

Ground Water Quality Technical Report No. 13

An Evaluation of Methyl Tert-Butyl Ether (MTBE) in Groundwater at Leaking Underground Storage Tank Sites in Idaho



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TABLE OF CONTENTS

INTRODUCTION	1
METHODS	1
RESULTS	4
<i>Detections</i>	4
<i>Concentrations</i>	5
<i>Comparison with RBCA Groundwater Ingestion Criteria</i>	8
SUMMARY AND CONCLUSIONS	9
REFERENCES	9

FIGURES

Figure 1. Percentage of Sample Sites and Groundwater Impacted LUST Sites by IDEQ Regions.	2
Figure 2. Idaho Division of Environmental Quality Regional Offices	3
Figure 3. Percentage of Sample Sites with Detections for RBCA VOC Chemicals.	4
Figure 4. Actual vs. Predicted MTBE Concentrations ($\mu\text{g/l}$) at Group One Sites Where Both MTBE and Benzene Were Detected.	7

TABLES

Table 1. Sample Site Distribution for Petroleum Product Release Groupings Among IDEQ Regional Offices.	4
Table 2. Mean Chemical Concentrations ($\mu\text{g/l}$) of RBCA Chemicals at LUST Sites with Detections Compared to Tier 1 Groundwater Ingestion RBSL.	6
Table 3. Mean Concentrations ($\mu\text{g/l}$) of RBCA PAH Chemicals at LUST Sites with Detections Compared to Tier 1 Groundwater Ingestion RBSL.	6
Table 4. Mean Benzene and MTBE Concentrations ($\mu\text{g/l}$) Statewide at Sites with Detections in the Six IDEQ Regions.	7
Table 5. Number of Sites (Percent of Totals) with Detectable Benzene Concentrations Which Meet or Exceed Selected RBCA Groundwater Cleanup Criteria.	8
Table 6. Number of Sites with Detectable MTBE Concentrations Which Meet or Exceed Selected RBCA Groundwater Cleanup Criteria.	9

APPENDIX A	Table A-1 Chemical Concentrations ($\mu\text{g/l}$) Idaho MTBE Ground Water Evaluation
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INTRODUCTION

The implementation of the Idaho Risk Based Corrective Action (RBCA) Guidance document for Petroleum Releases in January 1997 resulted in the requirement for sampling for twenty chemicals of concern (COC). These chemicals include naphthalene, MTBE, ethylene dibromide, 1,2 dichloroethane, and twelve polycyclic aromatic hydrocarbons as well as the traditional chemicals benzene, toluene, ethylbenzene, and xylene.

The primary objective of the Groundwater Evaluation for Methyl Tert-Butyl Ether (MTBE) study was to evaluate the current magnitude of the MTBE threat to groundwater resources and risk to potential receptors from releases at leaking underground storage tank (LUST) sites in Idaho. It is intended to represent a snapshot in time and is not indicative of long-term trends. While the primary focus of the study was the chemical MTBE, other Idaho RBCA COC that historically have not been analyzed were also evaluated.

METHODS

From October through December 1997 the Idaho Division of Environmental Quality (IDEQ) collected groundwater samples from LUST sites across the state where petroleum contamination of groundwater had been detected. Samples collected by IDEQ staff were analyzed at the Idaho State Laboratory. In addition to the samples collected by IDEQ staff, ground water monitoring data received from sampling of additional LUST sites by responsible parties were added to the data set.

The sample collection was distributed among three types or groups: Group 1 samples represent sites with gasoline releases of "recent" origin (within the last 5 years), Group 2 samples are from diesel release sites, and Group 3 samples are from gasoline releases of historical origin (> 5 years old). Samples from all groups were analyzed for the following Idaho RBCA constituents: benzene, toluene, ethylbenzene, xylene, MTBE, and naphthalene. In addition Group 2 samples were analyzed for polycyclic aromatic hydrocarbons (PAH) and Group 3 samples were analyzed for the lead scavenger additives ethylene dibromide (EDB) and 1,2 dichloroethane (EDC).

EPA analytical methods used for IDEQ samples were 8021 for volatile organic compounds (VOC), including EDB and EDC, and 8270 for PAH. Other methods used for VOC by other laboratories included 8020 and 8260.

A total of 100 groundwater samples were obtained from 100 sites with known groundwater contamination. Where sample results were available for several wells at a given site the well with the highest concentrations was generally selected.

This sample population represents approximately one third of all the Idaho LUST sites with known groundwater impacts. The distribution of sites across the state in each IDEQ regional office is presented in Figure 1. A map showing the area represented by each IDEQ regional office is presented in Figure 2.

Figure 1. Percentage of Sample Sites and Groundwater Impacted LUST Sites by IDEQ Regions.

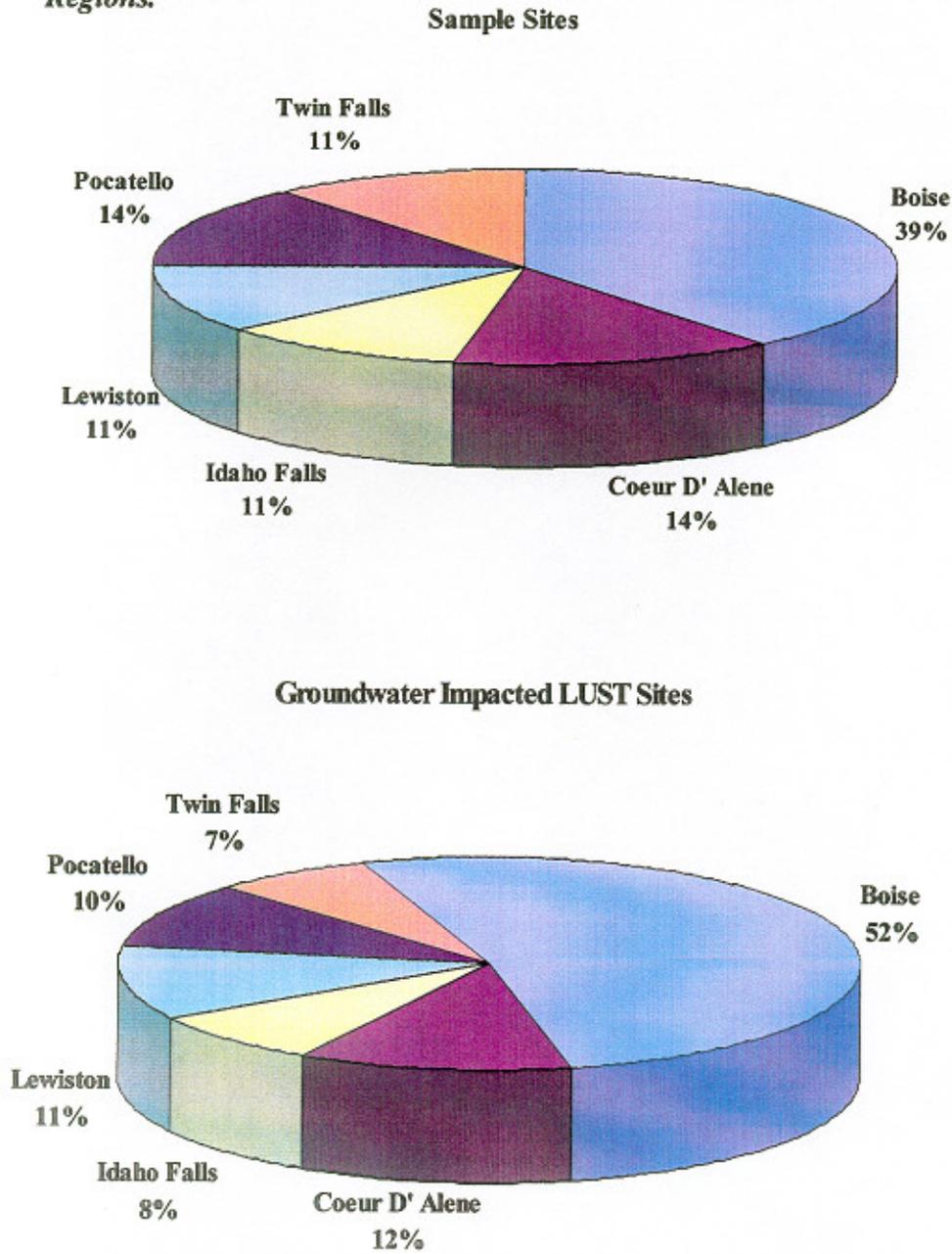
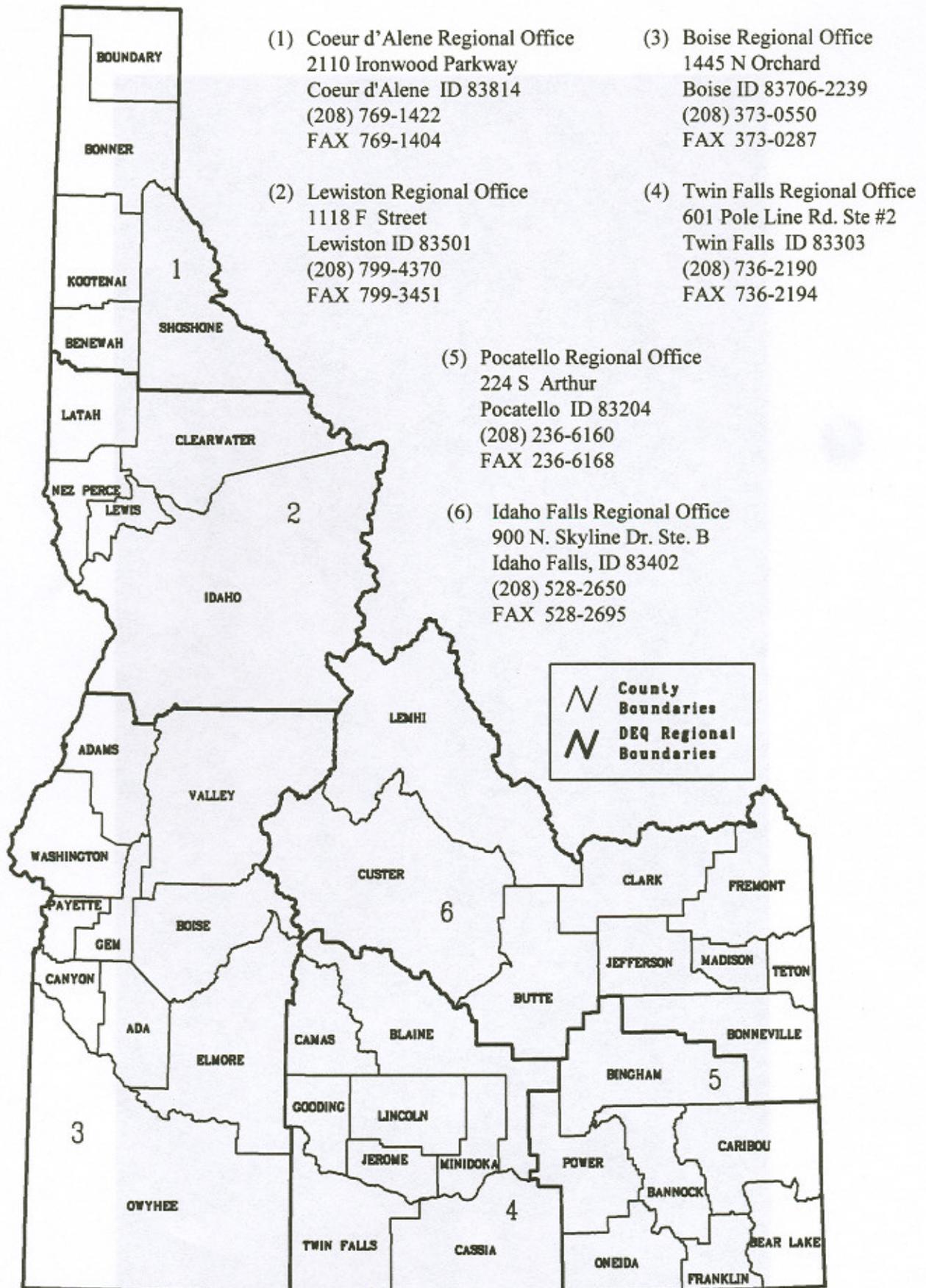


Figure 2. Idaho Division of Environmental Quality Regional Offices



When compared to the percentage of all LUST sites with groundwater contamination found in each region the sampling distribution appears representative. The distribution of samples among the product release groups and within IDEQ regions is shown in Table 1.

Table 1. Sample Site Distribution for Petroleum Product Release Groupings Among IDEQ Regional Offices.

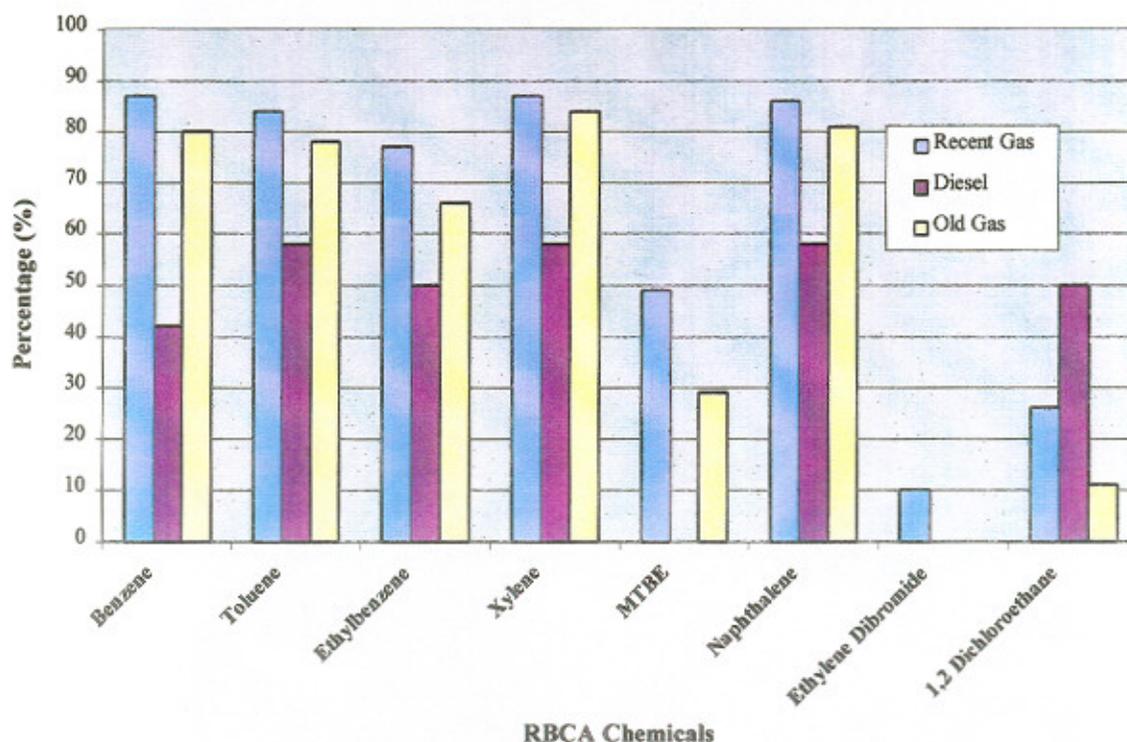
Group Type	All Sites	Boise	Coeur d' Alene	Idaho Falls	Lewiston	Pocatello	Twin Falls
1- Recent Gasoline	56	31	8	7	3	3	4
2- Diesel	12	5	2	1	0	4	0
3- Old Gasoline	32	3	4	3	8	7	7

RESULTS

Detections

Although hydrocarbon chemicals were detected in the past at all sites sampled, during this sampling event some sites had no detections for all constituents analyzed. The percentages of sites with detections for various chemicals for the three groups of sites is presented in Figure 3.

Figure 3. Percentage of Sample Sites with Detections for RBCA VOC Chemicals.



Detections varied by chemical. Benzene, toluene, ethylbenzene, xylene, and naphthalene (BTEX+N), as expected, were detected with much greater frequency at Groups 1 and 3 (gasoline) sites than at diesel release sites. MTBE was detected at about fifty percent of recent gas release sites and thirty percent of older sites. This finding supports a conclusion that in recent years MTBE use in Idaho has increased and is widespread, even though Idaho is not required to use reformulated gasoline to address air quality concerns.

Compared to other states surveyed by EPA, the overall percentage of MTBE detections (forty percent) places Idaho in the lower third to lower half nationwide (USEPA, 1998). MTBE was detected at group 1 sites in all IDEQ regions and all regions except Boise and Lewiston at Group 3 sites. The lack of detections at Group 3 sites in the Boise region is probably the result of the low sample size (3 sites).

The lead scavenger additives EDB and EDC were commonly added to regular, leaded gasoline. The use of these petroleum products have declined since the early 1980s with the phaseout of leaded gasoline. The additives showed anomalous patterns of detections in this evaluation with EDB only being found at recent gasoline sites and EDC being found at all types of sites. EDC was found least frequently at older gasoline release sites, contrary to expectations.

At twenty-two sites samples were analyzed for PAH. Eight sites, nine sites, and five sites were sampled in Groups 1, 2, and 3, respectively. Across all sites detections of at least one of the twelve RBCA PAH chemicals occurred at 7 sites (32%). The percentage of sites with detections in individual Groups was 13%, 55%, and 20% in Groups 1, 2, and 3. For the diesel release sites, Group 2, the PAH chemicals which were detected most frequently were fluorene (44%), fluoranthene (44%), pyrene (44%), and phenanthrene (33%).

Concentrations

The chemical concentration data for all sites is presented in Appendix Table A-1. The mean groundwater concentrations of the RBCA COC found in each group of sites is presented in Tables 2 and 3. These mean concentrations were calculated using only those sites which had detections for that chemical. Mean concentrations for most chemicals were lower for Group 3 sites compared to Group 1 sites. This very likely reflects the effect of remediation and/or natural attenuation.

Table 2. Mean Chemical Concentrations ($\mu\text{g/l}$) of RBCA Chemicals at LUST Sites with Detections Compared to Tier 1 Groundwater Ingestion RBSL.

Chemical	Group1 Recent Gasoline	Group 2 Diesel	Group 3 Old Gasoline	Tier 1 RBSL
Benzene	2835	150	599	5
Toluene	5500	289	1234	1000
Ethylbenzene	851	188	357	700
Xylene	4169	1434	3213	10,000
MTBE	2271	---	312	52
Naphthalene	258	101	249	417
Ethylene Dibromide	2.5	---	---	0.05
1,2 Dichloroethane	17	1.3	21	5

Table 3. Mean Concentrations ($\mu\text{g/l}$) of RBCA PAH Chemicals at LUST Sites with Detections Compared to Tier 1 Groundwater Ingestion RBSL.

Chemical	Group 1 Recent Gasoline	Group 2 Diesel	Group 3 Old Gasoline	Tier 1 RBSL
Benzo (a) Anthracene	0.002	0.36	---	0.6
Fluorene	0.005	9.6	2.0	417
Phenanthrene	---	2.3	27.0	417
Fluoranthene	---	13.0	---	237
Acenaphthene	---	7.2	1.0	626
Anthracene	---	5.7	---	45
Pyrene	---	9.8	---	148
Benzo (b) Fluoranthene	---	0.44	---	0.6
Benzo (k) Fluoranthene	---	0.16	---	4.3
Benzo (a) Pyrene	---	0.46	---	0.2
Chrysene	---	0.73	---	2
Benzo (ghi) Perylene	---	0.29	---	0.3

The mean concentrations of benzene and MTBE are similar for the group 1 sites. A site by site comparison of concentrations showed little statistical correlation however. At twenty-seven group 1 sites both MTBE and benzene were detected.

Figure 4 presents the results of a linear regression of benzene vs. MTBE concentrations at these sites. The linear regression of this data yielded an r-squared of 0.48. Benzene concentrations exceeded mtbe concentrations at nineteen of the sites (76%).

Figure 4. Actual vs. Predicted MTBE Concentrations (µg/l) at Group One Sites Where Both MTBE and Benzene Were Detected.

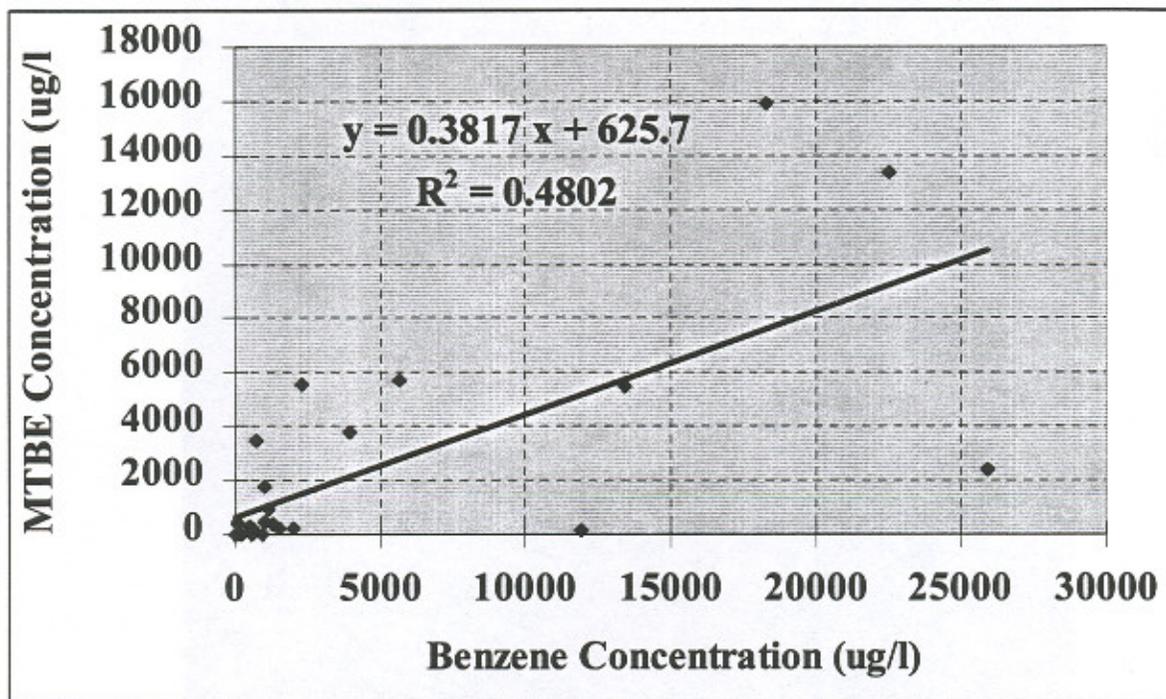


Table 4. Mean Benzene and MTBE Concentrations (µg/l) Statewide at Sites with Detections in the Six IDEQ Regions.

IDEQ Regional Office	Benzene (µg/l)	MTBE (µg/l)
Boise	2545	2839
Coeur D' Alene	710	588
Idaho Falls	4288	2240
Lewiston	1902	2141
Pocatello	1157	1673
Twin Falls	327	81

Comparison with RBCA Groundwater Ingestion Criteria

Tables 5 and 6 present a comparison of detected concentrations of benzene and MTBE with relevant groundwater cleanup criteria for the groundwater ingestion pathway from the Idaho RBCA Guidance Document.

For sites where benzene was detected ninety-three percent of these sites had concentrations which exceeded one or all of the relevant RBCA groundwater ingestion criteria. For MTBE the same value is sixty-two percent. A significantly greater percentage of sites with MTBE detections fell below the most stringent criteria than sites with benzene detections (thirty-eight vs. eight percent).

These data would suggest that, at the present time, when impacts occur at petroleum release sites with benzene and/or MTBE it is more likely that the benzene concentrations will dictate the need for corrective action than mtbe concentrations. If the use or percentage of MTBE in unleaded gasoline increases in Idaho in the future the potential for increasing numbers of MTBE-driven remedial actions is likely.

Table 5. Number of Sites (Percent of Totals) with Detectable Benzene Concentrations Which Meet or Exceed Selected RBCA Groundwater Cleanup Criteria.

	RBSL/SSTL Concentration Criteria (µg/l)	Group 1 Recent Gasoline	Group 2 Diesel	Group 3 Old Gasoline	All Sites
< Tier 1 RBSL	< 5	3 (6)	0 (0)	3 (12)	6 (8)
Tier 1 RBSL	>5 < 140	14 (29)	3 (60)	8 (31)	25 (31)
Tier 2 Class 2 Residential	> 140 < 617	10 (20)	2 (40)	10 (38)	22 (28)
Tier 2 Class 2 Commercial	> 617	22 (45)	0 (0)	5 (19)	27 (34)
Totals		49	5	26	80

Data gathered for PAH constituents showed very few instances where concentrations exceeded the RBCA groundwater ingestion criteria. For sites with detections only benzo(a)pyrene and benzo(ghi)perylene concentrations met or exceeded the most stringent RBCA criteria. In the case of benzo(a)pyrene two sites had detections and concentrations at both of these sites exceeded the drinking water maximum contaminant level of 0.2 µg/l.

Table 6. Number of Sites with Detectable MTBE Concentrations Which Meet or Exceed Selected RBCA Groundwater Cleanup Criteria.

	RBSL/SSTL Concentration Criteria (µg/l)	Group 1	Group 2	Group 3	All Sites
< Tier 1 RBSL	<52	8 (30)	NA	6 (60)	14 (38)
Tier 1 RBSL	>52 < 261	4 (14)	NA	2 (20)	6 (16)
Tier 2 Class 2 Residential	> 261 < 511	5 (19)	NA	1 (10)	6 (16)
Tier 2 Class 2 Commercial	> 511	10 (37)	NA	1 (10)	11 (30)
Totals		27	NA	10	37

SUMMARY AND CONCLUSIONS

- ◆ MTBE was detected in approximately forty percent of all sites sampled and at fifty percent of sites believed to be unleaded gasoline releases of recent origin. These percentages place Idaho in the lower third to lower half of states reporting these figures in a recent EPA nationwide survey of MTBE impacts (USEPA, 1998).
- ◆ Both MTBE and benzene were detected at 36 sites or forty-one percent of all gasoline sites. Benzene concentrations were typically higher than MTBE concentrations where both chemicals were present. Only weak correlations ($r^2 = 0.48$) were found between benzene and MTBE concentrations at those sites where both chemicals were detected.
- ◆ While all twelve PAH chemicals were detected, benzo(a)pyrene and benzo(ghi)perylene were the only PAH RBCA chemicals that were detected with concentrations at or exceeding the most stringent RBCA groundwater ingestion cleanup criteria.
- ◆ Based on comparison to RBCA groundwater ingestion cleanup criteria benzene is more likely to drive corrective action than MTBE. This conclusion is borne out by a review of RBCA evaluations and corrective action plans being implemented at Idaho LUST sites with ground water impacts. At these sites, which number over one hundred, less than ten percent of corrective actions are driven by MTBE detections and concentrations.

REFERENCES

USEPA, 1998. Memorandum from Anna Hopkins Virbick to State LUST Program Managers. Impacts of MTBE Releases on LUST Programs. Office of Underground Storage Tanks. August 5, 1998.

Appendix A. Table A-1 Chemical Concentrations (ug/l) Idaho MTBE Ground Water Evaluation

Region	Group	Benzene	Toluene	Ethyl Benzene	Xylene	MTBE	Naphthalene	EDB	EDC	PAH	BAA	FL	PH	FLA	AC	AN	PY	BBF	BKF	BAP	C	BGHP	
Boise	1	8.1	95.2	292	1350	0.5	171																
Boise	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5														
Boise	1	257	114	7	309	0.5	8.5																
Boise	1	99.1	513	162	749	0.5	52.2	0.5	0.5														
Boise	1	143	11.9	273	23.5	0.5	552																
Boise	1	514	2360	2811	19320	0.5	567	0.5	0.5														
Boise	1	1040	2150	840	4660	1790	351																
Boise	1	404	518	0.5	896	0.5	62.5	0.5	0.5	0.5													
Boise	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Boise	1	64	19	7	76	0.5	13																
Boise	1	2980	1510	985	4640	0.5	145																
Boise	1	1520	6910	925	5130	0.5	79.4																
Boise	1	78.3	1.2	540	14.8	9.3	24.4	0.5	1														
Boise	1	0.5	0.5	0.5	0.5	0.5	16	0.5	0.5	0.5													
Boise	1	52	22.3	131	92.5	0.5	55.7																
Boise	1	18300	47900	2660	17600	15900	369																
Boise	1	1290	1260	494	729	376	58.2	0.5	0.5	0.5													
Boise	1	4280	3090	395	2160		195	0.21	99.3	0.5													
Boise	1	8320	53500	3850	32700	0.5	73																
Boise	1	25900	33600	6000	9400	2410	1070																
Boise	1	1540	1190	440	2880	215	115																
Boise	1	2000	1240	450	2040	240	435																
Boise	1	103	19.3	331	79.2	403	333																
Boise	1	11900	40200	2880	18700	162	775	1.63	4.1														
Boise	1	200	730	780	3200	0.5	1510	0.5	0.5														
Boise	1	15.9	8.35	28.6	110.7	0.5	9.27	0.5	0.5														
Boise	1	3.7	1	7.5	7.5	0.5	22.1																
Boise	1	2270	3910	137	6680	5530	164																
Boise	1	1150	2360	124	705	910	235																
Boise	1	725	665	695	2560	3500	230																
Boise	1	42	170	45	250	0.5	0.5																
Boise	2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Boise	2	0.5	1.1	0.5	0.5		0.5				0.5	0.064	0.2	0.11	0.5	0.061	0.5	0.5	0.5	0.5	0.5	0.5	
Boise	2	8.7	0.6	7.7	7.9		45.6				0.5	0.5	0.5	6.44	0.5	0.5	29.8	0.5	0.5	0.5	0.5	0.5	
Boise	2	200	1700	770	9100	0.5	214					1.4	2.6		0.6		0.3						
Boise	2	489	310	339	824	0.5	172	0.5	1.3	0.5													
Boise	3	592	513	1.78	751	0.5	52.8	0.5	0.5	0.5													
Boise	3	0.53	0.1	0.33	16.3	0.5	24.1	0.5	0.5	0.5													
Boise	3	35.1	24.7	9.5	1874	0.5	183	0.5	0.5	0.5													
CDA	1	601	22.5	89.4	277	14.5	43.7																
CDA	1	58	68	11	27	0.5	2	0.5		0.5													
CDA	1	29.6	4.3	9.3	188.2	33.3	35.8	0.5	0.5														
CDA	1	0.21	0.5	0.5	0.57	0.45	1	0.5	0.5														
CDA	1	925	0.5	0.5	1.6	5.27	0.5																
CDA	1	313	1120	252	1570	0.5	111																
CDA	1	3930	95	2000	3210	3800	263																
CDA	1	676	1770	172	1650	126	0.5																
CDA	2	0.5	0.5	3.39	22.91	0.5	264	0.5	0.5	0.5													
CDA	2	0.5	9	4	45	0.5	3.5				0.36	10	4.2	43	0.5	0.5	1.9	0.44	0.22	0.71	0.66	0.29	
CDA	3	270	1080	0.5	3740	0.5	250																

Values of 0.5 indicate results below detection limits.

Appendix A. Table A-1 Chemical Concentrations (ug/l) Idaho MTBE Ground Water Evaluation

Region	Group	Benzene	Toluene	Edhyl Benzene	Xylene	MTBE	Naphthalene	EDB	EDC	PAH	BAA	FL	PH	FLA	AC	AN	PY	BBF	BKF	BAP	C	BGHIP
CDA	3	513	1000	1680	15390	0.5	1380	0.5	0.5													
CDA	3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5												
CDA	3	492	1920	498	1890	137	79					2	27		1							
Idaho Falls	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5														
Idaho Falls	1	0.5	0.5	0.5	0.5	0.5	14.3	0.5			0.002	0.005										
Idaho Falls	1	27	66.5	40.5	766	3.51	144	0.5	0.5													
Idaho Falls	1	185	0.7	1.31	12.9	11.8	18	0.5	0.99	0.5												
Idaho Falls	1	559	527	1.95	806	1.6	1.3	0.5	0.5													
Idaho Falls	1	3190	8860	727	6280	0.5	152	5.7	6.5													
Idaho Falls	1	22500	24200	2850	14300	13400	1890	0.5	0.5													
Idaho Falls	2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5												
Idaho Falls	3	1.52	4.08	0.5	61.08	0.5	12.3	0.5	0.5													
Idaho Falls	3	0.5	1.2	38.8	110.8	0.35	15	0.5	0.5													
Idaho Falls	3	3550	9960	1740	9680	25	595	0.5	0.5													
Lewiston	1	1000	10	440	1500	480	85	0.5	0.5													
Lewiston	1	13400	9580	0.5	20140	5490	812	0.5	8.6													
Lewiston	1	65	4519	1270	7416	454	314	0.5	0.5													
Lewiston	3	9.7	0.68	5.67	50.4	0.5	56.5	0.5	0.5													
Lewiston	3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Lewiston	3	237	69.3	387	502	0.5	102	0.5	0.5													
Lewiston	3	132	56.1	0.74	1118	0.5	314	0.5	0.5													
Lewiston	3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Lewiston	3	68	120	0.5	10	0.5	650	0.5	0.5													
Lewiston	3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Lewiston	3	307	321	288	610	0.5	81.2	0.5	43.9													
Pocatello	1	0.5	0.5	0.5	0.81	0.5	1.14	0.5	0.5													
Pocatello	1	8.3	0.5	0.5	0.5	0.5	0.5															
Pocatello	2	0.5	0.5	0.5	0.5	0.5	0.5															
Pocatello	2	7	2.7	0.5	21.5	0.5	4.3															
Pocatello	2	0.5	0.5	0.5	0.5		1.23				NA	26.9	0.5	2.5	13.8	11.4	7.1	0.5	0.1	0.2	0.8	
Pocatello	2	51	1.6	5.1	15.2	0.5	0.5															
Pocatello	3	2370	2100	0.5	3900	491	308	0.5	0.5													
Pocatello	3	3.1	0.5	29.2	79.9	6.7	16.1	0.5	0.5													
Pocatello	3	114	1730	256	28380	0.5	1500	0.5	0.5													
Pocatello	3	281	3	120	120	175																
Pocatello	3	1110	7800	1210	11000	0.5	245	0.5	0.5													
Pocatello	3	3060	2580	4.94	3370	1940	42.9	0.5	15.3													
Pocatello	3	24	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Pocatello	1	5700	3010	1740	4660	5750	567															
Twin Falls	1	468	537	1.11	983	292	13.5	0.5	0.5													
Twin Falls	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Twin Falls	1	2.63	2.99	0.5	38.54	0.5	8.56	0.5	0.5													
Twin Falls	1	58.2	58.1	702	3372	0.5	235	0.5	1.26													
Twin Falls	3	86	13.3	205	227.5	0.5	90.2	0.5	0.5	0.5												
Twin Falls	3	1300	670	870	1120	0.5	55	0.5	0.5	0.5												
Twin Falls	3	616	295	146	668	11.9	64.8															
Twin Falls	3	222	23.4	1.26	679	17	15	0.5	3.65													
Twin Falls	3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5													
Twin Falls	3	177	564	0.5	1254	0.5	90.7	0.5	0.5													
Twin Falls	3	11.7	6.6	1.3	157.1	2.99	12.3	0.5	0.5													

Values of 0.5 indicate results below detection limits.