

Dioxin QAPP Development

RMP TRC March 10 2009

Dioxin Strategy Mgmt Q's

- Similar to other contaminants
 - 1. Are the beneficial uses impaired by dioxins?
 - 2. What is the distribution of dioxin impairment?
 - 3. What is the dioxin reservoir sediments/water?
 - 4. Have dioxin loadings/concentrations changed?
 - 5. What are the relative contributions of loading pathways?
 - 6. What future impairment is predicted?

Tissue Challenges

- Blank contamination
 - Hp- & O-, but sample concentrations < tetra- & penta-
- Recovery issues for some congeners
 - esp. Hx- Hp- O- CDFs
- Previously some precision issues
 - OCDD (maybe contam issues?)
- On positive side, Hx, Hp, O congeners total <5% of TEQs in tissue

Water Challenges

- Blank contamination
 - Hp- & O- even with higher sample concentrations
- (Previously) No precision measures
 - Previously limited sample material for duplicates
 - Tweaks to pump now allow parallel collection, field replicates ~10-20% difference for PCBs
- No standard reference materials
 - 100L XAD setup not conducive to “matrix” spike
 - Blank spikes (into XAD media) possible and have been done but capture only extraction recovery
 - Collection efficiency on XAD ~50-60% (for PCBs)
- Without preconc, all but Hp O congeners ND
 - Hx, Hp, O congeners only ~10+% of TEQs in water

Sediment Challenges

- Blank contamination (?)
 - Hp- & O- probably not an issue given relatively higher concentrations
- **NDs for many congeners, esp T, Pe, Hx**
 - Axy MDLs, avg MDL < avg FS assuming NOAA ND results were 0 conc (worst case assumption)
 - 2x larger (20g) samples will help some

Preliminary Sediment Results

SampleID	Total Of Result	2,3,7,8-TCDD	1,2,3,7,8-PECDD	1,2,3,4,7,8-HXCDD	1,2,3,6,7,8-HXCDD	1,2,3,7,8,9-HXCDD	1,2,3,4,6,7,8-HPCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PECDF	2,3,4,7,8-PECDF	1,2,3,4,7,8-HXCDF	1,2,3,6,7,8-HXCDF	1,2,3,7,8,9-HXCDF	2,3,4,6,7,8-HXCDF	1,2,3,4,6,7,8-HPCDF	1,2,3,4,7,8,9-HPCDF	OCDF
Method Blank					0.026	0.024	0.042	0.074										
MDL		0.024	0.024	0.024	0.024	0.024	0.026	0.029	0.032	0.024	0.024	0.025	0.025	0.025	0.025	0.024	0.024	0.024
BG30	27.792	0.059	0.143	0.189	0.316	0.775	3.930	30.100	0.073	0.028	0.034	0.038	0.024			0.128	0.024	0.283
CB001	36.531	0.183	0.473	0.548	2.190	1.970	25.400	181.000	1.374	0.407	0.726	0.824	0.469	0.073	0.427	5.840	0.404	10.900
SPB011	43.693	0.149	0.453	0.477	2.330	1.880	29.000	190.000	1.495	0.506	0.883	1.110	0.578	0.072	0.570	7.770	0.501	14.700
Blank Spike	57.321	10.400	53.700	57.400	58.100	56.200	49.600	95.900	11.600	49.800	50.600	52.500	48.200	52.200	53.900	54.800	50.400	97.800
average conc		0.130	0.356	0.405	1.612	1.542	19.443	133.700	0.981	0.314	0.548	0.657	0.357	0.073	0.499	4.579	0.453	8.628

red means the blank value > MDL

blue means the result is <3x the max of either the blank result or the MDL

- red means the blank value > MDL
- blue means the result is <3x the max of either the blank result or the MDL
- (BG30 is among lowest expected concentrations)

MQOs Proposed

- Dioxin targets similar to those for other organics
 - Non detects (<MDL) for all blanks
 - Reference (not certified) material or matrix/blank spike recoveries within $\pm 35\%$
 - Replicate RPDs/RSDs <35%
- Flagging for mild/moderate failures
 - All blank hits flagged,
 - Recovery failures flagged
 - Replicate failures flagged
- Censoring for serious failures
 - Results <3x blank
 - Recovery outside 30-170%
 - Replicates outside 70% RPD/RSD

Next Steps

- Send out draft QAPP (within ~1 week)
- Get back comments from stakeholders and labs
 - What is achievable?
 - Can data meet needs?
 - ~2-3 weeks for comments
- Finalize QAPP (~ mid April)

QC for laboratory analyses of 2000 fish tissue (dioxins)

abundant congeners have low TEQs – blue highlighted have one or more QC issues

Parameter	# Samples	Median Field Sample	Units	MDL	# Replicates	SD Replicates	Precision (RSD%)	Accuracy (% Error)	Blank Mean	TEQ impact (2005 WHO)
2,3,7,8-TCDD	38	0.1	pg/g wet	0.02	1	0.03	22	13	0.016	14.08%
1,2,3,7,8-PCDD	38	0.22	pg/g wet	0.02	1	0.06	12	12	0.021	30.97%
1,2,3,4,7,8-HxCDD	38	ND	pg/g wet	0.02	0	NA		44	0.026	0
1,2,3,6,7,8-HxCDD	38	0.05	pg/g wet	0.02	1	0.02	6	30	0.03	0.70%
1,2,3,7,8,9-HxCDD	38	ND	pg/g wet	0.02	0	NA		31	0.023	
1,2,3,4,6,7,8-HpCDD	38	0.09	pg/g wet	0.04	0	NA		25	0.05	0.13%
1,2,3,4,6,7,8,9-OCDD	38	0.27	pg/g wet	0.1	2	0.3	70	77	0.295	0.01%
2,3,7,8-TCDF	38	1.71	pg/g wet	0.02	3	0.16	14	21	0.061	24.07%
1,2,3,7,8-PCDF	38	0.21	pg/g wet	0.02	1	0.02	8	61	0.017	0.89%
2,3,4,7,8-PCDF	38	0.69	pg/g wet	0.02	2	0.09	22	12	0.022	29.14%
1,2,3,4,7,8-HxCDF	38	ND	pg/g wet	0.02	0	NA		44	0.024	0
1,2,3,6,7,8-HxCDF	38	ND	pg/g wet	0.02	0	NA		19	0.019	
1,2,3,7,8,9-HxCDF	38	ND	pg/g wet	0.02	0	NA		28	0.024	
2,3,4,6,7,8-HxCDF	38	ND	pg/g wet	0.02	0	NA		75	0.023	0
1,2,3,4,6,7,8-HpCDF	38	ND	pg/g wet	0.04	0	NA		82	0.051	0
1,2,3,4,7,8,9-HpCDF	38	ND	pg/g wet	0.04	0	NA		82	0.038	0
1,2,3,4,6,7,8,9-OCDF	38	ND	pg/g wet	0.1	0	NA		37	0.087	0
sum TEQ		0.71		0.064					0.069	

QC for laboratory analyses of 2000 fish tissue (dioxins)

abundant congeners have low TEQs

		Avg Blank	min MDL	Max M D L	Avg M D L	Avg FS	MED F S	MAX F S	REC	RSD	%of T E Q
TCDD, 2,3,7,8-	ng/g	ND	0.048	0.05	0.049	0.382	0.4	0.6	12%	5%	19.3%
PeCDD, 1,2,3,7,8-	ng/g	ND	0.048	0.05	0.049	0.748	0.8	1.1	13%	10%	37.8%
HxCDD, 1,2,3,4,7,8-	ng/g	ND	0.048	0.05	0.049	0.095	0.1	0.1	21%		0.5%
HxCDD, 1,2,3,6,7,8-	ng/g	ND	0.048	0.05	0.049	0.402	0.4	0.5	4%	8%	2.0%
HxCDD, 1,2,3,7,8,9-	ng/g	ND	0.048	0.05	0.049	0.077	0.1	0.1	11%		0.4%
HpCDD, 1,2,3,4,6,7,8-	ng/g	ND	0.048	0.066	0.052	0.164	0.2	0.2	7%	23%	0.1%
OCDD, 1,2,3,4,6,7,8,9-	ng/g	0.179	0.048	0.059	0.051	0.216		0	33%	0%	0.003%
TCDF, 2,3,7,8-	ng/g	ND	0.048	0.156	0.080	2.427	1.7	3.6	5%	9%	12.3%
PeCDF, 1,2,3,7,8-	ng/g	ND	0.048	0.05	0.049	0.409	0.4	0.5	23%	10%	0.6%
PeCDF, 2,3,4,7,8-	ng/g	ND	0.048	0.05	0.049	1.710	1.6	2.7	9%	0%	25.9%
HxCDF, 1,2,3,4,7,8-	ng/g	ND	0.048	0.054	0.050	0.045	0.1	0.1	5%		0.2%
HxCDF, 1,2,3,6,7,8-	ng/g	ND	0.048	0.054	0.050	0.072	0.1	0.1	8%		0.4%
HxCDF, 1,2,3,7,8,9-	ng/g	ND	0.048	0.054	0.050	0.000	0.0	0.0	10%		0.0%
HxCDF, 2,3,4,6,7,8-	ng/g	ND	0.048	0.054	0.050	0.100	0.1	0.1	44%		0.5%
HpCDF, 1,2,3,4,6,7,8-	ng/g	ND	0.048	0.098	0.058	0.060	0.1	0.2	26%		0.03%
HpCDF, 1,2,3,4,7,8,9-	ng/g	ND	0.048	0.098	0.056	0.000		0	180%		0.0%
OCDF, 1,2,3,4,6,7,8,9-	ng/g	0.072	0.048	0.059	0.051	0.049		0	23%	0%	0.001%

Axys 100L Samples

Hepta/Octa more of TEQ but not majority

PARAMETER	Sacramento River	Yerba Buena Island	Dumbarton Bridge	Blank	LAB MDL	max(3xblank or MDL)	avg % of TEQ
2003-08	pg/L	pg/L	pg/L	pg/L			
2,3,7,8-TCDD	<	e 0.008	e 0.005	<	0.005	0.005	16%
1,2,3,7,8-PeCDD	e 0.008	0.011	e 0.008	<	0.005	0.005	21%
1,2,3,4,7,8-HxCDD	0.009	0.011	0.008	<	0.005	0.005	2%
1,2,3,6,7,8-HxCDD	0.029	0.04	e 0.025	<	0.005	0.005	7%
1,2,3,7,8,9-HxCDD	0.024	0.035	0.022	0.0050	0.005	0.01509	6%
1,2,3,4,6,7,8-HpCDD	b 0.410	b 0.500	b 0.281	e 0.012	0.005	0.0348	9%
OCDD	b 3.050	b 2.850	b 2.110	0.035	0.006	0.105	2%
2,3,7,8-TCDF	0.032	0.054	0.046	<	0.005	0.005	11%
1,2,3,7,8-PeCDF	0.006	e 0.016	0.009	<	0.005	0.005	1%
2,3,4,7,8-PeCDF	0.011	0.023	0.021	0.0055	0.005	0.01641	13%
1,2,3,4,7,8-HxCDF	0.014	0.017	e 0.011	<	0.005	0.005	3%
1,2,3,6,7,8-HxCDF	0.009	0.014	0.009	<	0.005	0.005	3%
1,2,3,7,8,9-HxCDF	<	<	<	<	0.005	0.005	0%
2,3,4,6,7,8-HxCDF	0.007	0.013	0.01	<	0.005	0.005	2%
1,2,3,4,6,7,8-HpCDF	b 0.090	b,e 0.139	b 0.076	0.0071	0.005	0.02127	2%
1,2,3,4,7,8,9-HpCDF	B, e	B	B, e	0.0070	0.005	0.02109	0%
OCDF	b 0.165	b 0.205	b 0.106	0.018	0.005	0.0528	0%

NOAA Sediment Samples

Most MDLs almost good enough

	avg FS ND 0	avg FS detects	maxFS	#results	avgMDL	#MDL	Axys M DL s	avg %of TE Q	%NDs
	pg/g dry								
2,3,7,8-TCDD	0.00	0.00	0.00	0	0.45	56	0.03	0%	100%
1,2,3,7,8-PCDD	0.08	0.49	0.61	8	0.36	52	0.13	7%	85%
1,2,3,4,7,8-HxCDD	0.11	0.48	0.81	12	0.30	51	0.19	1%	76%
1,2,3,6,7,8-HxCDD	1.73	2.07	4.76	36	0.38	54	0.18	15%	33%
1,2,3,7,8,9-HxCDD	1.30	1.64	3.25	34	0.34	53	0.17	11%	36%
1,2,3,4,6,7,8-HpCDD	24.05	24.05	108.26	50	0.55	65	0.17	21%	23%
1,2,3,4,6,7,8,9-OCDD	159.06	159.06	773.52	50	0.61	72	0.83	4%	31%
2,3,7,8-TCDF	1.73	2.02	4.61	41	0.47	54	0.02	15%	24%
1,2,3,7,8-PCDF	0.17	0.91	1.83	8	0.27	51	0.10	0%	84%
2,3,4,7,8-PCDF	0.28	0.89	1.40	12	0.26	51	0.10	7%	76%
1,2,3,4,7,8-HxCDF	0.92	1.01	2.55	42	0.24	50	0.09	8%	16%
1,2,3,6,7,8-HxCDF	0.34	0.72	1.97	20	0.31	52	0.12	3%	62%
1,2,3,7,8,9-HxCDF	0.00	0.00	0.00	0	0.35	52	0.09	0%	100%
2,3,4,6,7,8-HxCDF	0.38	1.15	4.02	16	0.32	52	0.12	3%	69%
1,2,3,4,6,7,8-HpCDF	5.04	5.15	22.16	48	0.38	56	0.10	4%	14%
1,2,3,4,7,8,9-HpCDF	0.05	0.78	0.78	2	0.46	58	0.09	0%	97%
1,2,3,4,6,7,8,9-OCDF	8.70	9.08	32.98	46	0.65	71	0.28	0%	35%
sum TEQs	1.16	2.05	4.84		1.18		0.30		