June 21, 2005

MEMORANDUM

To: Technical Review Committee

From: Don Yee

Re: Discussion of PAH Contamination

Background

Based on a review of 2003 water data set, significant blank contamination was observed in the dissolved and particulate fractions. The particulate fraction had the highest and most pronounced contamination. Further discussions with the laboratory and discussions among staff suggested that the cause of this blank contamination may be the result of the extraction method used for the glass filters.

Discussion of Data

A number of PAHs have blank contamination, but certain compounds are particularly bad (>10x MDL). In dissolved phase, naphthalene is a possible contaminant in dissolved phase from XAD. Minimizing time between initial exampling and cleaning will help minimize the leaching/release of naphthalene from the XAD resin. For particulate phase, biphenyl and anthracene are among the worst, possibly the result of formation reactions from toluene at elevated temperatures.

Table 1 PAH contamination water organics

DISSOLVED	AvgOfRESULT	MinOfRESULT	MaxOfRESULT	AvgOfMDL	xMDL
1-Methylnaphthalene	86	61.6	123	37	2
2-Methylnaphthalene	114	77.1	177	32	4
Acenaphthylene	40	0	62.4	28	1
Anthracene	30	0	58.7	29	1
Biphenyl	47	35.6	65.6	31	2
Naphthalene	**1049**	**447**	**2010**	**76**	**14**
Phenanthrene	98	66	115	24	4
Benzo(ghi)perylene	48	0	103	25	2
Chrysene	17	0	42.1	10	2
Indeno(1,2,3-cd)pyrene	44	0	69.3	26	2
Pyrene	18	0	36.7	15	1
C1-Fluorenes	**625**	**365**	**917**	**36**	**17**
C1-Naphthalenes	202	140	301	36	6
C2-Dibenzothiophenes	**600**	**135**	**1490**	**20**	**30**
C2-Fluorenes	**551**	**0**	**1000**	**36**	**15**
C2-Naphthalenes	**954**	**670**	**1250**	**60**	**16**
C2-Phenanthrenes_Anthracenes	105	0	283	44	2
C3-Dibenzothiophenes	63	0	98.2	23	3
C3-Fluorenes	**1913**	**1620**	**2330**	**78**	**24**
C3-Naphthalenes	**605**	**31**	**1440**	**39**	**15**
C3-Phenanthrenes_Anthracenes	23	0	69	20	1
C4-Naphthalenes	**651**	**473**	**817**	**45**	**14**
C4-Phenanthrenes_Anthracenes	354	0	758	38	9
PARTICULATE					
1-Methylnaphthalene	210	165	297	51	4
2,6-Dimethylnaphthalene	167	131	185	54	3
2-Methylnaphthalene	236	200	307	45	5
Acenaphthylene	106	79.7	120	40	3
Anthracene	**806**	**558**	**1290**	**33**	**25**
Biphenyl	**4747**	**1680**	**7320**	**38**	**124**
Dibenzothiophene	245	45.4	390	32	8
Naphthalene	506	357	741	76	7
Phenanthrene	132	0	324	27	5
Benz(a)anthracene	34	22.5	44.6	18	2
Benzo(ghi)perylene	36	0	109	32	1
Chrysene	29	23.1	34.6	18	2
Dibenz(a,h)anthracene	101	41.8	186	31	3
Indeno(1,2,3-cd)pyrene	102	36.5	166	34	3
Pyrene	25	23	28.9	18	1
C1-Dibenzothiophenes	218	81	347	63	3
C1-Fluoranthenes_Pyrenes	33	0	99	20	2
C1-Fluorenes	**28393**	**9980**	**60900**	**96**	**297**
C1-Naphthalenes	447	365	606	51	9
C1-Phenanthrenes_Anthracenes	200	99	307	33	6

C2-Benz(a)anthracenes_Chrysenes	33	0	71.7	20	2
C2-Dibenzothiophenes	316	255	348	36	9
C2-Fluorenes	**3350**	**1930**	**4100**	**68**	**50**
C2-Naphthalenes	**1447**	**1240**	**1630**	**54**	**27**
C2-Phenanthrenes_Anthracenes	174	108	278	27	6
C3-Dibenzothiophenes	170	0	317	38	4
C3-Fluorenes	**2137**	**1470**	**2690**	**185**	**12**
C3-Naphthalenes	**1103**	**988**	**1170**	**50**	**22**
C3-Phenanthrenes_Anthracenes	**310**	**0**	**813**	**23**	**13**
C4-Naphthalenes	**49333**	**21100**	**71500**	**82**	**600**
C4-Phenanthrenes_Anthracenes	**881**	**832**	**944**	**45**	**20**

The solution of going to whole water samples has its negatives- a number of the compounds may become unmeasureable due to a drop in sensitivity. Two sets of 4L whole water and dissolved water samples per site would result in 8L per site per sample in each phase. Compared to the ~20L samples taken now (100L divided 5 ways), the approximate decrease in sensitivity would be around one half. Table 2 highlights results that would become unreportable in the whole water analysis if MDLs double.

Table 2

MATRIX	PARAMETER	AvgOfFS	MinOfFS	MaxOfFS	AvgOfMDL	doubleMDL	avgFS/2xMDL
DISSOLVED	Dibenz(a,h)anthracene	67	ND	186	41	82	0.8
PARTICULATE	Acenaphthene	113.55484	0	305	61	122	0.9
PARTICULATE	C2-Dibenzothiophenes	0	0	0	36	71	0.0
PARTICULATE	C3-Benz(a)anthracenes_Chrysenes	10.83871	0	182	14	28	0.4
PARTICULATE	C4-Benz(a)anthracenes_Chrysenes	1.2806452	0	39.7	17	33	0.0

The average FS result for relatively few compounds falls below the <2xMDL threshold (the approx new MDL if we went to 8L whole water samples). In general these compounds near their MDL will contribute less overall to the PAH total for each sample and thus have little effect even if qualified or not reported.

Corrective Measures Under Consideration

1)8L whole water and dissolved, for all stations
Pros: no need for toluene, less potential contamination synthesis of PAHs (liquid extraction). Could implement for 2005
Cons: large unwieldy samples, possible change in definition of "dissolved' (1µm fiber cartridge filter vs ~0.45 µm for filter, MDLs double.
Concentrations are high enough that relatively few compounds have results that would be rendered unreportable because of blank contamination, even with MDL doubled.
A variant of this alternative is to skip dissolved phase (total only) in analysis.

B) Flat disc filters
Pros: less water retention, no need for toluene to extract. Could be ready for 2005.
Cons: not field or blank tested yet, potential frequent clogging requiring multiple filter exchanges within one station (currently typically only 1 filter per station)
Cost of filter holder apparatus and filters prepped for field use not yet known.

C) Change in filter extraction solvents
Axys is considering multiple solvent extractions, either at room temp or in Soxhlets.
Pros: If this works, we could get good PAH results without sacrificing MDLs or other compounds
Cons: Axys has not indicated a specific solvent extraction that they think would work. Development may not occur in time for 2005 samples.

D) Stay with the Status Quo
Not really an option beyond 2004- only proceeding for 2004 to not hold up other analyses, at the cost of biphenyl and a number of alkPAHs essentially being unreportable. Axys have suggested ascorbic acid reduces the formation, but not to below MDL, so we are not too hopeful.