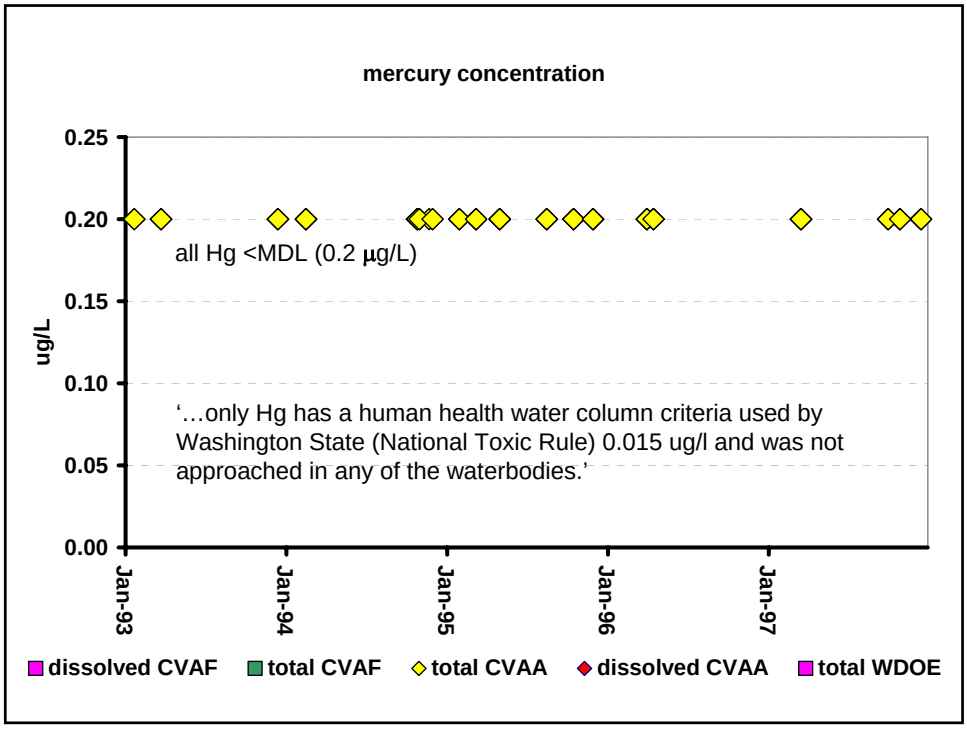

copper concentration
Ecology changed from total to dissolved metals occurred in the 1997 WDOE Water Quality Standards update
King County instituted dissolved metals in 1998 and switched from ICP to ICP-MS
MDL decreased from 4 µg/L to 0.5 µg/L
ug/L
0
10
20
30
40
50
60
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
total ICP
total ICP-MS
dissolved ICP-MS
dissolved WDOE


ICP-MS
Method Detection Limits (µg/L)
copper 0.5
lead 0.5
zinc 0.5
Copper
Lead
Zinc


copper total ICP (hardness corrected)
'However, the dissolved concentrations which exceeded the standards were calculated values, not measured directly (King County, 1994).'
above water quality criteria
below water quality criteria
chronic =((0.96)*(EXP(0.8545*(LN(Hardness))-1.465)))
acute =((0.96)*(EXP(0.9422*(LN(Hardness))-1.464)))
ug/L
10
8
6
4
2
0
-2
-4
-6
-8
-10
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
chronic total ICP
acute total ICP


copper (hardness corrected)
exceeds water quality criteria
acute =((0.96)*(EXP(0.9422*(LN(Hardness))-1.464)))
chronic =((0.96)*(EXP(0.8545*(LN(Hardness))-1.465)))
the data that resulted in the listings were for calculated dissolved, not [dissolved]
meets water quality criteria
Ecology data
ug/L
25
20
15
10
5
0
-5
-10
-15
-20
-25
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
chronic total ICP
acute total ICP
acute dissolved ICP-MS
chronic dissolved ICP-MS
dissolved acute WDOE
dissolved chronic WDOE


Mercury
CVAA
Method Detection Limits
Hg 0.2 (μg/L)
0.05 (μg/L) Teflon bottles



When the RAMIS database was downloaded off of the VAX…..

Locator	Collectdate	Matrix	Qual	Mercury, Dissolved, CVAA	Units
484	5/27/98	LG STORM WTR	<MDL	<0.2	ug/L
440	5/27/98	LG STORM WTR	<MDL	<0.2	ug/L
440	9/3/98	SE FRSHWTRSED			
484	9/2/98	SE FRSHWTRSED			
484	9/18/98	LG STORM WTR	<MDL	<0.2	ug/L
440	9/18/98	LG STORM WTR	<MDL	<0.2	ug/L
484	10/28/98	LG STORM WTR	<MDL	<0.2	ug/L
440	10/28/98	LG STORM WTR	<MDL	<0.2	ug/L
484	12/7/98	LG STORM WTR	<MDL	<0.2	ug/L
440	12/7/98	LG STORM WTR	<MDL	<0.2	ug/L

this data

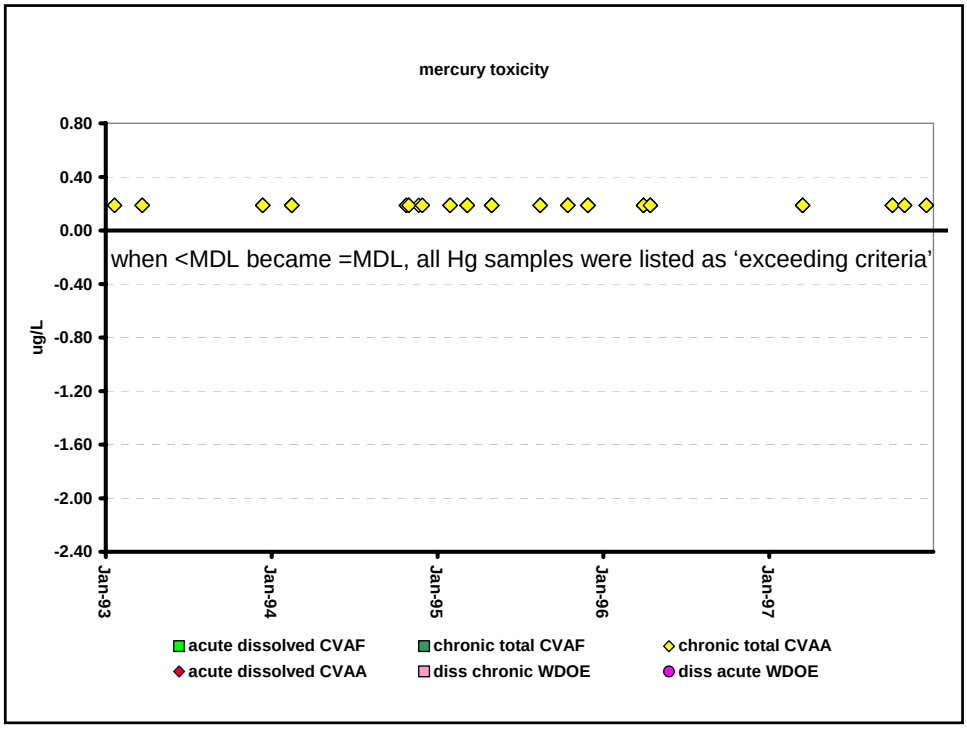
becomes……

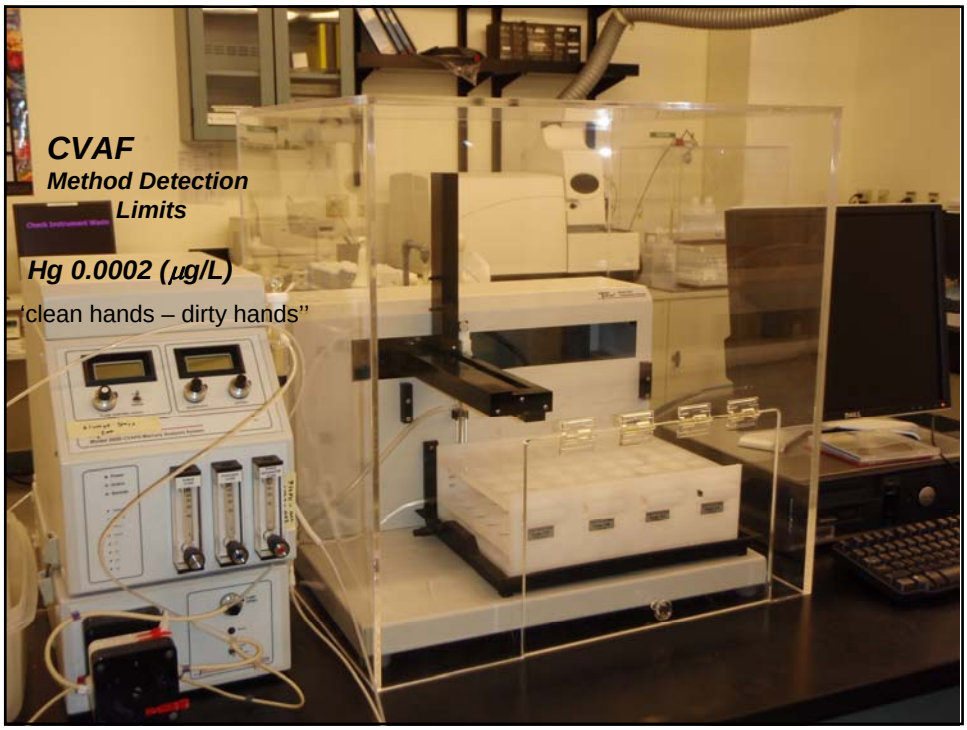
Qual	Mercury, Dissolved, CVAA
<	0.2
<	0.2
<	0.2
<	0.2
<	0.2
<	0.2
<	0.2
<	0.2

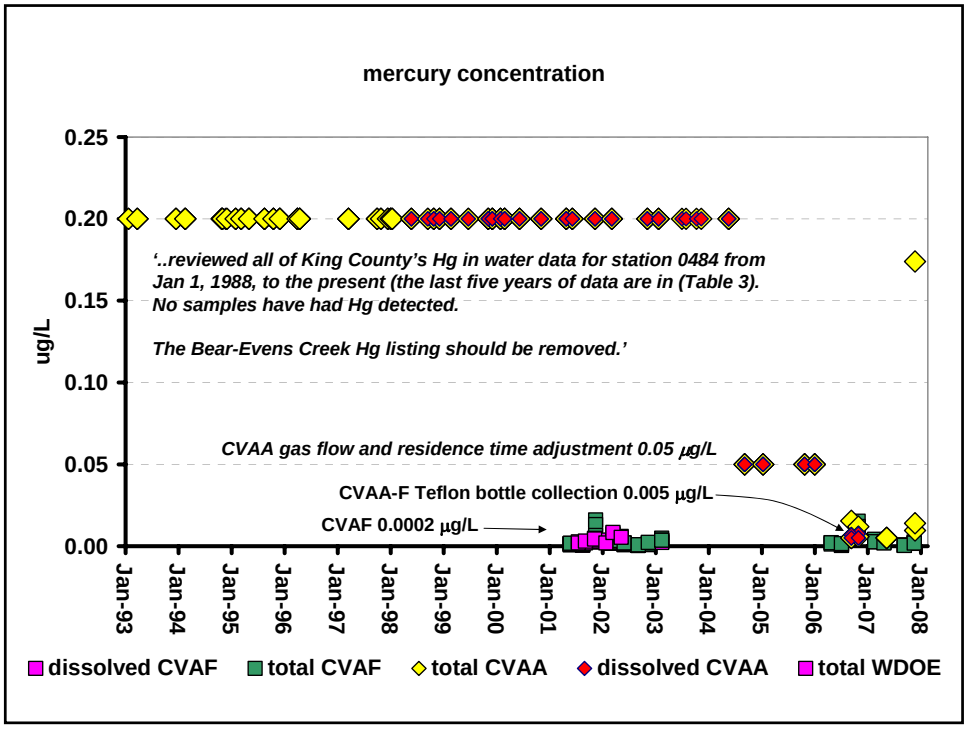
this

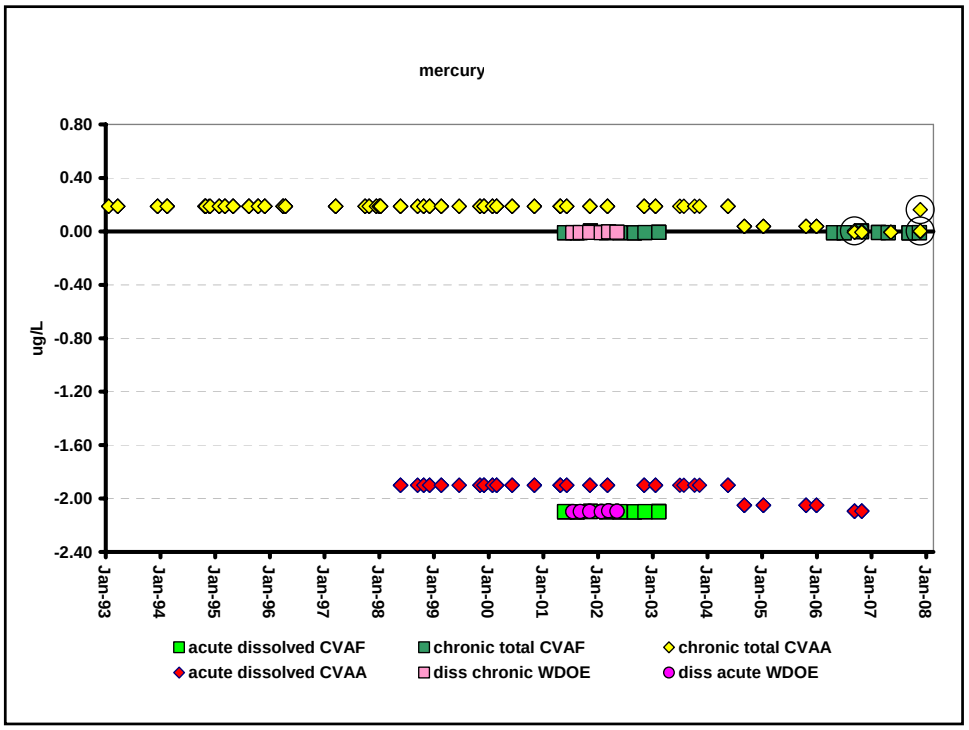
Mercury, Dissolved, CVAA
0.2
0.2
0.2
0.2
0.2
0.2
0.2
0.2

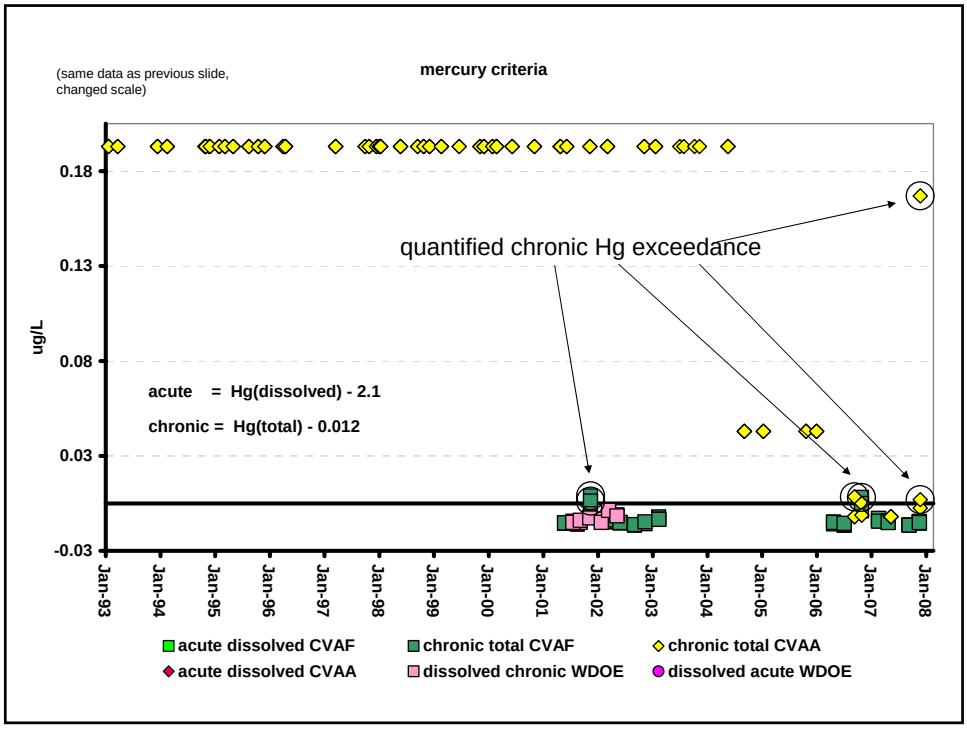
using this data as a quantification, instead of <MDL resulted in erroneous listings, and would be really high concentrations

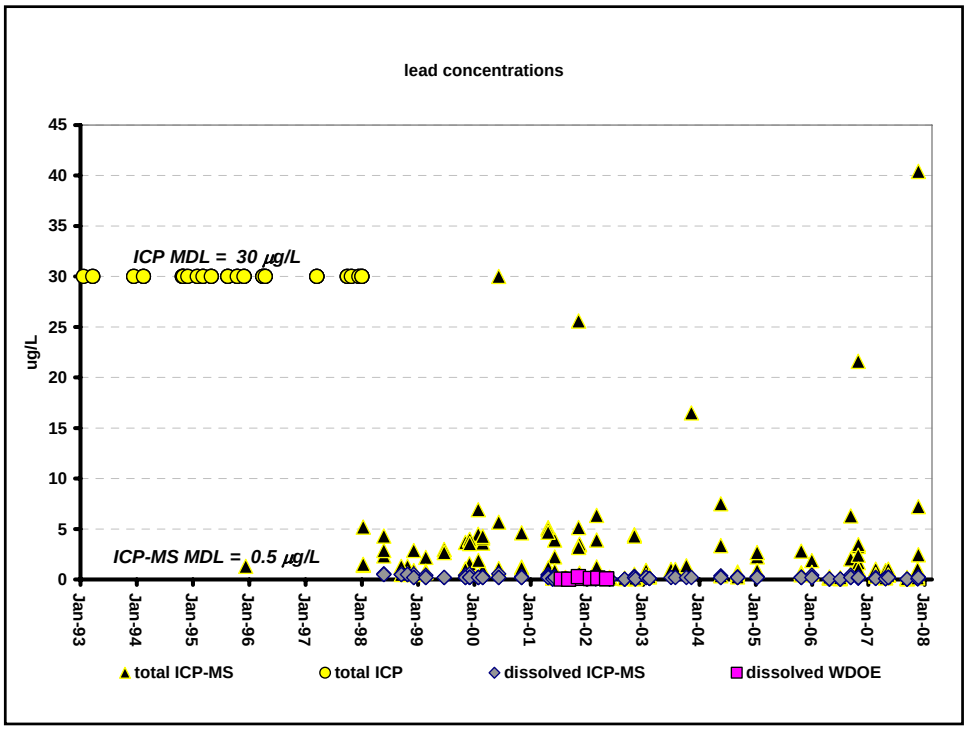

mercury toxicity
0.80
0.40
0.00
-0.40
-0.80
-1.20
-1.60
-2.00
-2.40
ug/L
when <MDL became =MDL, all Hg samples were listed as 'exceeding criteria'
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
acute dissolved CVAF
chronic total CVAF
chronic total CVAA
acute dissolved CVAA
diss chronic WDOE
diss acute WDOE

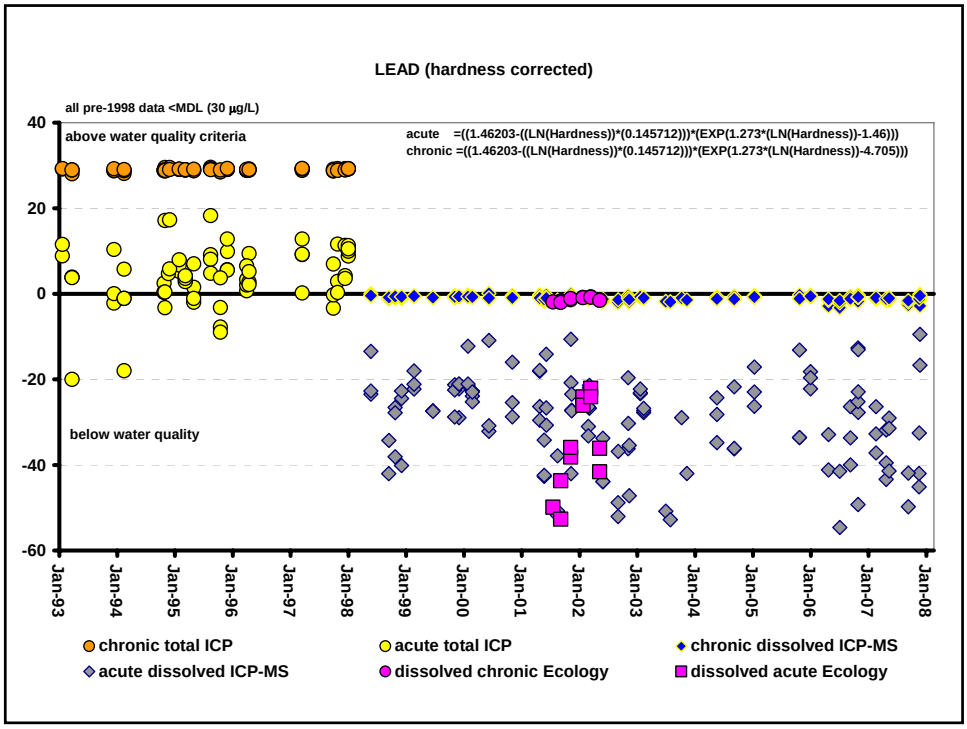

CVAF
Method Detection Limits
Hg 0.0002 (μg/L)
"clean hands – dirty hands"

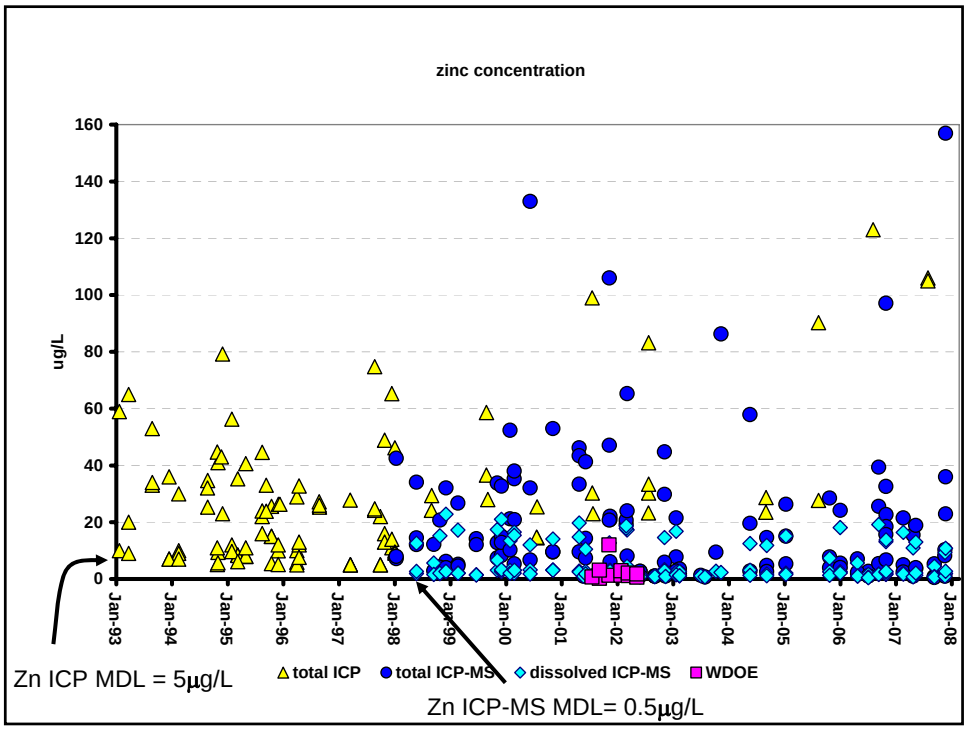

mercury concentration
0.25
0.20
0.15
0.10
0.05
0.00
ug/L
'..reviewed all of King County's Hg in water data for station 0484 from Jan 1, 1988, to the present (the last five years of data are in (Table 3). No samples have had Hg detected.
The Bear-Evens Creek Hg listing should be removed.'
CVAA gas flow and residence time adjustment 0.05 µg/L
CVAA-F Teflon bottle collection 0.005 µg/L
CVAF 0.0002 µg/L
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
dissolved CVAF
total CVAF
total CVAA
dissolved CVAA
total WDOE

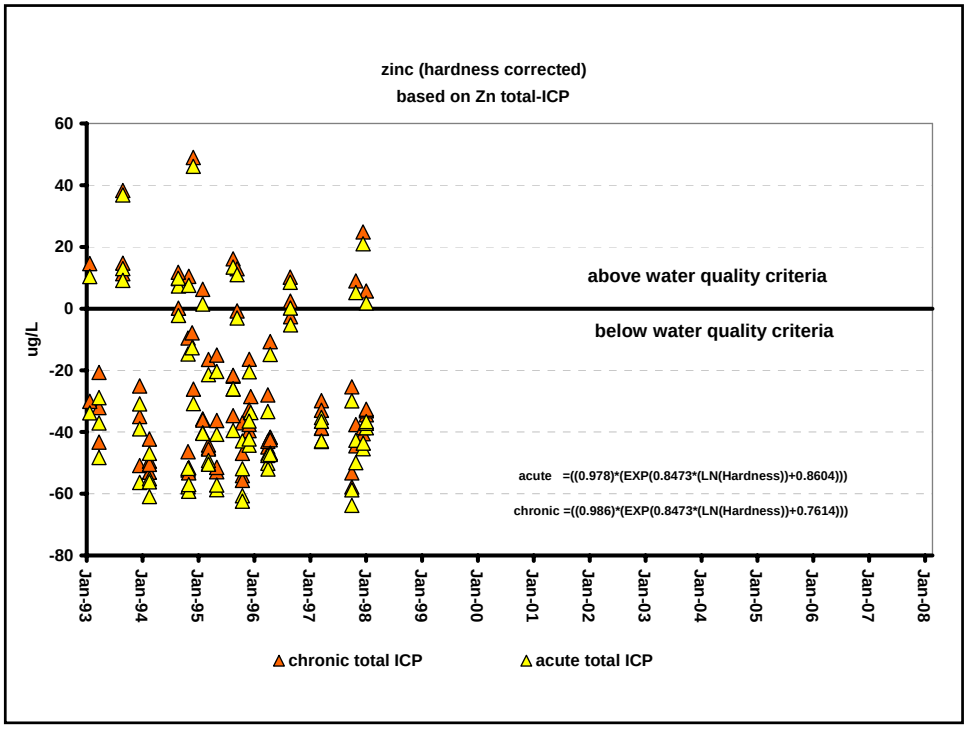

mercury
0.80
0.40
0.00
-0.40
-0.80
-1.20
-1.60
-2.00
-2.40
ug/L
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
acute dissolved CVAF
chronic total CVAF
chronic total CVAA
acute dissolved CVAA
diss chronic WDOE
diss acute WDOE

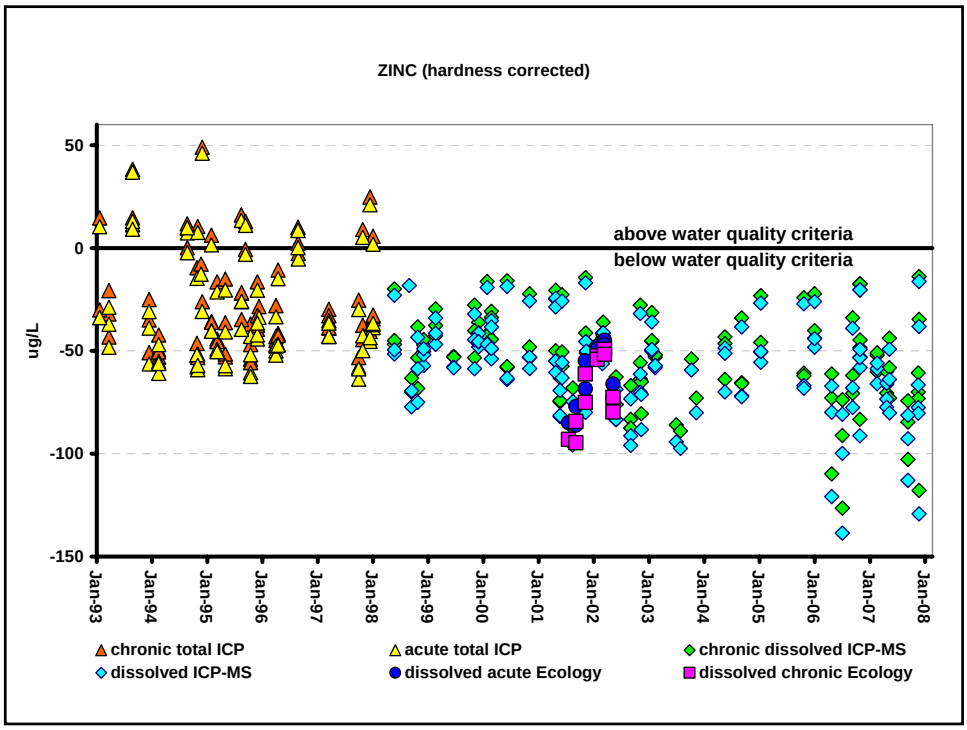

(same data as previous slide, changed scale)
mercury criteria
quantified chronic Hg exceedance
acute = Hg(dissolved) - 2.1
chronic = Hg(total) - 0.012
ug/L
0.18
0.13
0.08
0.03
-0.03
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
acute dissolved CVAF
chronic total CVAF
chronic total CVAA
acute dissolved CVAA
dissolved chronic WDOE
dissolved acute WDOE


lead concentrations
ICP MDL = 30 µg/L
ICP-MS MDL = 0.5 µg/L
ug/L
45
40
35
30
25
20
15
10
5
0
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
total ICP-MS
total ICP
dissolved ICP-MS
dissolved WDOE


LEAD (hardness corrected)
all pre-1998 data <MDL (30 µg/L)
above water quality criteria
acute =((1.46203-((LN(Hardness))*(0.145712)))*(EXP(1.273*(LN(Hardness))-1.46)))
chronic =((1.46203-((LN(Hardness))*(0.145712)))*(EXP(1.273*(LN(Hardness))-4.705)))
below water quality
40
20
0
-20
-40
-60
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
chronic total ICP
acute total ICP
chronic dissolved ICP-MS
acute dissolved ICP-MS
dissolved chronic Ecology
dissolved acute Ecology


zinc concentration
ug/L
160
140
120
100
80
60
40
20
0
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
Zn ICP MDL = 5µg/L
total ICP
total ICP-MS
dissolved ICP-MS
WDOE
Zn ICP-MS MDL= 0.5µg/L


zinc (hardness corrected)
based on Zn total-ICP
60
40
20
0
-20
-40
-60
-80
ug/L
above water quality criteria
below water quality criteria
acute =((0.978)*(EXP(0.8473*(LN(Hardness))+0.8604)))
chronic =((0.986)*(EXP(0.8473*(LN(Hardness))+0.7614)))
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
chronic total ICP
acute total ICP


ZINC (hardness corrected)
50
0
-50
-100
-150
ug/L
above water quality criteria
below water quality criteria
Jan-93
Jan-94
Jan-95
Jan-96
Jan-97
Jan-98
Jan-99
Jan-00
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Jan-06
Jan-07
Jan-08
chronic total ICP
acute total ICP
chronic dissolved ICP-MS
dissolved ICP-MS
dissolved acute Ecology
dissolved chronic Ecology

So, what did this cost?

(just for the King County mis-listed streams)

•Cu, Pb, Zn	*$60/ICP-MS X12*	*720*
•mercury	*$75/CVAF X12*	*900*
•hardness	*$40 X12*	*480*
•field sampling	*~48 hours x $75/hr*	*3,600*
•analysis and reporting	*~2 months*	*12,000*
		$ 17,700

Having accurate data to report to the public, media and explaining to your boss….

painless!

- ***why does this happen?***

  the problem in this case was a failure to communicate, both with the database and between organizations

- ***what is the cost of inappropriate listings***

  best guess this time, ~$20K, with a TMDL? $$$$

- ***does anyone really care?***

  this is an issue of Information quality we are responsible ***CONTENT****, as well as* ***DELIVERY***

- ***how do we minimize the probability that it will happen again?***

  Internal Controls - error detection

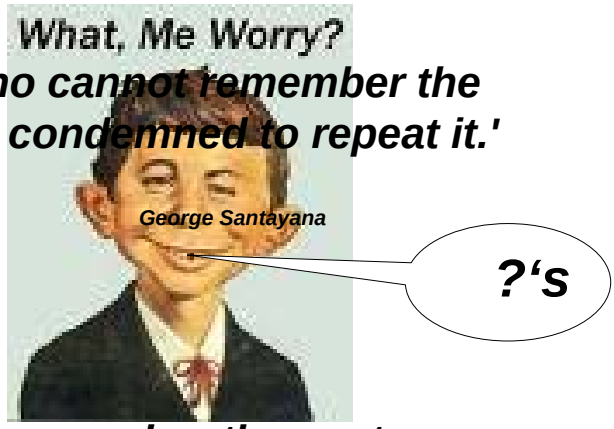
  Customer Service – service, timing

  Efficiency - effective use of resources

  External Failure Cost - costs associated with defects that are found after product is shipped to the customer. These costs also would disappear if there were no defects.

(stolen from Worthington, 2008)

Why worry about data quality?



'Those who cannot remember the past are condemned to repeat it.'

George Santayana

'Those who remember the past are condemned to repeat it with all those who can not remember the past.'

Jonathan Frodge