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CNC CHARLESTON  
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BACKGROUND CHRONOLOGY ALL ZONES THROUGH JUNE 1997 CNC CHARLESTON SC  
6/1/1997  
NAVFAC SOUTHERN

BACKGROUND CHRONO

# FAX COVER SHEET

# EN SAFE

DATE: 6-10-97

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TO: Dave Backus  
Jay Bassett  
Paul Bergstrand  
Daryle Fontenot  
Todd Haverkost  
Tony Hunt  
Johnny Tapia

FROM: Barry Doll

FAX:

SUBJECT: BG values for all zones so far

DOCUMENTS ATTACHED:

TOTAL PAGES FAXED: 5

## COMMENTS:

Here are the latest accepted numbers.  
Values for As, Mn, and Cr in Zone E  
groundwater are pending acceptance by Jay  
(after he sees the maps showing distribution of  
detections). Values for Cr in Zone C subsurface  
soil and Zone I surface soil apply to  
non-clay-rich samples only.

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A comparison of background reference values for surface soil at Charleston Naval Base.

I. Surface soil (mg/kg)

6-9-97

Inorganic chemical	Zone A (n=13)	Zone B (n=15)	Zone C (n=45)	Zone D (n=6)	Zone E (n=25)	Zone F (n=6)	Zone G (n=6)	Zone H (n=104)	Zone I (n=15)
Aluminum	12800 P	15500P	9990 P	8700 M	26600 P			26000 P	27400 N
Antimony	ND	X	0.55 N	0.92 M	1.77 N			X	ND
Arsenic	9.44 P	17.1 P	14.2 P	5.55 M	23.9 N			15.6 P	21.6 P
Barium	53.0 P	98.7 P	77.2 P	30.1 M	130 P			40.3 P	54.2 P
Beryllium	X	1.23 P	X	0.19 M	1.7 P			1.37 P	0.95 N
Cadmium	X	ND	0.65 N	0.07 M	1.5 N			1.05 N	0.61 N
Chromium	50.4 P	75.7 P	26.4 P	12.4 M	94.6 P			59.1 P	34.5 P
Cobalt	4.4 N	21.9 P	3.22 P	9.46 M	19.0 P			5.86 P	5.8 N
Copper	165 P	225 P	34.7 P	40.6 M	66.0 P			27.6 P	240 P
Lead	140 P	114 P	330 P	18.8 M	265 N			118 P	203 N
Manganese	98.1 P	464 P	92.5 P	28.6 M	302 N			583 P	419 N
Mercury	0.3 N	1.55 N	0.24 N	0.05 M	2.60 P			0.485 P	0.47 N
Nickel	13.55 P	43.6 P	12.3 P	4.68 M	77.1 P			33.4 P	23.9 P
Selenium	1.2 N	2.8 N	1.44 P	0.91 M	1.7 N			2.0 N	1.49 P
Silver	ND	1.7 N	X	0.43 M	X			X	X
Thallium	ND	ND	ND	ND	2.8 N			1.1 N	ND
Tin	ND	14.8 N	2.95 P	ND	59.4 P			X	7.5 N
Vanadium	29.24 P	52.6 P	23.4 P	9.73 M	94.3 P			73.0 P	113 P
Zinc	207.6 P	366 P	159 P	25.1 M	827 P			214 P	206 P
Cyanide	ND	ND	ND	0.18 M	0.5 N			ND	ND

Notes:

- P Parametric UTL
- N Nonparametric UTL
- X No UTL calculated (ND>90%)
- M Twice the mean
- ND Not detected

A comparison of background reference values for subsurface soil at Charleston Naval Base.

II. Subsurface soil (mg/kg)

6-9-97

Inorganic chemical	Zone A (n=12)	Zone B (n=14)	Zone C (n=30)	Zone D (n=6)	Zone E (n=24)	Zone F (n=6)	Zone G (n=4)	Zone H (n=63)	Zone I (n=6)
Aluminum	28240 P	17700 P	23700 P	10300 M	41100 P			46200 P	18900 M
Antimony	ND	X	0.92 N	ND	1.6 N			X	ND
Arsenic	9.836 P	10.8 N	14.1 N	4.08 M	19.9 P			22.5 P	6.45 M
Barium	40.01 P	65.0 N	68.5 P	29.7 M	94.1 P			43.8 P	36.0 M
Beryllium	ND	1.61 P	0.98 N	0.75 M	2.71 P			1.62 P	0.67 M
Cadmium	ND	ND	0.28 N	0.38 M	0.96 N			1.1 N	0.54 M
Chromium	63.4 P	48.1 N	12.5 P	22.3 M	75.2 N			84.2 P	51.3 M
Cobalt	1.7 N	10.6 N	7.1 N	2.89 M	14.9 N			14.9 P	3.48 M
Copper	33.69 P	47.0 P	42.2 P	ND	152 P			31.6 P	11.5 M
Lead	22.01 P	145 P	73.2 P	7.87 M	173 N			68.7 P	123 M
Manganese	85.54 P	288 N	106 P	29.9 M	881 P			1,410 P	118 M
Mercury	ND	2.0 N	0.30 N	0.05 M	1.59 P			0.735 P	ND
Nickel	35.0 P	29.9 N	16.7 P	6.76 M	57.0 P			29.9 P	15.7 M
Selenium	1.74 P	3.8 N	2.90 N	1.46 M	2.4 N			2.7 N	1.77 M
Silver	X	1.8 N	ND	0.36 M	ND			X	ND
Thallium	ND	ND	X	0.57 M	ND			1.3 N	ND
Tin	X	1.3 N	2.37 P	ND	9.23 P			ND	ND
Vanadium	77.32 P	102 N	56.9 N	15.1 M	155 P			132 P	38.1 M
Zinc	164.6 P	238 N	243 P	30.1 M	886 P			130 P	36.2 M
Cyanide	ND	ND	ND	0.16 M	X			ND	ND

Notes:

- P Parametric UTL
- N Nonparametric UTL
- X No UTL calculated (ND>90%)
- M Twice the mean
- ND Not detected

A comparison of background reference values for shallow groundwater at Charleston Naval Base.

III. Shallow groundwater ( $\mu\text{g/L}$ )

6-9-97

Inorganic chemical	Zone A (n=12)	Zone B (n=4)	Zone C (n=8)	Zone D (n=1)	Zone E (n=100)	Zone F (n=2)	Zone G (n=2)	Zone H (n=44)	Zone I (n=76)
Aluminum	3210 M		410 M	1410 D	2810 P			X	1440 N
Antimony	ND		ND	ND	X			ND	X
Arsenic	7.4 N		6.07 M	5.4 D	18.7 N			21.5 P	23.0 N
Barium	104 M		16.7 M	17.6 D	211 P			323 P	110 P
Beryllium	ND		0.33 M	0.8 D	0.43 N			ND	1.1 N
Cadmium	ND		ND	ND	X			ND	X
Chromium	8.7 M		1.99 M	3.8 D	12.3 N			ND	14.3 N
Cobalt	ND		1.33 M	ND	2.5 N			X	2.2 N
Copper	15.7 M		1.9 M	ND	2.7 N			ND	4.4 N
Lead	4.7 M		3.27 M	3.8 D	4.8 N			4.7 P	4.4 N
Manganese	577 N		608 M	30.6 D	2560 N			2440 P	5460 P
Mercury	ND		ND	ND	X			ND	X
Nickel	ND		3.59 M	3.4 D	15.2 N			X	13.3 P
Selenium	ND		ND	ND	X			3.2 P	ND
Silver	ND		1.26 M	ND	X			ND	X
Thallium	ND		ND	ND	5.4? N			5.3? N	6.6? N
Tin	NA		ND	ND	X			ND	X
Vanadium	5.4 M		1.96 M	7.2	11.4 P			X	14.1 P
Zinc	83.2 M		13.2 M	ND	27.3 N			ND	24.4 N
Cyanide	ND		ND	ND	7.9 N			X	25.2 N

Notes:

- P Parametric UTL
- N Nonparametric UTL
- X No UTL calculated (ND>90%)
- M Twice the mean
- ND Not detected
- NA Not analyzed

A comparison of background reference values for deep groundwater at Charleston Naval Base.

IV. Deep groundwater ( $\mu\text{g/L}$ )

6-3-97

Inorganic chemical	Zone A (n=12)	Zone B (n=2)	Zone C (n=8)	Zone D (n=1)	Zone E (n=100)	Zone F (n=2)	Zone G (n=2)	Zone H (n=44)	Zone I (n=76)
Aluminum	245 M		22.2 M	ND	319 N			723 MN	
Antimony	ND		ND	ND	X			ND	
Arsenic	11.1 N		ND	8.4 D	16.4 N			8.2 N	
Barium	179 N		52.2 M	31.8 D	218 P			237 P	
Beryllium	ND		0.32 M	ND	1.2 N			ND	
Cadmium	ND		ND	ND	X			X	
Chromium	7.3 N		ND	ND	15.5 N			X	
Cobalt	12.1 M		ND	ND	12.9 N			3.2 MN	
Copper	5.8 M		ND	ND	X			ND	
Lead	ND		ND	ND	X			4.3 MN	
Manganese	2,690 N		147 M	320 D	869 P			998 P	
Mercury	ND		ND	ND	0.2 N			X	
Nickel	21.1 M		ND	ND	42.2 N			X	
Selenium	ND		ND	ND	X			2.1 MN	
Silver	ND		ND	ND	X			ND	
Thallium	?		ND	ND	6.5? N			X	
Tin	NA		ND	ND	X			ND	
Vanadium	10.9 M		0.54 M	ND	5.3 N			9.3 MN	
Zinc	66.2 M		ND	ND	11.8 N			X	
Cyanide	0.05 M		ND	ND	37.3 N			ND	

Notes:

- P Parametric UTL
- N Nonparametric UTL
- MN Modified nonparametric UTL
- X No UTL calculated (ND>90%)
- M Twice the mean
- ND Not detected
- NA Not analyzed

## A comparison of background values for surface soil at Charleston Naval Base.

## I. Surface soil (mg/kg)

4-28-97

Inorganic chemical	Zone A (n=13)	Zone B (n=15)	Zone C (n=44)	Zone D (n=6)	Zone E (n=25)	Zone F (n=6)	Zone G (n=6)	Zone H (n=104)	Zone I (n=15)
Aluminum	12800 P	15500P			26600 P			26000 P	
Antimony	ND	X			1.77 N			X	
Arsenic	9.44 P	17.1 P			23.9 N			15.6 P	
Barium	53.0 P	98.7 P			130 P			40.3 P	
Beryllium	X	1.23 P			1.7 P			1.37 P	
Cadmium	X	ND			1.5 N			1.05 N	
Chromium	50.4 P	75.7 P			94.6 P			59.1 P	
Cobalt	4.4 N	21.9 P			19.0 P			5.86 P	
Copper	165 P	225 P			66.0 P			27.6 P	
Lead	140 P	114 P			265 N			118 P	
Manganese	98.1 P	464 P			302 N			583 P	
Mercury	0.3 N	1.55 N			2.6 P			0.485 P	
Nickel	13.55 P	43.6 P			77.1 P			33.4 P	
Selenium	1.2 N	2.8 N			1.7 N			2.0 N	
Silver	ND	1.7 N			X			X	
Thallium	ND	ND			2.8 N			1.1 N	
Tin	ND	14.8 N			59.4 P			X	
Vanadium	29.24 P	52.6 P			94.3 P			73.0 P	
Zinc	207.6 P	366 P			827 P			214 P	
Cyanide	ND	ND			0.5 N			ND	

## Notes:

- P Parametric UTL  
 N Nonparametric UTL  
 X No UTL calculated (ND>90%)  
 M Twice the mean  
 ND Not detected

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<TapiaJM@columb34.dhec.state.sc.us>,<dbackus@ensafe.com>  
From: thaverkost@ensafe.com  
Cc:  
Bcc:  
Subject: Todd, -Reply  
Attachment: Headers.822  
Date: 2/25/97 2:37 PM

Johnny,

As for background organics we feel like this has been settled to with the agreement that we weren't using the data for screening but rather just discussing in the risk uncertainty section. It was on the agenda because I asked Daryle to put it on before I went back and looked at decisions already reached. We would like to talk about several aspects of the inorganic background. Barry faxed out a memo in which the arsenic background was calculated seven different ways for zones B, C, H, and I. We would like feedback on which method appears to generate numbers you can live with. At the 60% progress update for F and G more background numbers were presented for those zones. Are they acceptable or do we need to provide you more info?=20 There was also another memo that has been generated which identified background values above RBCs that was done at Jay's request (I think). I hope this helps you prepare for the discussion. Let me know if you have any more questions.

Todd=20

>>> "TapiaJM@columb34.dhec.state.sc.us" 2/25/97, 03:21pm >>>  
Received: from IPCDOM01-Message\_Server by gw.state.sc.us with  
Novell\_GroupWise; Tue, 25 Feb 1997 15:10:55 -0500  
Message-Id: <s31300ff.016@gw.state.sc.us>  
X-Mailer: Novell GroupWise 4.1  
Date: Tue, 25 Feb 1997 15:13:11 -0500  
From: Johnny Tapia <TapiaJM@columb34.dhec.state.sc.us>  
To: bkstockmaster@efdsouth.navfac.navy.mil,  
dlfontenot@efdsouth.navfac.navy.mil,  
mahunt@efdsouth.navfac.navy.mil,DBackus@Ensafe.com,  
THaverkost@Ensafe.com, BASSET.JAY@epamail.epa.gov,  
Dearhart\_Earl\_R@mlink.repair.navy.mil,  
Subject: Todd,  
Mime-Version: 1.0  
Content-Type: text/plain

Content-Disposition: inline  
Todd,

I need to know what the discussions about background are going to focus on.

For organics I thought the matter was settled.

For Inorganics I need to know what you are looking for to move forward in the process.

Johnny

MEMO

*Tom*

2-20-97

TO: Project Team members  
FROM: EnSafe

RE: Benzo(a)pyrene and total BEQs at AOC 507 in Zone B. Information specifically requested at Project Team Meeting of 2-11-97 appears in boldface type.

*Concentrations in AOC 507 upper interval soil samples*

Benzo(a)pyrene and total BEQs were detected at 8 of 13 upper interval soil sampling locations and 0 of 5 lower interval locations at AOC 507. Concentrations in upper interval samples were as follows:

	<u>Benzo(a)pyrene</u>	<u>Total BEQs</u>
507SB00201	230 $\mu\text{g}/\text{kg}$	272 $\mu\text{g}/\text{kg}$
507SB00301	1200 "	1544 "
507SB00601	170 "	214 "
507SB00701	150 "	196 "
507SB00801	730 "	1225 "
507SB01101	360 "	426 "
507SB01201	290 "	335 "
507SB01301	330 "	402 "

At AOC 507, the concentration of benzo(a)pyrene and/or total BEQs corresponding to 1E-06 risk is 60  $\mu\text{g}/\text{kg}$ , which is the residential RGO. The concentration corresponding to 1E-05 risk is 600  $\mu\text{g}/\text{kg}$ . These risk calculations include the dermal pathway as well as ingestion. Since the relationship of risk to concentration is considered to be linear, the risk corresponding to any concentration of benzo(a)pyrene or total BEQs in upper interval soil at AOC 507 can be expressed as:

$$\text{risk} = ([\text{B(a)P}] / 60 \mu\text{g}/\text{kg}) \times (1\text{E}-06) \quad \text{or} \quad \text{risk} = ([\text{total BEQs}] / 60 \mu\text{g}/\text{kg}) \times (1\text{E}-06)$$

According to the formulas above, risk based on total BEQs in the listed samples at AOC 507 ranges from 3E-06 (for sample 507SB00701) to 3E-05 for sample 507SB00301). Since EPA risk assessment guidance requires combining the effects of carcinogenic PAHs to calculate risk, separate calculations were not performed for benzo(a)pyrene.

*Concentrations in grid-based soil samples*

Benzo(a)pyrene was detected in 2 of 15 upper interval soil grid samples and 0 of 14 lower interval soil grid samples. Total BEQs were detected in the same two upper interval soil samples and in one lower interval soil sample. Concentrations in soil grid samples were as follows:

	<u>Benzo(a)pyrene</u>	<u>Total BEQs</u>
GDBSB00601	210 $\mu\text{g}/\text{kg}$	272 $\mu\text{g}/\text{kg}$
GDBSB00801	150 "	179 "
GDBSB01302	ND	19 "

*Background reference values*

**Background reference value for benzo(a)pyrene in Zone B upper interval soil, based on twice the mean value, using zero for nondetects:**

Mean concentration =  $(360 \mu\text{g}/\text{kg}) / 15 = 24 \mu\text{g}/\text{kg}$  *ppb*

Twice the mean =  $48 \mu\text{g}/\text{kg}$  *ppb* (Residential RBC for benzo(a)pyrene =  $88 \mu\text{g}/\text{kg}$ )

**Background reference value for total BEQs in Zone B upper interval soil, based on twice the mean value, using zero for nondetects:**

Mean concentration =  $(451.44) / 15 = 30.1$

Twice the mean =  $60 \mu\text{g}/\text{kg}$  (Residential RBC for total BEQs =  $88 \mu\text{g}/\text{kg}$ )

The residential RBC ( $88 \mu\text{g}/\text{kg}$ ) for benzo(a)pyrene and/or total BEQs considers the ingestion pathway only, while the RGO ( $60 \mu\text{g}/\text{kg}$ ) for AOC 507 considers both ingestion and dermal pathways.



ENVIRONMENTAL AND SAFETY DESIGNS, INC.

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Todd Haverkost
Tony Hunt
Ann Ragan
Brian Stockmaster
Johnny Tapia
Kevin Tunstall

FROM:
Barry Doll

DATE:
February 14, 1997

Fax to number:

Number of pages: 3

Remarks:

The tables present calculated background reference values (from previously submitted RFI reports) that exceed corresponding residential RBCs, generic SSLs, or tap water RBCs.

2-14-97

The following tables present selected background reference values from previously submitted RFI reports on Zones A, B, C, H, and I at NAVBASE. The values shown are all those that exceed corresponding residential RBCs (for upper interval soil), generic SSLs (for lower interval soil; assumes DAF of 20), or tap water RBCs (for shallow and deep groundwater). RBC and SSL values for chromium are shown with asterisks because they represent hexavalent chromium, while the calculated background reference values are based on total chromium analyses. Figures for iron were not tabulated because iron has been considered an essential nutrient. RBCs for noncarcinogens have been divided by 10 (THQ = 0.1) to allow for possible additive effects of multiple contaminants.

**Upper interval (surface) soil:**

Element	Residential RBC	Zone A	Zone B	Zone C	Zone H	Zone I
Aluminum	7,800	12,786	15,500	10,017	25,310	
Antimony	3.1					8.98
Arsenic	0.43	9.439	17.1	24.96	14.81	73.5
Beryllium	0.15		1.34		1.466	3.17
Chromium	39*	50.43	80.2		85.65	131.65
Manganese	180		589		636.4	1,980
Thallium	0.63				0.63	
Vanadium	55		156		77.38	114.16

*Blanks mean blank was not higher than RBC*

**Lower interval (subsurface) soil:**

Element	Generic SSL (DAF = 20)	Zone A	Zone B	Zone H
Arsenic	29		48.9	35.52
Chromium	38*	175.7	75.7	83.86
Thallium	0.7			1.3

Background reference values were not calculated for Zones C and I.

**Shallow groundwater:**

Element	Tap water RBC	Zone A	Zone C	Zone H	Zone I
Arsenic	0.045	53.5		27.99	35.01
Barium	260			323	393.57
Manganese	84	378.5	557.4	3,391	23,445
Thallium	0.29			7.66	

10,400

Because no monitoring wells were installed at the only site in Zone B (AOC 507), no groundwater background reference values were calculated for the zone.

**Deep groundwater:**

Element	Tap water RBC	Zone A	Zone H
Arsenic	0.045	10.67	14.98
Manganese	84	2,786	776.2
Thallium	0.29	165	

only two hits (4,163) - should not be considered as background: look at subsequent sample data.

Because no deep monitoring wells were installed at any sites in Zones B, C, or I, no deep groundwater background reference values were calculated for those zones.

The following tables present selected background reference values from previously submitted RFI reports on Zones A, B, C, H, and I at NAVBASE. The values shown are all those that exceed corresponding residential RBCs (for upper interval soil), generic SSLs (for lower interval soil; assumes DAF of 20), or tap water RBCs (for shallow and deep groundwater). RBC and SSL values for chromium are shown with asterisks because they represent hexavalent chromium, while the calculated background reference values are based on total chromium analyses. Figures for iron were not tabulated because iron has been considered an essential nutrient. RBCs for noncarcinogens have been divided by 10 (THQ = 0.1) to allow for possible additive effects of multiple contaminants.

**Upper interval (surface) soil:**

*n = 44*

Element	Residential RBC	Zone A	Zone B	Zone C	Zone H	Zone I
Aluminum	7,800	12,786	15,500	10,017	25,310	
Antimony	3.1					8.98
Arsenic	0.43	9.439	17.1	24.96	14.81	73.5
Beryllium	0.15		1.34		1.466	3.17
Chromium	39*	50.43	80.2		85.65	131.65
Manganese	180		589		636.4	1,980
Thallium	0.63				0.63	
Vanadium	55		156		77.38	114.16

**Lower interval (subsurface) soil:**

Element	Generic SSL (DAF = 20)	Zone A	Zone B	Zone H
Arsenic	29		48.9	35.52
Chromium	38*	175.7	75.7	83.86
Thallium	0.7			1.3

Background reference values were not calculated for Zones C and I.

**Shallow groundwater:**

Element	Tap water RBC	Zone A	Zone C	Zone H	Zone I
Arsenic	0.045	53.5		27.99	35.01
Barium	260			323	393.57
Manganese	84	378.5	557.4	3,391	23,445
Thallium	0.29			7.66	

Because no monitoring wells were installed at the only site in Zone B (AOC 507), no groundwater background reference values were calculated for the zone.

**Deep groundwater:**

Element	Tap water RBC	Zone A	Zone H
Arsenic	0.045	10.67	14.98
Manganese	84	2,786	776.2
Thallium	0.29	165	

Because no deep monitoring wells were installed at any sites in Zones B, C, or I, no deep groundwater background reference values were calculated for those zones.

**Zone H grid-based upper interval soil samples (n=104): Background reference concentrations of cPAHs**

Background reference concentration expressed as 2 x mean of sample concentrations.

Methods for handling nondetect values:

Method A: Substitute the lesser of one-half the SQL of the sample or one-half the lowest J-qualified value among the grid samples. (using the lowest J)

Method B: Substitute as above in all samples with any cPAH detections; for samples with all seven cPAHs not detected, substitute zero.

Method C: Substitute zero for all nondetects.

cPAH	No. of Detects	ND Estimator	RBC	Method A		Method B		Method C	
				Mean	2 x Mean	Mean	2 x Mean	Mean	2 x Mean
Benzo(a)anthracene	17	24	880	116	232	96.4	193	96.0	192
Benzo(a)pyrene	16	40.5	88	125	249	91.5	183	90.3	181
Benzo(b)fluoranthene	14	20.3	880	122	244	105	211	104	209
Benzo(k)fluoranthene	11	44	8,800	123	247	87.4	175	84.0	168
Dibenz(a,h)anthracene	7	42	88	54.5	109	20.1	40.3	15.3	30.6
Indeno(1,2,3-cd)pyrene	12	47	880	82.2	165	43.8	87.6	40.7	81.3
Chrysene	18	25	88,000	121	243	101	202	101	201

(All concentration values expressed in  $\mu\text{g}/\text{kg}$ )  $\leftarrow \frac{1}{2}$  of the lowest J in all samples

Using Method A, only benzo(a)pyrene and dibenz(a,h)anthracene have background levels higher than their RBCs; using Methods B and C, only benzo(a)pyrene has a background level higher than its RBC.

4  
 Applied using BoP.  
 7 sites drop + 2 other OIA  
 2 other sites where risk

**Suggested alternative method for calculating background reference values for arsenic and beryllium.**

The UTL approach (specifically,  $UTL_{95,95}$ ) has served as an effective screening tool for concentrations of inorganics in individual soil and groundwater samples in all of the investigatory zones where it has been applied at NAVBASE. Due to the large RBC exceedances of arsenic and beryllium, however, a somewhat more conservative screening method may be appropriate for these two trace metals *only*. EnSafe recommends that a statistically based approach continue to be used because the variance of the background dataset is always a critical factor in distinguishing contamination from ambient conditions. We suggest that using the lower of  $UTL_{90,90}$  and mean plus two standard deviations as the background reference value for arsenic and beryllium in both soil and groundwater might be appropriate. The effect of the alternative formulation would be to keep the tolerance factor from rising too high in small datasets. For a  $UTL_{90,90}$ , the tolerance factor exceeds 2.0 when datasets are smaller than  $n = 12$ . Freezing the tolerance factor at 2.0 prevents inflated UTLs due solely to the size of the dataset, at the cost of some loss of coverage and/or confidence. When  $n \geq 12$ , use of the  $UTL_{90,90}$  should produce a false positive rate of roughly 10%; for zones with smaller background datasets, it will be somewhat higher.

Application of the recommended method produces the following background reference values for arsenic in upper interval soil:

Zone B	12.3 mg/kg (previously 17.1)
Zone C	13.1 mg/kg (previously 26.0)
Zone H	12.6 mg/kg (previously 14.8)
Zone I	18.8 mg/kg (previously 26.4)

Background reference values for arsenic in upper interval soil at NAVBASE.

2-7-97

A comparison of possible methods for calculating background reference values, showing results of applying them as screening values to upper interval grid samples and site samples in each of four zones (all site samples combined for each zone). Zone B grid-based dataset excludes four samples collected on the golf course. Grid and site exceedances of background reference values are shown as both percentages and actual numbers (in parentheses).

Zone	B			C			H			I		
	Grid Hits/Samples	10/11		31/45			93/104			14/15		
Grid % Hits		89%		69%			89%			93%		
Site Hits/Samples			5/5		75/107			202/270				122/144
Site % Hits			100%		70%			75%				85%
	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.
UTL <sub>95,95</sub>	17.1	0	0	26.0	2% (1)	4% (4)	15.6	4% (4)	5% (14)	26.4	0	4% (6)
UTL <sub>95,99</sub>	14.4	0	0	22.6	2% (1)	4% (4)	15.2	5% (5)	6% (16)	23.7	0	5% (7)
UTL <sub>99,95</sub>	13.6	0	0	14.9	7% (3)	4% (4)	13.0	10% (10)	9% (24)	20.8	0	5% (7)
UTL <sub>99,99</sub>	12.3	9% (1)	0	13.1	7% (3)	6% (6)	12.6	10% (10)	10% (28)	18.8	7% (1)	6% (8)
Mean ± 2 Std. Dev.	12.3	9% (1)	0	23.0	2% (1)	4% (4)	16.1	3% (3)	5% (13)	20.1	0	6% (8)
Max. Value	12.3	9% (1)	0	39.4	2% (1)	3% (3)	18.4	1% (1)	3% (8)	19.7	7% (1)	6% (8)
2 x Mean	8.9	9% (1)	0	8.1	13% (6)	11% (12)	11.7	11% (11)	13% (35)	11.9	7% (1)	11% (16)

Notes:

BRV Background reference value

UTL<sub>95,95</sub> Upper tolerance limit with 95% coverage, 95% confidence

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MEMO

1/23/97

TO: Jay Bassett, USEPA, and Project Team members  
FROM: Barry Doll, EnSafe (Raleigh office)  
RE: Question posed at January project team meeting: "How many samples do we need to collect to have confidence in our background reference values?"

Jay, since I did not get what I consider to be a straight answer from our resident statistician, I'm going to attempt this one myself. Naturally, the answer is that the question *cannot* be answered as posed. In fact, it need not be answered, because we can predetermine the confidence level of the background value when we design it.

If we calculate a background reference value based on a statistical concept such as a 95% upper tolerance limit (UTL), it will always have a specified confidence level. Increasing the number of background data points on which the value is based would have one of two effects, depending on our approach:

1. Retain the existing UTL but (usually) increase the confidence level that it is correct (e.g., from the original specified 95% to perhaps 97.86%).
2. Retain the original specified confidence level but (usually) decrease the size of the calculated UTL.

By specifying a standard confidence level of 95% for background values in each zone at the Naval Base (i.e., we are 95% certain that our UTL is greater than 95% of the concentrations in the background population), we take the second approach described above. The value of each calculated UTL depends primarily on the sample concentrations, but secondarily on the sample size. Increasing the size of the dataset gives more confidence that the population has been sampled adequately, so that (usually) a somewhat lower value can serve as our UTL without sacrificing confidence in its accuracy. A larger dataset normally increases the accuracy of our estimates of the population mean and standard deviation, and therefore of the UTL; unless the original dataset was biased low, the result should be a lower UTL with equivalent confidence, reflecting our increased understanding of the data distribution.

Because we use the conventional approach of specifying our confidence level, the number of background samples in the dataset does not affect our confidence in the calculated UTL. What *is* affected by the number of samples is the *size* of the UTL: for a small background dataset, the value of a UTL must be set relatively high to ensure that it encloses the desired percentage of the population with 95% confidence. I have attached a table of tolerance factors for calculating one-sided normal tolerance intervals with 95% coverage and 95% confidence. The upper bounds of such intervals are UTLs such as the ones EnSafe uses to determine background reference levels at the Naval Base. Calculate a UTL by multiplying the sample standard deviation by the tolerance factor and adding the result to the sample mean ( $UTL = \bar{x} + Ks$ ). The table should give a feel for the effect of the sample size on the UTL. Whether a UTL with the above parameters (95% coverage, 95% confidence) that is based on a small dataset provides a reasonable reference value for background is, of course, a management decision. Other possible options for small datasets (i.e., fewer than 8 to 10 data points) include the use of the maximum observed value or twice the mean of the observed values as the background reference value.

**Background reference values for arsenic in upper interval soil at NAVBASE.**

2-7-97

A comparison of possible methods for calculating background reference values, showing results of applying them as screening values to upper interval grid samples and site samples in each of four zones (all site samples combined for each zone). Zone B grid-based dataset excludes four samples collected on the golf course. Grid and site exceedances of background reference values are shown as both percentages and actual numbers (in parentheses).

Zone	B			C			H			I		
Grid Hits/Samples		10/11			31/45			93/104			14/15	
Grid % Hits		89%			69%			89%			93%	
Site Hits/Samples			5/5			75/107			202/270			122/144
Site % Hits			100%			70%			75%			85%
	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.	BRV (mg/kg)	Grid Exceeds.	Site Exceeds.
UTL <sub>95,95</sub>	17.1	0	0	26.0	2% (1)	4% (4)	15.6	4% (4)	5% (14)	26.4	0	4% (6)
UTL <sub>95,90</sub>	14.4	0	0	22.6	2% (1)	4% (4)	15.2	5% (5)	6% (16)	23.7	0	5% (7)
UTL <sub>90,95</sub>	13.6	0	0	14.9	7% (3)	4% (4)	13.0	10% (10)	9% (24)	20.8	0	5% (7)
UTL <sub>90,90</sub>	12.3	9% (1)	0	13.1	7% (3)	6% (6)	12.6	10% (10)	10% (28)	18.8	7% (1)	6% (8)
Mean + 2 Std. Dev.	12.3	9% (1)	0	23.0	2% (1)	4% (4)	16.1	3% (3)	5% (13)	20.1	0	6% (8)
Max. Value	12.3	9% (1)	0	39.4	2% (1)	3% (3)	18.4	1% (1)	3% (8)	19.7	7% (1)	6% (8)
2 x Mean	8.9	9% (1)	0	8.1	13% (6)	11% (12)	11.7	11% (11)	13% (35)	11.9	7% (1)	11% (16)

**Notes:**

BRV Background reference value

UTL<sub>95,95</sub> Upper tolerance limit with 95% coverage, 95% confidence

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From: thaverkost@ensafe.com

Cc:

Bcc:

Subject: Organic Background

Attachment: Headers.822

Date: 12/30/96 4:08 PM

As promised at the last meeting we are providing the calculated carcinogenic PAH background values for zones in addition to zone H which was calculated at 424 ppb. =20

The values calculated using the 2X method as are as follows:

Zone A - 590 ppb  
Zone B - 232 ppb  
Zone C - 344 ppb  
Zone I - 160 ppb

November 8, 1996

Memorandum

TO: Tony Hunt

FROM: EnSafe

RE: Proposed method for comparing site sample values to background values for surface soils.

Part 1 - Inorganics (Appears as Appendix J in Final RFI Report for Zone H, NAVBASE)

Part 2 - Organics

Substantial background levels of some organic compounds are present in urban and near-urban environments. Polynuclear aromatic hydrocarbons (PAHs), in particular, are widely distributed in many urban surface soils as a result of airborne deposition. Formed mainly by incomplete combustion of organic materials, PAHs have numerous sources, both natural and anthropogenic. Specific sources of background PAHs include forest fires and volcanoes as well as vehicular and industrial emissions, energy production using hydrocarbons, wood treatment, waste incineration, and cooking (Wild and Jones, 1995). Bradley, et al. (1994) documented benzo(a)pyrene concentrations averaging 1323  $\mu\text{g}/\text{kg}$  in background samples of surface soil from three urban areas in New England. Corresponding concentrations of benzo(a)pyrene equivalents (BEQs) from the same samples were 2437  $\mu\text{g}/\text{kg}$ . Responsible risk management decisions and target cleanup levels for urban sites must consider the potential for non-site-related concentrations of organics. This memo discusses the issue as it relates to carcinogenic PAHs (cPAHs) at NAVBASE, Zone H. The seven PAHs known to be carcinogens are benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and chrysene.

Determination of background levels for PAHs such as benzo(a)pyrene, its equivalents, and other widespread but infrequently detected contaminants poses a greater challenge than determination of background levels for inorganics. The lower rate of detection means that little information is available on the majority of samples, so that parametric statistical assumptions are difficult to verify. Nonparametric methods are more appropriate, but simple tests like the Wilcoxon rank sum test for comparing two groups, which was used for inorganics, are not valid where nondetect rates are high, since the majority of the data (the nondetects) must be ranked as ties for purposes of the test. We therefore concentrate on the standard "2 X Background" test recommended by USEPA and on nonparametric tolerance limits as discussed in the previous memo (Zone H RFI Report, Appendix J) covering inorganics. For illustration, the BEQ results for Zone H surface soil grid samples will be examined. Of the 104 samples in this dataset, 18 samples reported detections of at least one cPAH.

The "2 X Background" comparison establishes twice the mean concentration of the background samples as a reference standard. To apply this rule, concentrations must be estimated for nondetects, which appear in the dataset as U-qualified values. A U-qualified value represents a sample quantitation limit, or SQL; the actual concentration in the sample is somewhere between zero and the SQL. The Zone H RFI Human Health Risk Assessment recommended using the lower of one-half the SQL value or one-half the lowest estimated (J-qualified) detected value as the estimate for a nondetect. One-half the lowest estimated detected value is included as a potential estimator for the sake of conservatism, since organic compounds are often detected at levels well below the SQL. Applying this procedure to BEQ values in Zone H surface soil background samples results in an estimated mean concentration of 212  $\mu\text{g}/\text{kg}$  total BEQs, thereby yielding an estimated background reference level of 424  $\mu\text{g}/\text{kg}$ . As an alternative approach, using one-half the SQL without adjusting (as above) for the lowest estimated detected value results in higher estimated concentrations; for Zone H BEQs, the estimated mean concentration using this method is 1910  $\mu\text{g}/\text{kg}$ . The mean of the detected concentrations only (no estimated values for nondetects) is 1430  $\mu\text{g}/\text{kg}$ . This range of estimated mean values (212-1910  $\mu\text{g}/\text{kg}$ ) shows that calculation of a background number depends strongly on the manner in which censored data (nondetects) are incorporated.

Another option for determining a reference standard is a nonparametric tolerance limit, which directly estimates a quantile of the underlying background distribution, using the actual data collected. Nonparametric methods generally require greater amounts of data to draw comparable conclusions, but this approach is possible with the large sample sizes used in Zone H. Calculation of a nonparametric tolerance limit is a two-step procedure. The first is to directly calculate the equivalent percentile in the sample data, and the second is to allow for sampling variability. With an infinite amount of data, we could estimate the desired quantile directly, with complete accuracy; when estimating from sample data, however, we must account for variability.

If we assume that all nondetect values are lower than detected values, the 95th percentile of BEQ values in background surface soil samples from Zone H is 1028  $\mu\text{g}/\text{kg}$ . The 90th percentile is 310  $\mu\text{g}/\text{kg}$ . As explained in the previous memo, the 95th percentile nonparametric upper tolerance limit (UTL) for this sample size (95% coverage, 95% confidence) is estimated by using the second-highest data value (USEPA, 1992, Table A-6). For the example dataset, this value is 2006  $\mu\text{g}/\text{kg}$ . Although a UTL with 95% coverage has been used as the background estimator for inorganics at NAVBASE, a UTL with 90% coverage might be considered more appropriate for organic compounds, for added conservatism. Unfortunately, USEPA's statistical tables provide coverage percentages for only the largest and second-largest values in datasets of various sizes, so that data values corresponding to lower coverages cannot be identified. Nevertheless, the sampling variability in this estimate may still be calculated using the statistical technique known as the bootstrap<sup>1</sup>. Applying bootstrap techniques, using the "BCANON" code in the statistical language S-Plus (developed by the authors mentioned in footnote 1), an upper tolerance limit for the 90th percentile (90% coverage, 95% confidence) was determined to be 814  $\mu\text{g}/\text{kg}$ <sup>2</sup>.

From this discussion, we have three preferred estimators for BEQ background reference concentrations:

Type	Value ( $\mu\text{g}/\text{kg}$ )
2 X Background	424
90% UTL (Bootstrap)	814
95% UTL	2006

Given the relatively high percentage of BEQ nondetects and the greater level of uncertainty about the sources of organic compounds in soils (site-related vs. background), the UTL approach that was applied to inorganics in Zone H soil could be considered insufficiently conservative for organics. If nondetects are treated as recommended in the Zone H Human Health Risk Assessment (described above), then a reasonable mean background concentration can be estimated for the grid samples. As recommended by USEPA in other situations, twice the estimated mean background concentration would serve as a conservative background reference value.

Analysis of their spatial distribution and frequency of detection, along with knowledge of potential offsite sources, allow us to differentiate with some confidence between background presence and widespread site-related contamination by organic compounds. Choosing an appropriate technique to estimate background screening levels of organics is a risk-management decision. Although a particular technique will likely be selected resulting in specific background values for cPAHs and possibly other organics, the full range of concentrations in grid-based samples as well as potential anthropogenic sources should be considered in the risk management decision making process.

<sup>1</sup> The bootstrap is a simulation-based technique that has been shown capable of producing confidence intervals for a wide range of statistics. Very briefly, the bootstrap uses resampling from the observed data values, with replacement. In other words, a data value is picked from all observed data values, its value recorded, and then returned to the pile. This procedure is repeated until there are as many resampled data points as there are original data points. This resampled set is called a bootstrap sample. The value of the desired statistic is then calculated from the bootstrap sample. If this procedure is repeated a number of times, an approximate distribution for the statistic is constructed. A confidence interval may then be calculated from this distribution. It can be shown that these confidence intervals are extremely accurate, particularly if a somewhat refined version of the simple algorithm is used. Several introductory treatments of these techniques are available. *An Introduction to the Bootstrap* by B. Efron and R. Tibshirani is especially good and quite readable.

<sup>2</sup> The bootstrap may also be used to calculate the 95th percentile UTL, giving a value of 1850  $\mu\text{g}/\text{kg}$ . Theoretical derivations show that this upper limit is probably more accurate than the

value of 2006  $\mu\text{g}/\text{kg}$  derived from the table.

*References:*

Bradley, L.J.N, B.H. Magee, and S.L. Allen (1994): Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils. *Journal of Soil Contamination*, v.3, n.4, pp.349-361.

USEPA (1992): Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Draft Addendum to Interim Final Guidance. Office of Solid Waste.

Wild, S.R. and K.C. Jones (1995): Polynuclear Aromatic Hydrocarbons in the United Kingdom Environment: A Preliminary Source Inventory and Budget. *Environmental Pollution*, v.88, pp.91-108.

0064-00001 - NAVAL BASE CHARLESTON ZONE H (NBCH)

Samples by Chemical Report

50-32-8 - Benzo(a)pyrene

>= 0.0000 for UG/KG - Hits Only

Sample ID	Ext.	Orig. ID	Type	Date	Result	VQual	Units	SDG #	
159-C-B001-01		159CB00101	Soil	06/19/95	19.5000		UG/KG	APX18	VAL
662-C-B002-01		662CB00201	Soil	08/15/94	48.1000	J	UG/KG	APX01	VAL
670-M-0002-01		670M00201	Soil	09/24/94	50.0000	J	UG/KG	APX09	VAL
670-C-B013-01		670CB01301	Soil	09/12/94	53.1000	J	UG/KG	APX03	VAL
662-S-B002-01		662SB00201	Soil	08/15/94	60.0000	J	UG/KG	CHS03	VAL
014-S-B007-01		014SB00701	Soil	09/22/94	60.1000	J	UG/KG	APX07	VAL
684-S-B005-01		684SB00501	Soil	09/19/94	61.6000	J	UG/KG	APX04	VAL
670-S-B019-01		670SB01901	Soil	09/14/94	68.4000	J	UG/KG	APX04	VAL
670-S-B020-02		670SB02002	Soil	09/14/94	71.5000	J	UG/KG	APX04	VAL
121-S-B004-01		121SB00401	Soil	08/26/94	77.0000	J	UG/KG	CHS07	VAL
665-S-B003-01		665SB00301	Soil	08/26/94	77.0000	J	UG/KG	CHS07	VAL
G80-C-B004-01		GDHCB09701	Soil	02/02/95	78.5000	J	UG/KG	APX16	VAL
650-S-B002-01		650SB00201	Soil	08/22/94	80.3000	J	UG/KG	CHS05	VAL
649-S-B002-01		649SB00201	Soil	08/22/94	80.9000	J	UG/KG	CHS05	VAL
GDH-S-B023-01		GDHSB02301	Soil	10/04/94	81.0000	J	UG/KG	CHS17	VAL
649-S-B001-01		649SB00101	Soil	08/22/94	81.2000	J	UG/KG	CHS05	VAL
GDH-S-B015-01		GDHSB01501	Soil	09/29/94	82.0000	J	UG/KG	CHS16	VAL
663-S-B001-01		663SB00101	Soil	08/31/94	82.9000	J	UG/KG	CHS09	VAL
019-S-B014-01		019SB01401	Soil	01/16/95	83.0000	J	UG/KG	CHS31	VAL
684-M-0002-01		684M00201	Soil	09/24/94	84.8000	J	UG/KG	APX09	VAL
670-S-B015-01		670SB01501	Soil	09/14/94	85.6000	J	UG/KG	APX04	VAL
020-S-B004-01		020SB00401	Soil	03/27/95	87.0000	J	UG/KG	CHS37	VAL
013-S-B005-01		013SB00501	Soil	08/12/94	91.0000	J	UG/KG	CHS02	VAL
121-S-B002-01		121SB00201	Soil	08/26/94	95.0000	J	UG/KG	CHS07	VAL
649-C-B001-01	RE	649CB00101	Soil	08/22/94	95.4000	J	UG/KG	APX02	VAL
013-S-B008-01		013SB00801	Soil	08/12/94	96.0000	J	UG/KG	CHS02	VAL
015-S-B007-01		015SB00701	Soil	01/20/95	96.0000	J	UG/KG	CHS32	VAL
684-S-B035-02		684SB03502	Soil	01/25/95	98.0000	J	UG/KG	CHS33	VAL
121-C-B002-01		121CB00201	Soil	08/26/94	99.7000	J	UG/KG	APX02	VAL
015-S-B001-01		015SB00101	Soil	09/10/94	100.0000	J	UG/KG	CHS11	VAL
121-S-B007-01		121SB00701	Soil	01/13/95	100.0000	J	UG/KG	CHS30	VAL
121-S-B014-01		121SB01401	Soil	03/22/95	100.0000	J	UG/KG	CHS35	VAL
159-S-B011-01		159SB01101	Soil	06/19/95	100.0000	J	UG/KG	CHS46	VAL
684-S-B018-01		684SB01801	Soil	09/21/94	102.0000	J	UG/KG	APX05	VAL
684-S-B017-01		684SB01701	Soil	09/21/94	103.0000	J	UG/KG	APX05	VAL
650-S-B001-01		650SB00101	Soil	08/22/94	107.0000	J	UG/KG	CHS05	VAL
684-S-B027-02		684SB02702	Soil	09/23/94	107.0000	J	UG/KG	APX09	VAL
019-S-B001-01		019SB00101	Soil	08/27/94	110.0000	J	UG/KG	CHS07	VAL
019-S-B009-01		019SB00901	Soil	01/17/95	110.0000	J	UG/KG	CHS31	VAL
649-S-B010-01		649SB01001	Soil	01/19/95	110.0000	J	UG/KG	CHS32	VAL
653-S-B001-01		653SB00101	Soil	08/26/94	110.0000	J	UG/KG	CHS08	VAL
G07-S-B001-01		GDHSB09801	Soil	02/02/95	110.0000	J	UG/KG	CHS33	VAL
GDH-S-B021-01		GDHSB02101	Soil	10/03/94	110.0000	J	UG/KG	CHS16	VAL
017-S-B009-01		017SB00901	Soil	08/17/94	116.0000	J	UG/KG	CHS04	VAL
665-S-B002-01		665SB00201	Soil	08/26/94	120.0000	J	UG/KG	CHS07	VAL
020-S-B010-01		020SB01001	Soil	03/28/95	130.0000	J	UG/KG	CHS37	VAL
020-C-B001-01		020CB00101	Soil	03/27/95	140.0000	J	UG/KG	CHS36	VAL
178-S-B005-01		178SB00501	Soil	08/23/94	140.0000	J	UG/KG	CHS06	VAL
653-S-B003-02		653SB00302	Soil	08/26/94	140.0000	J	UG/KG	CHS08	VAL

0064-00001 - NAVAL BASE CHARLESTON ZONE H (NBCH)

Samples by Chemical Report

50-32-8 - Benzo(a)pyrene

>= 0.0000 for UG/KG - Hits Only

Sample ID	Ext. Orig. ID	Type	Date	Result	VQual	Units	SDG #	
656-S-B011-01	656SB01101	Soil	01/10/95	140.0000	J	UG/KG	CHS29	VAL
670-S-B030-01	670SB03001	Soil	01/20/95	140.0000	J	UG/KG	CHS32	VAL
684-S-B032-01	684SB03201	Soil	01/25/95	140.0000	J	UG/KG	CHS33	VAL
G80-S-B003-01	GDHSB10101	Soil	02/03/95	140.0000	J	UG/KG	CHS34	VAL
GDH-S-B011-02	GDHSB01102	Soil	09/27/94	140.0000	J	UG/KG	CHS14	VAL
020-S-B007-01	020SB00701	Soil	03/27/95	150.0000	J	UG/KG	CHS37	VAL
684-S-B040-02	684SB04002	Soil	03/29/95	150.0000	J	UG/KG	CHS40	VAL
138-S-B003-01	138SB00301	Soil	08/29/94	153.0000	J	UG/KG	CHS09	VAL
019-S-B004-01	019SB00401	Soil	08/29/94	160.0000	J	UG/KG	CHS08	VAL
684-M-0001-01	684M00101	Soil	09/24/94	160.0000	J	UG/KG	APX09	VAL
684-S-B034-01	684SB03401	Soil	01/25/95	160.0000	J	UG/KG	CHS33	VAL
656-C-B009-01	656CB00901	Soil	08/10/94	161.0000	J	UG/KG	APX01	VAL
684-S-B019-01	684SB01901	Soil	09/21/94	164.0000	J	UG/KG	APX07	VAL
GDH-S-B007-01	GDHSB00701	Soil	09/27/94	170.0000	J	UG/KG	CHS15	VAL
017-C-B022-01	017CB02201	Soil	01/11/95	175.0000	J	UG/KG	APX15	VAL
GDH-S-B080-02	GDHSB08002	Soil	10/21/94	180.0000	J	UG/KG	CHS23	VAL
684-S-B028-01	684SB02801	Soil	09/23/94	181.0000	J	UG/KG	APX08	VAL
663-S-B002-01	663SB00201	Soil	08/31/94	190.0000	J	UG/KG	CHS09	VAL
670-S-B016-01	670SB01601	Soil	09/14/94	190.0000	J	UG/KG	CHS14	VAL
GDH-S-B025-01	GDHSB02501	Soil	10/04/94	190.0000	J	UG/KG	CHS17	VAL
019-C-B014-01	019CB01401	Soil	01/16/95	192.0000	J	UG/KG	APX15	VAL
663-C-B002-01	663CB00201	Soil	08/31/94	193.0000	J	UG/KG	APX02	VAL
666-S-B001-01	666SB00101	Soil	08/23/94	196.0000	J	UG/KG	CHS05	VAL
015-S-B005-01	015SB00501	Soil	01/20/95	200.0000	J	UG/KG	CHS32	VAL
121-S-B007-02	121SB00702	Soil	01/13/95	200.0000	J	UG/KG	CHS30	VAL
GDH-S-B080-01	GDHSB08001	Soil	10/21/94	200.0000	J	UG/KG	CHS23	VAL
663-S-B005-01	663SB00501	Soil	08/31/94	206.0000	J	UG/KG	CHS09	VAL
019-S-B017-01	019SB01701	Soil	03/22/95	210.0000	J	UG/KG	CHS35	VAL
020-S-B001-01	020SB00101	Soil	03/27/95	210.0000	J	UG/KG	CHS37	VAL
020-S-B003-01	020SB00301	Soil	03/27/95	210.0000	J	UG/KG	CHS37	VAL
684-S-B033-01	684SB03301	Soil	01/25/95	210.0000	J	UG/KG	CHS33	VAL
020-S-B006-01	020SB00601	Soil	03/27/95	220.0000	J	UG/KG	CHS37	VAL
GDH-C-B007-01	GDHCB00701	Soil	09/27/94	224.0000	J	UG/KG	APX06	VAL
GDH-S-B024-01	GDHSB02401	Soil	10/04/94	230.0000	J	UG/KG	CHS17	VAL
GDH-S-B032-01	GDHSB03201	Soil	10/04/94	230.0000	J	UG/KG	CHS17	VAL
684-S-B025-01	684SB02501	Soil	09/21/94	234.0000	J	UG/KG	APX07	VAL
649-S-B004-01	649SB00401	Soil	08/22/94	239.0000	J	UG/KG	CHS05	VAL
121-S-B015-01	121SB01501	Soil	03/22/95	240.0000	J	UG/KG	CHS35	VAL
670-S-B002-01	670SB00201	Soil	09/10/94	250.0000	J	UG/KG	CHS11	VAL
G38-S-B003-01	GDHSB09601	Soil	02/02/95	250.0000	J	UG/KG	CHS33	VAL
019-S-B005-01	019SB00501	Soil	01/17/95	260.0000	J	UG/KG	CHS31	VAL
684-S-B022-01	684SB02201	Soil	09/21/94	271.0000	J	UG/KG	APX07	VAL
GDH-S-B017-01	GDHSB01701	Soil	10/03/94	290.0000	J	UG/KG	CHS16	VAL
019-S-B018-01	019SB01801	Soil	03/22/95	310.0000	J	UG/KG	CHS35	VAL
015-S-B006-01	015SB00601	Soil	01/20/95	320.0000	J	UG/KG	CHS32	VAL
015-S-B003-01	015SB00301	Soil	09/10/94	330.0000	J	UG/KG	CHS11	VAL
GDH-S-B012-01	GDHSB01201	Soil	09/27/94	410.0000		UG/KG	CHS14	VAL
684-S-B027-01	684SB02701	Soil	09/23/94	416.0000	J	UG/KG	APX09	VAL
019-S-B011-01 RE	019SB01101	Soil	01/17/95	460.0000	J	UG/KG	CHS30	VAL

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11/07/96

ENVIRONMENTAL SAFETY & DESIGNS

0064-00001 - NAVAL BASE CHARLESTON ZONE H (NBCH)

Samples by Chemical Report

50-32-8 - Benzo(a)pyrene

>= 0.0000 for UG/KG - Hits Only

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Sample ID	Ext. Orig. ID	Type	Date	Result	VQual	Units	SDG #	
656-S-B001-01	656SB00101	Soil	08/09/94	460.0000		UG/KG	CHS01	VAL
159-M-0002-01	159M000201	Soil	06/20/95	470.0000	J	UG/KG	CHS46	VAL
020-S-B011-02	020SB01102	Soil	03/28/95	480.0000	J	UG/KG	CHS37	VAL
GDH-S-B032-02	GDHSB03202	Soil	10/04/94	480.0000	J	UG/KG	CHS17	VAL
670-S-B012-01	670SB01201	Soil	09/12/94	490.0000	J	UG/KG	CHS11	VAL
684-S-B040-01	684SB04001	Soil	03/29/95	490.0000		UG/KG	CHS40	VAL
019-S-B010-01	019SB01001	Soil	01/17/95	500.0000	J	UG/KG	CHS30	VAL
019-S-B002-01	019SB00201	Soil	08/27/94	540.0000		UG/KG	CHS07	VAL
121-S-B009-01	121SB00901	Soil	01/16/95	540.0000		UG/KG	CHS31	VAL
684-C-B036-01	684CB03601	Soil	01/25/95	540.0000		UG/KG	APX16	VAL
670-C-B003-01	670CB00301	Soil	09/13/94	556.0000		UG/KG	APX03	VAL
020-S-B009-01	020SB00901	Soil	03/28/95	570.0000		UG/KG	CHS37	VAL
020-S-B008-01	020SB00801	Soil	03/27/95	580.0000		UG/KG	CHS37	VAL
121-S-B010-01	121SB01001	Soil	01/16/95	620.0000		UG/KG	CHS31	VAL
121-S-B016-01	121SB01601	Soil	03/22/95	620.0000		UG/KG	CHS35	VAL
GDH-S-B081-01	GDHSB08101	Soil	10/21/94	620.0000	J	UG/KG	CHS23	VAL
019-C-B002-01	019CB00201	Soil	08/27/94	668.0000		UG/KG	APX02	VAL
650-S-B004-01	650SB00401	Soil	08/22/94	679.0000		UG/KG	CHS05	VAL
GDH-S-B027-01	GDHSB02701	Soil	10/04/94	710.0000		UG/KG	CHS17	VAL
670-S-B008-01	670SB00801	Soil	09/12/94	720.0000		UG/KG	CHS13	VAL
670-S-B032-01	670SB03201	Soil	09/14/94	722.0000	J	UG/KG	APX04	VAL
136-S-B002-01	136SB00201	Soil	08/31/94	733.0000		UG/KG	CHS09	VAL
670-S-B004-01	670SB00401	Soil	09/13/94	760.0000		UG/KG	CHS13	VAL
014-S-B106-01	GDHSB10601	Soil	02/06/95	780.0000	J	UG/KG	CHS34	VAL
020-S-B005-01	020SB00501	Soil	03/27/95	820.0000	J	UG/KG	CHS37	VAL
GDH-S-B056-01	GDHSB05601	Soil	10/07/94	860.0000		UG/KG	CHS19	VAL
684-S-B023-01	684SB02301	Soil	09/21/94	989.0000		UG/KG	APX07	VAL
684-S-B015-01	684SB01501	Soil	09/20/94	1010.0000		UG/KG	APX05	VAL
670-S-B005-01	670SB00501	Soil	09/13/94	1100.0000		UG/KG	CHS13	VAL
666-S-B002-01	666SB00201	Soil	08/23/94	1180.0000	J	UG/KG	CHS05	VAL
GDH-S-B026-01	GDHSB02601	Soil	10/04/94	1200.0000		UG/KG	CHS17	VAL
015-S-B004-01	015SB00401	Soil	09/12/94	1300.0000		UG/KG	CHS13	VAL
684-S-B036-01	684SB03601	Soil	01/25/95	1300.0000		UG/KG	CHS33	VAL
019-S-B004-02	019SB00402	Soil	08/29/94	1400.0000	J	UG/KG	CHS08	VAL
121-S-B013-01	121SB01301	Soil	03/22/95	1400.0000		UG/KG	CHS35	VAL
GDH-S-B001-01	GDHSB00101	Soil	09/27/94	1400.0000		UG/KG	CHS15	VAL
GDH-S-B028-01	GDHSB02801	Soil	10/04/94	1400.0000		UG/KG	CHS17	VAL
684-S-B020-01	684SB02001	Soil	09/21/94	1430.0000		UG/KG	APX07	VAL
015-C-B004-01	015CB00401	Soil	09/12/94	1500.0000		UG/KG	APX03	VAL
670-S-B034-01	670SB03401	Soil	03/29/95	1500.0000		UG/KG	CHS40	VAL
121-S-B011-01	121SB01101	Soil	01/16/95	1700.0000		UG/KG	CHS31	VAL
666-S-B002-02	666SB00202	Soil	08/23/94	1750.0000	J	UG/KG	CHS05	VAL
650-S-B006-01	650SB00601	Soil	01/19/95	2000.0000		UG/KG	CHS32	VAL
655-S-SGC9-01	SGCSB00901	Soil	10/12/94	2400.0000	J	UG/KG	CHS21	VAL
GDH-C-B025-01	GDHCB02501	Soil	10/04/94	2560.0000		UG/KG	APX10	VAL
670-S-B031-01	670SB03101	Soil	01/20/95	2700.0000		UG/KG	CHS32	VAL
684-S-B043-01	684SB04301	Soil	03/29/95	3100.0000		UG/KG	CHS40	VAL
663-S-B007-01	663SB00701	Soil	01/19/95	3200.0000		UG/KG	CHS31	VAL
684-S-B024-01	684SB02401	Soil	09/21/94	3490.0000		UG/KG	APX07	VAL

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11/07/96

ENVIRONMENTAL SAFETY & DESIGNS

0064-00001 - NAVAL BASE CHARLESTON ZONE H (NBCH)

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Samples by Chemical Report  
50-32-8 - Benzo(a)pyrene  
>= 0.0000 for UG/KG - Hits Only

Sample ID	Ext. Orig. ID	Type	Date	Result	VQual	Units	SDG #	
684-S-B004-01	684SB00401	Soil	09/19/94	3710.0000		UG/KG	APX04	VAL
670-S-B003-01	670SB00301	Soil	09/13/94	5200.0000		UG/KG	CHS13	VAL
670-S-B029-01	670SB02901	Soil	01/20/95	5600.0000		UG/KG	CHS32	VAL
684-C-B044-01	684CB04401	Soil	03/29/95	5800.0000		UG/KG	CHS36	VAL
684-S-B003-01	684SB00301	Soil	09/19/94	6710.0000		UG/KG	APX04	VAL
684-S-B044-01	684SB04401	Soil	03/29/95	7600.0000		UG/KG	CHS40	VAL
670-M-0001-01	670M00101	Soil	09/24/94	12100.0000		UG/KG	APX09	VAL
684-S-B021-01	684SB02101	Soil	09/21/94	18300.0000	J	UG/KG	APX07	VAL
684-S-B035-01	684SB03501	Soil	01/25/95	22000.0000		UG/KG	CHS33	VAL
GDH-S-W04D-07	GDHSW04D07	Soil	10/19/94	34000.0000	J	UG/KG	CHS22	VAL
670-C-B031-01	670CB03101	Soil	01/20/95	36800.0000	J	UG/KG	APX16	VAL

\*\*\* End of Report \*\*\*

Upper interval vs. lower interval concentrations  
of cPAHs. (x no. of detections)

Final RCRA Facility Investigation Report for Zone H  
NAVBASE Charleston  
Section 4: Nature of Contamination  
July 5, 1996

Table 4.22.1  
Zone H Grid-Based Soil Samples  
Organic Compounds in Soil (in µg/kg)

Compound Name	Number of Detections (Upper Interval/Lower Interval)	Range of Concentrations for Detections (Upper Interval/Lower Interval)	Risk-Based Screening Levels
<b>Volatile Organic Compounds (154 Samples Collected — 96 Upper Interval Samples, 58 Lower Interval Samples, 10 Samples Duplicated)</b>			
Acetone	44/39	8-12,000 / 11-2,300	780,000
Bromomethane	1/2	5 / 3-4.3	11,000
2-Butanone (MEK)	2/4	14-17 / 4-100	4,700,000
Carbon disulfide	1/1	1.3 / 15	780,000
Methylene chloride	20/14	3.8-11 / 3.7-18	85,000
Tetrachloroethene	4/4	7-22 / 7-25	12,000
Tetrahydrofuran	1/1	31 / 87	Not Listed
Toluene	45/28	2.1-67.5 / 3.3-26.0	1,600,000
1,1,1-Trichloroethane	2/2	6-9 / 7-10	700,000
Trichloroethene	5/2	2-3.5 / 2.5-6	47,000
Trichlorofluoromethane	1/0	7.3 / 0	2,300,000
Xylene (total)	1/0	1.6 / 0	16,000,000
<b>Semivolatile Organic Compounds (154 Samples Collected — 96 Upper Interval Samples, 58 Lower Interval Samples, 10 Samples Duplicated)</b>			
Acenaphthene	9/2	88-6,600 / 100-170	470,000
Acenaphthylene	1/0	460 / 0	470,000
Anthracene	13/2	41.4-840 / 74-310	2,300,000
BEHP	26/1	39-680 / 400	46,000
Benzo(a)anthracene	17/3	48-1,900 / 120-640	880
Benzo(b)fluoranthene	14/1	40.6-2,840 / 270	880
Benzo(k)fluoranthene	11/0	88-2,340 / 0	8,800
Benzo(a)pyrene	16/3	81-1,400 / 140-480	88
Benzo(g,h,i)perylene	11/1	97-1,110 / 220	310,000
Butylbenzylphthalate	5/0	65.8-580 / 0	1600,000
4-Chloro-3-methylphenol	1/0	170 / 0	Not Listed

**Table 4.22.1**  
**Zone H Grid-Based Soil Samples**  
**Organic Compounds in Soil (in µg/kg)**

Compound Name	Number of Detections (Upper Interval/Lower Interval)	Range of Concentrations for Detections (Upper Interval/Lower Interval)	Risk-Based Screening Levels
<b>Semivolatile Organic Compounds (154 Samples Collected — 96 Upper Interval Samples, 58 Lower Interval Samples, 10 Samples Duplicated)</b>			
2-Chlorophenol	1/0	160 / 0	39,000
Chrysene	18/3	50-1,700 / 140-580	88,000
Dibenzo(a,h)anthracene	7/0	84-456 / 0	88
Dibenzofuran	4/0	150-4,300 / 0	31,000
Di-n-butylphthalate	1/0	140 / 0	780,000
Di-n-octylphthalate	2/0	200-660	160,000
Fluoranthene	25/5	50.7-3,245 / 130-1,400	310,000
Fluorene	7/2	100-4,500 / 120-190	310,000
Indeno(1,2,3-cd)pyrene	12/1	94-1,110 / 220	880
2-Methylnaphthalene	3/0	91-4,200 / 0	310,000
Naphthalene	4/0	110-7,500 / 0	310,000
Phenanthrene	17/3	86-2,900 / 350-1,200	310,000
Phenol	1/0	160 / 0	4,700,000
Pyrene	25/4	45.8-2,940 / 120-1,100	230,000
<b>Pesticides (154 Samples Collected — 96 Upper Interval Samples, 54 Lower Interval Samples, 10 Samples Duplicated)</b>			
beta-BHC	0/1	4.2 / 0	350
Chlorobenzilate	1/0	124 / 0	2,400
alpha-Chlordane	20/5	1-330 / 2-19	470
gamma-Chlordane	19/6	1-260 / 3-73	(alpha + gamma)
4,4'-DDE	33/15	2-270 / 2-22	1,900
4,4'-DDD	7/4	6-130 / 7-120	2,700
4,4'-DDT	30/3	2.1-180 / 5-21	1,900
Dieldrin	5/1	4-300 / 8	40

October 8, 1996

DRAFT

Memorandum

TO: Tony Hunt  
FROM: EnSafe

RE: Proposed method for comparing site sample values to background values for surface soils.

Part 1 - Inorganics (Appears as Appendix J in Final RFI Report for Zone H, NAVBASE)

Part 2 - Organics

Substantial levels of organic compounds from natural and anthropogenic sources are present in urban environments. Polynuclear aromatic hydrocarbons (PAHs), in particular, are nearly ubiquitous in many urban soils. Sources of background PAHs include forest fires and volcanoes as well as vehicular and industrial emissions, wood treatment, waste incineration, and cooking. Bradley, et al. (1994) documented benzo(a)pyrene concentrations averaging 1323  $\mu\text{g}/\text{kg}$  in background samples of surface soil from three urban areas in New England. Corresponding concentrations of benzo(a)pyrene equivalents (BEQs) from the same samples were 2437  $\mu\text{g}/\text{kg}$ . Responsible risk management decisions and target cleanup levels for urban sites must consider the potential for non-site-related concentrations of organics. This memo discusses the problem as it relates to carcinogenic PAHs (cPAHs) at NAVBASE, Zone H.

Determination of background levels for PAHs such as benzo(a)pyrene (B(a)P) and other infrequently detected contaminants poses a greater challenge than determination of background levels for inorganics. The lower rate of detection means that little information is available on the majority of samples, so that parametric assumptions are difficult to verify. Nonparametric methods are more appropriate, but simple tests like the Wilcoxon rank sum test for comparing two groups, which was used for inorganics, are not valid where nondetect rates are high, since the majority of the data (the nondetects) must be ranked as ties. We therefore concentrate on the standard "2 X Background" test recommended by USEPA and on nonparametric tolerance limits as discussed in the previous memo (Zone H RFI Report, Appendix J) covering inorganics. For illustration, the BEQ results for Zone H surface soil grid samples will be examined. Of the 101 samples in this dataset, 19 samples reported detections of at least one cPAH.

The "2 X Background" comparison establishes twice the mean concentration of the background samples as a reference standard. To apply this rule, a concentration must be estimated for nondetects, which appear in the dataset as U-qualified values. A U-qualified value represents a sample quantitation limit, or SQL; the actual concentration in the sample is somewhere between zero and the SQL. The Zone H RFI Human Health Risk Assessment recommended

using the lower of one-half the SQL value or one-half the lowest estimated (J-qualified) detected value as the estimate for a nondetect. Applying this procedure to BEQ values in Zone H background samples results in an estimated mean concentration of 212  $\mu\text{g}/\text{kg}$  total BEQs, thereby yielding an estimated background reference level of 424  $\mu\text{g}/\text{kg}$ . Because many SQL values for nondetected organics are substantially higher than the lowest detected values, using one-half the SQL without adjusting (as above) for the lowest estimated detected value results in higher estimated concentrations; for Zone H BEQs, the estimated mean concentration using this method is 1910  $\mu\text{g}/\text{kg}$ . The mean of the detected concentrations only (no estimated values for nondetects) is 1430  $\mu\text{g}/\text{kg}$ . This range of estimated mean values shows that calculation of a background number depends strongly on the manner in which censored data (nondetects) are used.

Another option for determining a reference standard is a nonparametric tolerance limit, which directly estimates a quantile of the underlying background distribution, using the actual data collected. Nonparametric methods generally require greater amounts of data to draw comparable conclusions, but this approach is possible with the large sample sizes used in Zone H. Calculation of a nonparametric tolerance limit is a two-step procedure. The first is to directly calculate the equivalent percentile in the sample data, and the second is to allow for sampling variability. With an infinite amount of data, we could estimate the desired quantile directly, with complete accuracy; when estimating from sample data, however, we must account for variability.

If we assume that all nondetect values are lower than detected values, the 95th percentile of BEQ values in background surface soil samples from Zone H is 1028  $\mu\text{g}/\text{kg}$ . The 90th percentile is 310  $\mu\text{g}/\text{kg}$ . As explained in the previous memo, the 95th percentile nonparametric upper tolerance limit (UTL) for this sample size (95% coverage, 95% confidence) is estimated by using the second-highest data value (USEPA, 1992, Table A-6). For the example dataset, this value is 2006  $\mu\text{g}/\text{kg}$ . Although a UTL with 95% coverage has been used as the background estimator for inorganics at NAVBASE, a UTL with 90% coverage might be considered more appropriate for organic compounds, for added conservatism. Unfortunately, USEPA's statistical tables provide coverage percentages for only the largest and second-largest values in datasets of various sizes, so that data values corresponding to lower coverages cannot be identified. Nevertheless, the sampling variability in this estimate may still be calculated using the statistical technique known as the bootstrap<sup>1</sup>. Applying bootstrap techniques, using the "BCANON" code in the statistical language S-Plus (developed by the authors mentioned in footnote 1), an upper tolerance limit for the 90th percentile (90% coverage, 95% confidence) was determined to be 814  $\mu\text{g}/\text{kg}$ <sup>2</sup>.

From this discussion, we have three preferred estimators for BEQ background reference concentrations:

Type	Value ( $\mu\text{g}/\text{kg}$ )
2 X Background	424
90% UTL (Bootstrap)	814
95% UTL	2006

Given the relatively high percentage of BEQ nondetects and the greater level of uncertainty about the sources of organic compounds in soils (site-related vs. background), the UTL approach that was applied to inorganics in Zone H soil could be considered insufficiently conservative for organics. If nondetects are treated as recommended in the Zone H Human Health Risk Assessment (described above), then a mean background concentration can be estimated for the grid samples. As recommended by USEPA in other situations, twice the estimated mean background concentration would serve as a reasonable, conservative background reference value.

Choosing an appropriate technique to estimate background screening levels of organic compounds is a risk-management decision. Although a particular technique will likely be selected resulting in specific background values for PAHs and possibly other organics, the full range of concentrations in grid-based samples as well as potential anthropogenic sources should be considered in the risk management decision making process.

<sup>1</sup> The bootstrap is a simulation-based technique that has been shown capable of producing confidence intervals for a wide range of statistics. Very briefly, the bootstrap uses resampling from the observed data values, with replacement. In other words, a data value is picked from all data values, its value observed, and then returned to the pile. This procedure is repeated until there are as many resampled data points as there are data points. This resampled set is called a bootstrap sample. The value of the desired statistic is then calculated from the bootstrap sample. If this procedure is repeated a number of times, an approximate distribution for the statistic is constructed. A confidence interval may then be calculated from this distribution. It can be shown that these confidence intervals are extremely accurate, particularly if a somewhat refined version of the simple algorithm is used. Several introductory treatments of these techniques are available. *An Introduction to the Bootstrap* by B. Efron and R. Tibshirani is especially good and quite readable.

<sup>2</sup> The bootstrap may also be used to calculate the 95th percentile UTL, giving a value of 1850  $\mu\text{g}/\text{kg}$ . Theoretical derivations show that this upper limit is probably more accurate than the value of 2006  $\mu\text{g}/\text{kg}$  derived from the table.

*References:*

**Bradley, L.J.N, B.H. Magee, and S.L. Allen (1994): Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils. Journal of Soil Contamination, v.3, n.4, p.349-361**

**USEPA (1992): Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Draft Addendum to Interim Final Guidance. Office of Solid Waste.**

1/5/95

*Handwritten notes*

PAHs

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# Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils

L. J. N. Bradley,<sup>1\*</sup> B. H. Magee,<sup>2</sup> and S. L. Allen<sup>1</sup>

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**ABSTRACT:** Polycyclic aromatic hydrocarbons (PAH) are byproducts of combustion and are ubiquitous in the urban environment. They are also present in industrial chemical wastes, such as coal tar, petroleum refinery sludges, waste oils and fuels, and wood-treating residues. Thus, PAHs are chemicals of concern at many waste sites. Risk assessment methods will yield risk-based cleanup levels for PAHs that range from 0.1 to 0.7 mg/kg. Given their universal presence in the urban environment, it is important to compare risk-based cleanup levels with typical urban background levels before utilizing unrealistically low cleanup targets. However, little data exist on PAH levels in urban, nonindustrial soils. In this study, 60 samples of surficial soils from urban locations in three New England cities were analyzed for PAH compounds. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and seven metals. The upper 95% confidence interval on the mean was 3 mg/kg for benzo(a)pyrene toxic equivalents, 12 mg/kg for total potentially carcinogenic PAH, and 25 mg/kg for total PAH. The upper 95% confidence interval was 373 mg/kg for TPH, which exceeds the target level of 100 mg/kg used by many state regulatory agencies. Metal concentrations were similar to published background levels for all metals except lead. The upper 95% confidence interval for lead was 737 mg/kg in Boston, 463 mg/kg in Providence, and 378 mg/kg in Springfield.

← BEQS

**KEY WORDS:** background, PAH, metals, urban, anthropogenic, soil.

## I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are byproducts of combustion and are naturally occurring chemicals in the environment. Forest fires and volcanoes are major natural sources of PAHs, but there are anthropogenic sources as well due to burning of fossil fuels, including automobile and industrial emissions. PAHs are chemicals of concern in many waste site investigations that are undertaken pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Resource Conservation and Recovery Act (RCRA), and state

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They obtained totals for

- 1) BEQS - benzo(a)pyrene equivalents of the 7 cPAHs
- 2) Total concentrations of the 7 cPAHs
- 3) " " " " 17 PAHs on EPA's TCL

hazardous waste programs. Risk assessments performed according to federal guidance for former manufactured gas plant sites, wood treating facilities, petroleum refineries, and other sites generally conclude that PAHs pose unreasonable risks to human health and that remedial actions must be taken to reduce risks to acceptable levels. The majority of the risk posed by PAHs is generally due to benzo(a)pyrene and the other PAHs that have been shown to cause cancer in laboratory animals after repeated dosings. The U.S. EPA (1993a) currently identifies seven PAHs as "probable human (B2) carcinogens": benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-c,d)pyrene.

Because of the very health-protective assumptions used in regulatory risk assessments, very low risk-based clean-up levels for PAHs are derived for such sites. In Michigan, residential soil cleanup levels of 0.33 mg/kg for each carcinogenic PAH have been set (MDNR, 1993). In New Jersey, proposed residential soil cleanup levels are 0.66 mg/kg for benzo(a)pyrene (*New Jersey Register*, 1992). The use of standard CERCLA risk assessment guidance (U.S. EPA, 1993b) results in the derivation of a risk-based cleanup level for benzo(a)pyrene of 0.1 mg/kg.

→ All of these risk-based soil cleanup levels are below the urban, nonindustrial background soil concentrations presently reported in the literature. However, the availability of such data is very limited. Blumer (1961) reports that benzo(a)pyrene concentrations in Cape Cod, MA, soils range from 0.04 to 1.3 mg/kg. Menzie et al. (1992) report that urban background soil levels of total carcinogenic PAH range from 0.06 to 5.8 mg/kg. Butler et al. (1984) report that total PAH levels in soils alongside roadways in England range from 4 to 20 mg/kg, and potentially carcinogenic PAH range from 0.8 to 11.5 mg/kg. Blumer et al. (1977) report that total PAH levels in soils in a Swiss town range from 6 to 300 mg/kg.

It is very difficult to compare the data from these studies to the results of site risk assessments due to the limited dataset and the nonuniformity of the PAH compounds evaluated. Clearly, more data are required from nonindustrial urban locations to define the urban background level for PAH and to critically evaluate the role of risk assessment in setting remedial goals for PAH in soils. Accordingly, we have collected 60 samples of surficial soils from urban locations in three New England cities and analyzed them for all 17 PAH compounds present on the EPA's Target Compound List, which is used in the Superfund program. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and for seven metals: arsenic, barium, cadmium, chromium, lead, mercury, and selenium.

## II. METHODS

### A. Sample Collection

→ Samples of surficial soils from urban locations in three New England cities were collected: Boston, MA; Providence, RI; and Springfield, MA. Twenty independent

samples and duplicates of two samples were collected in each city. The samples were collected on July 21, 22, and 23, 1992, respectively. The samples were taken at a depth of 0 to 6 in. in areas considered to be not directly affected by industrial sites. Generally, the locations were along roads and sidewalks, and in parks and open lots. Each location was characterized in writing, including a soil description, and photographically documented. The samples were collected following standard environmental sampling protocols (U.S. EPA, 1986).

## B. Sample Analysis

Chemical analysis of the samples was performed by AnalytiKEM, Inc. (Cherry Hill, NJ). The samples were analyzed by GC-MS for the 17 PAH compounds present on the EPA's Target Compound List using the methods required by EPA Method 8270 for the analysis of semivolatile compounds. In addition, the samples were analyzed for the eight RCRA metals, total petroleum hydrocarbons (TPH; EPA Method 418.1), and total solids. The complete analyte list is given in Table 1.

## C. Data Validation

Validation of the data received from AnalytiKEM was performed according to U.S. EPA (1991) guidelines. The data were reviewed for completeness, holding times, GC-MS tuning and system performance, initial and continuing calibrations, laboratory method blank analysis, surrogate recoveries, matrix spike and matrix spike duplicate analysis, field duplication precision, and compound quantitation and detection limits.

## D. Data Analysis

The analytical data were summarized in accordance with U.S. EPA (1989) risk assessment guidance. If a compound was detected at least once in surface soil, one half the sample quantitation limit (SQL) was used as a proxy concentration for all samples reported as "below detection limit" in the estimation of exposure point concentrations. However, if a compound was not detected in any sample, that compound was omitted from further consideration. In addition, when a proxy concentration (i.e., one half the detection limit) was greater than the highest actual detected value for a compound in any sample, that concentration was considered to be an aberration and was omitted from the database. This is consistent with U.S. EPA (1989) guidance, which recognizes that high sample quantitation limits can lead to unrealistic concentration estimates.

*They treated nondetects somewhat differently than we did, but the difference should not be significant.*

**TABLE 1**  
**Chemical Analyses of Urban Soils**

Semivolatile Organics, EPA Target Compound List

- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Benzo(a)anthracene
- Chrysene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene
- 2-Methylnaphthalene

Metals

- Arsenic, total
- Barium, total
- Cadmium, total
- Chromium, total
- Lead, total
- Mercury, total
- Selenium, total
- Silver, total

Other

- Total petroleum hydrocarbons
- Solids

A slightly different method of analysis was used to evaluate PAH. Because PAH are generally found in groups, it was conservatively assumed that if one PAH was detected in a sample, other compounds in that class might also be present in that sample. Therefore, if one PAH was detected in a sample, all undetected PAH were assigned a proxy concentration equal to one half the SQL. If a sample had no detected PAH, no PAH were assumed to be present in the sample, and a concentration of zero was used for all nondetects.

Summary statistics (minimum, maximum, arithmetic mean, upper 95% confidence limit on the arithmetic mean, and frequency of detection) were generated for each compound for each city and for all three cities combined.

The data for PAH were summarized in several different ways. Of the 17 PAH analyzed in each sample, seven are considered to be probable human carcinogens (Group B2) by the U.S. EPA (1993a). The U.S. EPA has derived a cancer slope factor, which is a measure of the carcinogenic potency of a compound, only for benzo(a)pyrene (B(a)P) (U.S. EPA, 1993a). Review of the literature indicates that not all PAH are equally potent with respect to tumor induction. Several researchers have proposed toxic equivalency schemes that relate the tumorigenic potency of each PAH to that of B(a)P (ICF-Clement Associates, 1988; Woo, 1989). B(a)P toxic equivalency factors (B(a)P-TEFs) can be used to adjust either the B(a)P dose-response value to provide a compound-specific dose-response value, or the concentration of each PAH in a sample to be expressed in terms of B(a)P toxic equivalents (B(a)P-TE). The latter method was used here. B(a)P-TE were calculated using the B(a)P toxic equivalency factors recommended for use by the U.S. EPA (1993c), as shown in Table 2. For each sample, PAH concentrations were reported for each of the 17 PAH on the analyte list, for total PAH (tPAH), for total carcinogenic PAH (cPAH), and for B(a)P-TE, and these values were used to generate the summary statistics for each group of samples.

### III. RESULTS

Analysis of the laboratory results for the PAH indicates that quality control criteria were acceptable. The data were analyzed to determine if any statistically significant differences existed between the datasets for the three cities. A Hartley test for homogeneity of variances (Mendenhall, 1979) and a one-factor analysis of variance to test for equality of the means (Mendenhall, 1979) indicated no statistically significant differences. The results indicate that the PAH data can be pooled and treated as one dataset for further statistical analyses.

TABLE 2  
Benzo(a)Pyrene Toxic  
Equivalent Factors (BAP-TEF)

Compound	EPA TEF
Benzo(a)pyrene	1.0
Benzo(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Chrysene	0.001
Dibenzo(a,h)anthracene	1.0
Indeno(1,2,3-c,d)pyrene	0.1

*(Same scheme that we use to calculate BEQs)*

The results of the PAH analyses are presented in Table 3 for all cities combined. A summary of the PAH results by city and for all cities combined is presented in Table 4, which reports for each: tPAH, total cPAH, and total B(a)P-TE. The arithmetic mean and the upper 95% confidence limit concentration are reported for each. Table 4 provides a summary of the data by city, and the results are graphically presented in Figure 1.

Table 5 presents a summary of the metals, TPH, and solids data by city. A Hartley test for homogeneity of variances and a one-factor analysis of variance to test for equality of the means indicated that the metals and TPH data from the three cities cannot be combined. This is due to the fact that the concentrations in each city are not normally distributed and did not have equal variances. The concentrations of the metals are compared to the arithmetic mean concentrations in the eastern U.S. (ATSDR, 1992) in Table 5. Most notably, lead concentrations are much higher than background concentrations. This is most likely due to the effects of automobile exhaust.

In order to determine if sample location significantly affected PAH concentration results, individual samples were classified based on the sample location's

→ TABLE 3  
Summary Statistics for PAH — All Areas Combined

Compound	Minimum detect (mg/kg)	Maximum detect (mg/kg)	Arithmetic mean	Upper 95% Interval (mg/kg)	Frequency of detection*	
2-Methylnaphthalene	0.017	0.64	0.151	0.173	19	62
Acenaphthene	0.024	0.34	0.201	0.306	30	62
Acenaphthylene	0.018	1.10	0.173	0.208	24	62
Anthracene	0.029	5.70	0.351	0.535	54	62
Benzo(a)anthracene	0.048	15.00	1.319	1.858	58	62
Benzo(a)pyrene	0.040	13.00	1.323	1.816	57	62
Benzo(b)fluoranthene	0.049	12.00	1.435	1.973	55	62
Benzo(g,h,i)perylene	0.200	5.90	0.891	1.195	36	62
Benzo(k)fluoranthene	0.043	25.00	1.681	2.522	59	62
Chrysene	0.038	21.00	1.841	2.693	60	62
Dibenzo(a,h)anthracene	0.020	2.90	0.388	0.521	32	62
Fluoranthene	0.110	39.00	3.047	4.444	60	62
Fluorene	0.022	3.30	0.214	0.317	35	62
Indeno(1,2,3-c,d)pyrene	0.093	6.00	0.987	1.293	43	62
Naphthalene	0.018	0.66	0.125	0.149	35	62
Phenanthrene	0.071	36.00	1.838	2.982	61	62
Pyrene	0.082	11.00	2.398	2.945	61	62
Total BAP-TE	0.257	21.31	2.437	3.324	62	62
Total carcinogenic PAH	0.680	77.70	8.973	12.423	62	62
Total PAH	2.292	166.65	18.361	24.819	62	62

\* Frequency of detection = number detected: number samples.

These values are in mg/kg; ours are in µg/kg.

TABLE 4  
Background PAH Concentrations in Urban Surface Soils\*

Compound	Boston (n = 20)		Providence (n = 20)		Springfield (n = 20)		All cities (n = 60)	
	Arithmetic mean (ppm)	Upper 95% CI (ppm)						
Total B(a)P-TB	2.4	4.6	2.1	2.9	2.8	4.5	2.4	3.3
Total cPAH	8.4	16.0	7.8	11.0	10.6	18.3	9.0	12.4
Total PAH	18.7	35.9	16.8	23.5	19.1	29.9	18.4	24.8
TPH	474.9	652.6	267.4	338.2	184.4	233.3	306.2	372.8

\* 0 to 6 in.

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Mean BEQ = 2400 µg/kg.

Parts Per Million (ppm)

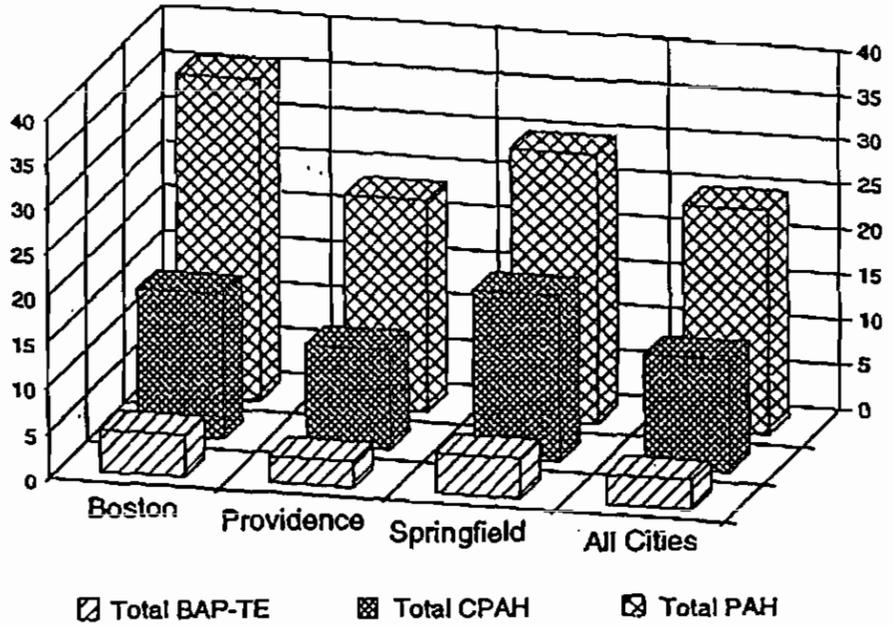


FIGURE 1. Background concentrations of PAH in urban soils. Data presented are the upper 95% confidence interval on the arithmetic mean. Data are presented numerically in Table 4.

proximity to asphalt pavement, based on both written and photographic documentation of sample location. Generally, samples collected within 4 to 6 ft of a road were considered to be near pavement. Of the 60 separate locations, 42 were considered to be near pavement and 18 were not. When tested for equality of variance and means as above, the two populations were determined to be significantly different. The mean total PAH concentration near pavement was 22 ppm compared to 8 ppm not near pavement. These results are shown in Table 6.

Similar analyses were performed to see if TPH or total organic carbon concentrations could be used as surrogates for PAH concentrations. The results showed that there is no correlation between PAH and TPH concentrations, nor between PAH and total organic carbon concentrations (data not shown).

The highest total PAH concentration detected was 166 mg/kg, taken from a street corner in Boston. The next highest PAH concentration was 109 mg/kg, taken at the base of a telephone pole. Four of the 60 samples were taken at the bases of telephone poles, with widely varying results. The total PAH concentrations in the other three locations were 62, 4, and 45 mg/kg.

*We did not see significant correlation between BEQ concentration and distance from pavement. We used Arc/Info to analyze this.*

TABLE 5  
Summary Statistics for Metals, TPH, and Soils by City

Compound	Boston (n = 20)		Providence (n = 20)		Springfield (n = 20)		Arithmetic mean in U.S. soils <sup>a</sup> (mg/kg)
	Arithmetic mean (mg/kg)	Upper 95% Interval (mg/kg)	Arithmetic mean (mg/kg)	Upper 95% Interval (mg/kg)	Arithmetic mean (mg/kg)	Upper 95% Interval (mg/kg)	
Arsenic, total	4.20	5.59	3.53	4.27	5.63	9.23	7.4
Barium, total	53.95	66.25	45.29	59.43	45.17	51.03	420
Cadmium, total	1.55	2.79	ND	ND	ND	ND	0.25 <sup>b</sup>
Chromium, total	23.00	27.69	12.08	14.35	12.62	14.45	52
Lead, total	398.70	737.44	305.76	462.98	261.69	377.76	17
Mercury, total	0.29	0.39	0.19	0.24	0.20	0.25	0.12
Selenium, total	0.51	0.57	0.39	0.48	0.53	0.55	0.45
Total petroleum hydrocarbons	474.90	652.62	267.43	338.19	184.38	233.27	—
Total solids	90%	93%	93%	95%	90%	92%	—

<sup>a</sup> ATSDR. 1992. *Public Health Assessment Guidance Manual*. PB92-147164. U.S. Department of Health and Human Services.

<sup>b</sup> ATSDR. 1991. *Toxicological Profile for Cadmium*. PB92-147164. Draft. U.S. Department of Health and Human Services.

\* All of these values except lead are higher than mean values observed in Zone H surface soil grid samples. Zone H lead values averaged 23.3 mg/kg, vs. 17 shown here!

**TABLE 6**  
**Comparison of Background PAH Concentrations in Urban Soils: The Effects of Proximity to Pavement**

Compound	Near pavement		Not near pavement		Results of statistical analysis					
	Arithmetic mean (ppm)	Standard deviation	Arithmetic mean (ppm)	Standard deviation	Test for homogeneity of variances			Test of equality of means		
					Sample F-statistic	Associated degrees of freedom	Statistically significant at 0.05 level of significance	Sample Student's t	Associated degrees of freedom	Statistically significant at 0.05 level of significance
Total B(a)P-TE	2.9	4.2	1.1	0.92	21.3	41, 17	Yes	2.69	50	Yes
Total PAH	21.9	30.7	8.3	7.2	18.4	41, 17	Yes	2.69	50	Yes

#### IV. CONCLUSION

In this study, 20 surface soil samples were collected from each of three New England cities and analyzed for PAH, TPH, and metals. The results of the statistical analyses described in the previous section show that, with respect to PAH, the three datasets are not significantly different and can be considered as one dataset representative of urban environments. The samples were taken in typical urban areas but not near known industrial sites. Therefore, these data are considered to be representative of the generalized effects of urban activities.

It is clear from the results presented here that common regulatory target cleanup levels for cPAH and B(a)P-TE (0.1 to 0.66 mg/kg) are much below the background concentrations of these compounds in urban surface soils (upper 95% confidence interval of 3.3 and 12.4 mg/kg for total B(a)P-TE and total cPAH, respectively). Figure 2 graphically compares the "bright line" target cleanup level for B(a)P of 0.1 mg/kg with the total B(a)P-TE (upper 95% confidence interval on the arithmetic mean) measured in urban environments.

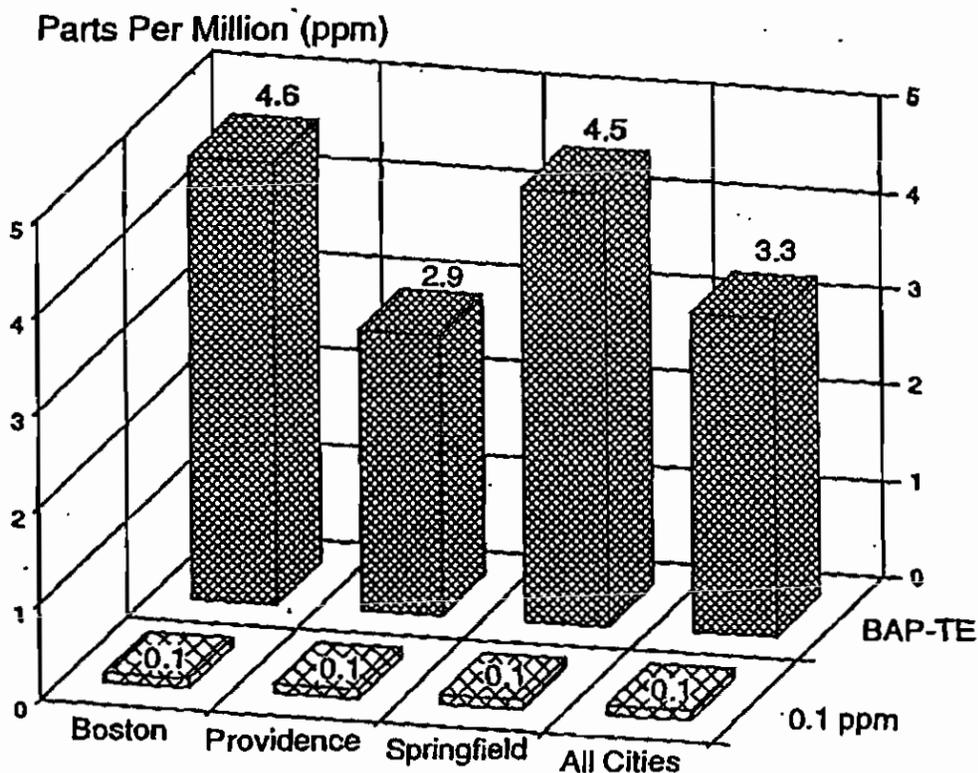


FIGURE 2. Comparison of B(a)P-TE with U.S. EPA Region III<sup>4</sup> risk-based concentration for B(a)P. B(a)P data presented are the upper 95% confidence interval on the arithmetic mean.

Upper 95% confidence intervals are compared because this is the statistic preferred by EPA and many states for risk assessment. Moreover, the State of Massachusetts defines its background concentrations of metals based on the upper 95% confidence limit on the arithmetic mean concentration (Massachusetts Department of Environmental Protection, 1992). For all cities combined, the background level of B(a)P-TE of 3.3 mg/kg is approximately ten times greater than the target cleanup level of 0.33 mg/kg and approximately 30 times higher than the target cleanup level of 0.1 mg/kg. For those regulatory situations in which the use of B(a)P-TEFs in determining site risk is not allowed, the background level of cPAH is approximately 40 to 100 times greater than these target cleanup levels.

An analysis of the data comparing samples taken near pavement with those determined to be not near pavement indicated that those samples designated near pavement had significantly higher, approximately threefold higher, PAH concentrations for both total PAH and total B(a)P-TE. This is most likely due to the presence of diesel and automobile exhaust particles, perhaps influenced by the presence of asphalt and runoff of vehicular oil from the roads.

Total petroleum hydrocarbons (TPH) were also found at consistently high levels in each city. The commonly applied regulatory cleanup level for TPH is 100 mg/kg. This cleanup level is not risk based and is three times lower than the background concentration of TPH found in this study (arithmetic mean of 306 mg/kg and upper 95% confidence interval on the mean of 373 mg/kg).

It is incumbent upon the regulatory agencies to recognize that substantial background levels of PAH and TPH exist in our urban environments and to acknowledge this information in the development of realistic target cleanup levels. The use of these background data in setting more realistic target cleanup levels may result in better allocation of remedial and regulatory dollars in site investigations.

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To: Tony Hunt

From: Todd

Date: 8/28

Fax to Number:

Number of Pages: 4

Remarks:

Here's the background memo at last. If you have questions I'll have to defer them to Barry Doll to explain.

August 28, 1996

DRAFT

Memorandum

TO: Tony Hunt  
FROM: EnSafe  
RE: Proposed method for comparing site sample values to background values for surface soils.

Part 1 - Inorganics (Appears as Appendix J in Final RFI Report for Zone H, NAVBASE)

Part 2 - Organics

Substantial levels of organic compounds from natural and anthropogenic sources are present in urban environments. Polynuclear aromatic hydrocarbons (PAHs), in particular, are ubiquitous in many urban soils. Sources of background PAHs include forest fires and volcanoes as well as vehicular and industrial emissions, wood treatment, and waste incineration. Bradley, et al. (1994) documented benzo(a)pyrene concentrations averaging 1323  $\mu\text{g}/\text{kg}$  in background samples of surface soil from three urban areas in New England. Corresponding concentrations of benzo(a)pyrene equivalents (BEQs) from the same samples were 2437  $\mu\text{g}/\text{kg}$ . Responsible risk management decisions and target cleanup levels for urban sites must consider the potential for non-site-related concentrations of organics. This memo discusses the problem as it relates to carcinogenic PAHs at NAVBASE, Zone H.

Determination of background levels for PAHs such as benzo(a)pyrene (B(a)P), and other infrequently detected contaminants poses a greater challenge than determination of background levels for inorganics. The low rate of detection means that little information is available on the majority of samples, so that parametric assumptions are difficult to verify. Nonparametric methods are more appropriate, but simple tests like the Wilcoxon rank sum test for comparing two groups, which was used for inorganics, are not valid where nondetect rates are high, since the majority of the data (the nondetects) must be ranked as ties. We therefore concentrate on the standard "2 X Background" test recommended by USEPA and on nonparametric tolerance limits as discussed in the previous memo (Zone H RFI Report, Appendix J) covering inorganics. For illustration, the BEQ results for Zone H surface soil grid samples will be examined. Of the 101 samples in this dataset, 19 samples reported detections of at least one carcinogenic PAH.

The "2 X Background" comparison uses twice the mean concentration of the background samples as a reference standard. To apply this rule, a concentration must be estimated for nondetects. The Zone H RFI Risk Assessment recommended using the lower of one-half the SQL value or lowest estimated (J-flagged) detected value as the estimate for nondetects. Applying this procedure to BEQ values in Zone H background samples results in an estimated mean concentration of 212  $\mu\text{g}/\text{kg}$ , thereby yielding an estimated background level of 424  $\mu\text{g}/\text{kg}$ .

Because many SQL values for nondetected organics are substantially higher than the lowest detected values, using one-half the SQL without adjusting for lowest estimated detected value gives an estimated mean concentration of 1910  $\mu\text{g}/\text{kg}$ . Using the mean of only the detected values gives an estimated mean concentration of 1430  $\mu\text{g}/\text{kg}$ . This range of estimated mean values shows that calculation of a background number depends strongly on the manner in which censored data are used.

Another option is a nonparametric tolerance limit, which directly estimates a quantile of the underlying background distribution, using the actual data collected. Nonparametric methods generally require greater amounts of data to draw comparable conclusions, but this approach is possible with the large sample sizes used in Zone H. Calculation of a nonparametric tolerance limit is a two-step procedure. The first is to directly calculate the equivalent percentile in the sample data, and the second is to allow for sampling variability. With an infinite amount of data, we could estimate the tolerance limit directly, with complete accuracy; when estimating from sample data, we must account for variability. If we assume that all nondetect values are lower than the detected values, the 95th percentile of BEQ values in background samples is 1028  $\mu\text{g}/\text{kg}$ . The 90th percentile is 310  $\mu\text{g}/\text{kg}$ .

As mentioned in the previous memo, the 95th percentile nonparametric upper tolerance limit (UTL) for this sample size (95% coverage, 95% confidence) is estimated by using the second-highest data value (USEPA, 1992, Table A-6). For the example dataset, this value is 2006  $\mu\text{g}/\text{kg}$ . Although a UTL with 95% coverage has been used as the background estimator for inorganics at NAVBASE, a UTL with 90% coverage might be considered more appropriate for organic compounds, for added conservatism. Unfortunately, USEPA's statistical tables provide coverage percentages for only the largest and second-largest values in datasets of various sizes, so that data values corresponding to lower coverages cannot be identified. Nevertheless, the sampling variability in this estimate may still be calculated using the statistical technique known as the bootstrap<sup>1</sup>. Applying bootstrap techniques, using the "BCANON" code in the statistical language S-Plus (developed by the authors mentioned in footnote 1), an upper tolerance limit for the 90th percentile (90% coverage, 95% confidence) was determined to be 814  $\mu\text{g}/\text{kg}$ .

From this discussion, therefore, we have three potential estimators for organic background concentrations:

Type	Value ( $\mu\text{g}/\text{kg}$ )
2 X Background	424
90% UTL (Bootstrap)	814
95% UTL	2006

Choosing an appropriate technique to estimate background screening levels of organic compounds is a risk-management decision. Although a particular technique will likely be

selected resulting in specific background values for PAHs and possibly other organics, the full range of concentrations in grid-based samples as well as potential anthropogenic sources should be considered in the risk management decision making process.

<sup>1</sup> The bootstrap is a simulation-based technique that has been shown capable of producing confidence intervals for a wide range of statistics. Very briefly, the bootstrap uses resampling from the observed data values with replacement. In other words, a data value is picked from all data values, its value observed, and then returned to the pile. This procedure is repeated until there are as many resampled data points as there are data points. This resampled set is called a bootstrap sample. The value of the desired statistic is then calculated from the bootstrap sample. If this procedure is repeated a number of times, an approximate distribution for the statistic is constructed. A confidence interval may then be calculated from this distribution. It can be shown that these confidence intervals are extremely accurate, particularly if a somewhat refined version of the simple algorithm is used. Several introductory treatments of these techniques are available. *An Introduction to the Bootstrap* by B. Efron and R. Tibshirani is especially good and quite readable.

<sup>2</sup> The bootstrap may also be used to calculate the 95th percentile UTL, giving a value of 1850  $\mu\text{g}/\text{kg}$ . Theoretical derivations show that this upper limit is probably more accurate than the value of 2006  $\mu\text{g}/\text{kg}$  derived from the table.

*References:*

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