# Cabot and Koppers COC Ratios using data from Cabot Hawthorn Group Investigation, April & June 2014

By GRU DNAPL Team, July 21, 2014

#### **Observations:**

Samples are analyzed in the attached tables based on a series of ratios of reported concentrations between compounds and on the presence of certain tracers.

Criterion	Koppers origin	Cabot origin
Naphthalene : 3&4 Methyl Phenol	Ratio > 1	Ratio < 1
Benzene : Toluene	Ratio > 0.4	Ratio < 0.4
2,4-DMP : 3&4 MP	Ratio > 1	Ratio < 1
Naphthalene : Benzene	Not predictive	Not predictive
Acetone	No tests @ Koppers	Abundant
Phenol	Low	Abundant
Terpenoids & Terpenes	No tests @ Koppers	Abundant
Pentachlorophenol	Present	Absent

The utility of the ratios appears to come from the relative abundance of *benzene*, *naphthalene* and 24-DMP in the creosote and *toluene*, 3&4-MP, acetone and phenol being associated with the Cabot pine tar. Unfortunately *terpene* and the *terpenoids* that are a major distinguishing feature of the pine tar are not measured by Cabot any more. A reference data set is shown in Table 1.

Thus ratios of **K**oppers to **C**abot compounds provide guidance, but if you choose a ratio pair like naphthalene and benzene from the same source, the results are unreliable. The Naphthalene: Benzene ratio may be helpful in 'age dating' a plume migrating from Koppers in that benzene would likely lead and naphthalene follow based on octanol/water partition coefficients. Acetone and phenol are the most soluble and therefore the most mobile, according to their octanol-water partition coefficients (see Table 1), consequently these are now found in the UHG. Table 2 contains the results from groundwater samples around the Cabot ponds conducted by Gradient during the April and June 2014.

## **Surficial Aquifer Plume**

There is clear evidence of Cabot contamination 600 ft east of the former Cabot ponds at WS-28 and 700 ft northeast at WS-29. In addition, in both of these samples there is evidence of

Koppers fingerprint in the form of pentachlorophenol (no longer measured), *benzene*, *naphthalene* and *2,4-dimethyphenol*. Similar contamination exists at WS-30 and the possibility arises that the Koppers fingerprint in any of these surficial aquifer samples may be due to the former disposal pond at ITW-13/14.

To the south of the former Cabot ponds, WS-31 – near the Former Processing and Storage Area – is contaminated with both Cabot and Koppers wastes. Nearer the RR tracks, WS-32 clearly reflects contamination from Koppers.

#### **UHG Plume**

Generally speaking the UHG remains contaminated with Cabot wastes beneath the former Cabot ponds. This is confirmed the UHG samples HG-29S and HG-30S as well as HG-28S, which is 400 ft to the northeast of the ponds. The presence of high concentrations of *2,4-DMP* and *benzene* in all three of these UHG monitoring wells raises the possibility that Koppers wastes have also migrated through the UHG.

### **LHG Plume**

Cabot asserts that the UHG and the LHG have been cross-connected by a faulty well installation at HG-29D and that elevated COC concentrations reported at HG-29D the result. GRU is evaluating that assertion.

### **MNA**

The ROD (section 11.2.1.12) says that Monitored Natural Attenuation (MNA) is being used "to demonstrate plume stability and decreasing constituent concentrations in groundwater". EPA should direct Cabot and Koppers to demonstrate that this is occurring with separate reports to stakeholders by the end of the year. This will likely demonstrate that the present sampling frequency is insufficient for Cabot and Koppers to demonstrate "decreasing constituent concentrations in groundwater".

Analyte		SA-29	SA-29	ITW-7	HG-29S	M-25B	HG-15S	HG-4I	HG-4D	HG-6S	HG-6D
Sample date	Log K <sub>ow</sub>	Nov-2011	Mar-2012	Nov-2011	Jun-2014	Aug-2011	Jul-2004	Dec-2007	Dec-2007	Dec-2007	Dec-2007
Screened Interval (ft bgs)		26-31	26-31	7-17	46-56	25TD <sup>†</sup>	64-74	75-85	95-105	40-50	95-105
Acetone (in µg/L)	-0.24	50U	78	50U	16,000	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported
Benzene	2.13	6	8.2	42	400	320	839	15	0.8J	14	37
Toluene	2.73	200	350	260	1,900	610	766	1.7	ND	3.4	18
24-DMP	2.35	56	98U	990	11,000	510	4,340	270	430	8.6	490
3&4-MP	1.98	360	470	380	63,000	310	4,730	ND	ND	ND	ND
Naphthalene	3.35	54U	98U	99U	600U	30,000	8,690	2,600	1,300	450	3,850
Phenol	1.50	54U	98U	99U	71,000	73	368	ND	ND	ND	ND
Benzene/ Toluene		0.03	0.02	0.2	0.2		1.1	8.8		4.1	2.1
24-DMP/ 3&4-MP		0.16	<0.21	2.6	0.2		0.9	>>1	>>1	>>1	>>1
Naphthalene/ 3&4-MP		<0.15	<0.21	<0.26	<0.01		1.8	>>1	>>1	>>1	>>1
PRIMARY SOURCE OF CONTAMINANTS	С	С	С	C/K	С	K	К	K	K	K	К

**Table 1: Reference Data Set: Typical Compositions** 

**Source of Contaminants: K**=Koppers and **C**=Cabot, †: total depth of MW

Table 1.1 Tar Fingerprinting Results 2013 HG Investigation

	2013 HG Hivesugau						
	Location	SB-10A		SB-10B		SB-10B	
5	Sample Depth (feet bgs)	24		3		5	
	Sample Date	4/8/13		4/11/13		4/11/13	
Analyte	Max Detect						
Volatile Organic Compounds (VOCs) (mg/kg)							
1,2,4-Trimethylbenzene	30	16		11		30	
1,3,5-Trimethylbenzene	2.4	1.5		2.1		2.4	
Benzene	12	5.2		5.8		12	
Ethylbenzene	52	22		29		52	
Isopropylbenzene	5.3	5.3		4.0		4.2	
m+p-Xylenes	84	36		48		84	
Naphthalene	40	11		9.7		40	
n-Butylbenzene	0.68	0.52		0.59		0.68	
n-Propylbenzene	4.2	4.2		2.7		3.0	
o-Xylene	17	7.0		9.5		17	
P-isopropyl toluene	590	430		440		590	
sec-Butylbenzene	15	15		0.12	U	0.12	
Toluene	230	130		100		230	
Trichloroethene	1.6	0.96		0.12	U	1.6	
Xylenes (Total)	100	43		57		100	
Semi-Volatile Organic Compounds (SVOCs) (mg	/kg)						
2,4-Dimethylphenol	170	140		170		26	
2-Methylnaphthalene	31	31		28		14	
2-Methylphenol	99	99		98		25	
3+4-Methylphenol	250	190		250		54	
Isophorone	15	15		12	J	25	
Naphthalene	18	18		25	U	25	
Phenanthrene	36	22		36		23	
Phenol	13 J	3.0	U	13	J	25	
Terpenes (mg/kg)							
alpha-Pinene	75	75		5.9	J	8.3	
alpha-Terpineol	810	810		770		26	
Borneol	520	520		310		7.8	
Camphene	220	220		21		20	
Camphor	170	160		100		170	
Cineole	82	82		12	U	8.8	
Dipentene	63	63		8.3	J	8.8	
Isoborneol	61	61		12	U	8.8	
Limonene	1,000	1,000		190		75	
trans-Anethol	25	25		12	U	8.8	
Total Petroluem Hydrocarbons (TPH) (mg/kg)							
TPH - C10 - C11	1,600	1,600		1,200		390	
TPH - C12 - C14	2,400	2,400		1,400		330	
TPH - C15 - C16	2,000	2,000		660		300	
TPH - C17 - C18	1,000	1,000		340		180	
TPH - C19 - C20	2,600	2,600		1,300		730	
TPH - C21 - C22	3,600	3,600		1,500		940	
TPH - C23 - C28	8,000	8,000		4,800		1,200	
TPH - C29 - C32	1,500	1,500		370		180	
TPH	22,000	22,000		12,000		4,200	
General Chemistry (percent)	,						
Percent Moisture	14.4	NT		9.42		14.4	
Percent Solid	90.6	NT		90.6		85.6	

From Gradient's key findings of 2013 HG Investigation August 2013

Note the general nature of the ratios

#### Tar Fingerprinting (Table 1.1)

- During the source area investigation, samples of tar-affected were collected from the vadose zone (<5 feet bgs) and saturated zone (~24 feet bgs) at borings SB-10A and SB-10B advanced in the eastern lagoon. These samples were submitted for laboratory analysis of a comprehensive suite of analytes (volatile organic compounds, semi-volatile organic compounds, terpenes, and total petroleum hydrocarbons) in order to better understand the composition of pine tar observed in the surficial aquifer.
- Analytical results showed that the composition of the vadose zone and saturated zone samples were generally comparable to each other, with few exceptions (Table 1.1). Additionally, contaminant concentrations in the vadose zone sample (i.e., SB-10B-3' bgs) were on the same order of magnitude as concentrations in the saturated zone sample (SB-10B-24' bgs). Lower concentrations in the vadose zone sample collected from 5 feet bgs at SB-10B may be attributed to the compositing of tar-impacted soils with cleaner soils in the soil core.

U = Analyte not detected, detection limit shown.

J = Value estimated.

NT = Analyte not tested.

Well	HG-28S	HG-28S	HG-28S	HG-28D	HG-28D	HG-29S	HG-29S	HG-29D	HG-29D	HG-30S	HG-30S	HG-30D	HG-30D	HG-31D	HG-31D
Sample Date	April-14	April-14	June-14	April-14	April-14										
Sample depth	45-54	45-54	56-66	82-92	82-92	46-56	46-56	87-97	87-97	56-66	56-66	93-103	93-103	94-104	94-104
	(UHG)	(UHG)	(UHG)	(LHG)	(LHG)	(UHG)	(UHG)	(LHG)	(LHG)	(UHG)	(UHG)	(LHG)	(LHG)	(LHG)	(LHG)
		dup													dup
Acetone	4,300	4,300	17,000	130U	80U	6,900	16,000	6,600	5,400	3,400	7,000	50U	1,400U	76	85
Benzene	25U	20U	330U	86	77	190	400	120	110	56	130	46	140U	130	130
Toluene	77	79	880	5U	8U	920	1,900	440	390	190	570	8	140U	13	13
Naphthalene	1,000U	2,000U	780U	970U	140	4,100U	600U	4300U	380U	3900U	290U	NT	2,700	32	30
2,4-DMP	14,000	20,000U	11,000	9,700U	1,100	41,000U	11,000	43,000U	3,800U	39,000U	5,300	10,000U	780	1,900	1,800
3 & 4 MP	64,000	20,000U	55,000	9,700U	78U	41,000U	63,000	43,000U	41,000	39,000U	37,000	10,000U	97U	200U	640
Phenol	96,000	12,000	87,000	4,900U	43	20,000U	71,000	22,000U	19,000	20,000U	42,000	5,000U	49U	260	210
Benz/Tol	<0.32	<0.25	<0.38	17	>9.6	0.2	0.2	0.27	0.28	0.29	0.23	5.8		10	10
Napth/Benz				<11	1.8	10	>1.5	<36	3.4	<70	<2.2		>19	0.25	0.23
24DMP/3&4MP	0.22		0.20		>14		0.17		0.09		0.14		8.0	>9.5	2.8
Napth/3&4MP	<0.20				>1.8		<0.01		0.01		0.01		>27	>0.16	0.05
SOURCE OF CONTAMINANTS	С	С	С	К	К	С	С	С	С	С	С	К	К	K&C	K&C

# Table 2A: Hawthorn Group monitoring wells, 2014 data

Notes: Identification of source based on (1) Benzene:Toluene ratio; (2) 24-DMP:3&4 MP ratio and (3) Napthalene:3&4Methyl Phenol ratio as indicators. Acetone and Phenol are tracers that identify a Cabot source.

## **K**=Koppers and **C**=Cabot

Soil Sample	HG-31D	HG-31D	WS-25	WS-25	WS-25	WS-26	WS-26	WS-26	WS-26	WS-27	WS-27	WS-27	WS-27
Sample Date	June-14	June-14	April-14										

Sampled by	94-104	94-104	13-15	40-42	50-52	18-20	38-40	48-50	58-60	18-20	41-43	50-52	58-60
	(LHG)	(LHG) dup	(SA)	(UHG)	(UHG)	(SA)	(UHG)	(UHG)	(UHG)	(SA)	(UHG)	(UHG)	(UHG)
Acetone	290	270	2,500U	130U	130U	25U	56	2,300	3,300	170	130	160	87
Benzene	120	130	340	350	260	20	8.2	280	190	100	19	200	12
Toluene	30	32	6,700	63	68	100	42	1,400	740	890	110	28	44
Naphthalene	69	72	320	570	480	180	20U	200U	200U	97U	9.9U	77U	3.9U
2,4-DMP	2,200	2,500	5,000	480	520	730	200U	2,000U	2,100	2,300	250	4,400	120
3 & 4 MP	3,000	3,700	4,700	97U	96U	220	450	11,000	10,000	6,100	700	770U	240
Phenol	1,000	1,200	480U	48U	48U	50U	110	5,100	6,200	2,900	600	390U	160
Benz/Tol	4.0	4.1	0.05	5.6	3.8	0.20	0.20	0.20	0.26	0.26	0.17	7.1	0.27
Napth/Benz	0.58	0.55	0.94	1.6	1.8	9.0	<2.4	<0.7	<1.0	<1.0	<0.5	<0.4	<0.3
24DMP/3&4MP	0.7	0.68	1.1	>5	>5	3.3	<0.5	<0.2	0.21	0.38	0.36	>5.7	0.5
Napth/3&4MP	0.02	0.02	0.07	>5.9	>5.0	0.8	<0.04	<0.02	<0.02	<0.02	<0.01	<0.1	<0.02
SOURCE OF CONTAMINANTS	K&C	K&C	K&C	К	К	K&C	С	С	С	С	С	K&C	С

# Table 2B: Hawthorn Group monitoring wells, 2014 data

Notes: Identification of source based on (1) Benzene:Toluene ratio; (2) 24-DMP:3&4 MP ratio and (3) Napthalene:3&4Methyl Phenol ratio as indicators. Acetone and Phenol are tracers that identify a Cabot source.

## **K**=Koppers and **C**=Cabot

Soil Sample	WS-28	WS-28	WS-28	WS-28	WS-28	WS-29	WS-29	WS-29	WS-29	WS-29
Sample Date	April-14									
	18-20	42-44	52-54	52-54	62-64	18-20	18-20	42-44	51-53	58-60

Sampled by	(SA)	(UHG)	(UHG)	(UHG) dup	(UHG)	(SA)	(SA) dup	(UHG)	(UHG)	(UHG)
Acetone	500U	25U	25U	25U	25U	130U	130U	50U	25U	25U
Benzene	20U	1U	1U	1U	1U	12	11	50	30	5.5
Toluene	20U	1.2	1U	1U	1	670	590	320	100	32
Naphthalene	99U	1.9U	1.9U	1.9U	0.27	24	23	2U	2U	1.9U
2,4-DMP	2,000	19U	19U	19U	8.5	210	200	38	150	19U
3 & 4 MP	9,700	19U	19U	19U	2U	1,300	1,100	130	97	65
Phenol	6,800	9.7U	9.6U	9.6U	1U	99U	100U	86	76	45
Benz/Tol		<1			<1	0.02	0.02	0.16	0.30	0.17
Napth/Benz						2.0	2.1	<0.04	<0.07	0.35
24DMP/3&4MP	0.21				>4	0.16	0.18	0.29	1.6	<0.3
Napth/3&4MP	<0.01					0.02	0.02	<0.02	<0.02	<0.03
SOURCE OF CONTAMINANTS	С	?	?	?	K?	С	С	С	C, K?	С

Table 2C: Hawthorn Group monitoring wells, 2014 data

Notes: Identification of source based on (1) Benzene:Toluene ratio; (2) 24-DMP:3&4 MP ratio and (3) Napthalene:3&4Methyl Phenol ratio as indicators. Acetone and Phenol are tracers that identify a Cabot source.

## **K**=Koppers and **C**=Cabot

SOURCE OF	0.13 <b>C</b>		С	<0.06	0.46 C & K	0.2 C & K	0.14 C & K	0.03	>3 <i>K</i>	>1 <b>K</b>	>5 <i>K</i>	>4 <b>K</b>
24DMP/3&4MP  Napth/3&4MP	<0.5			<0.6	0.62	0.26	1.1 0.14	0.28	>4	>1	 >5	>1
Napth/Benz	5.9				1.5	3.1	1.2	1.2	14	>1	>380	>50
Benz/Tol	1.1			<1	0.11	0.30	0.77	0.4	~1		<1	>1.5
Phenol	53	9.7U	9.9U	62	160	500U	64U	1,300	9.2U	9.9U	190U	190U
3 & 4 MP	200	19U	20U	160	390	3,900	280	4,300	18U	20U	390U	380U
2,4-DMP	96U	19U	20U	98U	240	1,000	300	1,200U	73	20U	390U	390
Naphthalene	26	1.9U	2.2	9.8U	180	920	40	120U	58	24	2,300	1,700
Toluene	4	1U	5U	6	1,100	1,000	43	240	3.5	1.4	10	20U
Benzene	4.4	1U	5U	5U	120	300	33	96	4	1U	6	30
Acetone	25U	25U	470	320	250U	890	170	6,200	25U	25U	25U	500U
	(SA)	(UHG)	(UHG)	(UHG)	(SA)	(UHG)	(UHG)	(UHG)	(SA)	(UHG)	(UHG)	(UHG)
Sampled by	18-20	43-45	55-57	66-68	23-25	38-40	50-52	58-60	15-17	32-34	45-47	58-60
Soil Sample Sample Date	WS-30 April-14	WS-30 April-14	WS-30 April-14	WS-30 April-14	WS-31 April-14	WS-31 April-14	WS-31 April-14	WS-31 April-14	WS-32 April-14	WS-32 April-14	WS-32 April-14	WS-32 April-14

# Table 2D: Hawthorn Group monitoring wells, 2014 data

Notes: Identification of source based on (1) Benzene:Toluene ratio; (2) 24-DMP:3&4 MP ratio and (3) Napthalene:3&4Methyl Phenol ratio as indicators. Acetone and Phenol are tracers that identify a Cabot source.

## **K**=Koppers and **C**=Cabot