NATURALLY OCCURRING CONCENTRATIONS OF INORGANIC CHEMICALS IN GROUND WATER AND SOIL AT CALIFORNIA AIR FORCE INSTALLATIONS

Philip M. Hunter, P.G., Air Force Center for Environmental Excellence, Brooks AFB, Texas 78235
Brian Davis, Ph.D., Department of Toxic Substances Control, Sacramento, California

ABSTRACT

Risk assessment and risk management must differentiate between naturally occurring and anthropogenic inorganic chemicals. Naturally occurring or background concentrations of inorganic chemicals are important for site characterization, determining chemicals of concern, establishing cleanup levels, and long-term monitoring programs. Analysis of the Air Force's Environmental Resources Program Information Management System (ERPIMS) database identified uncontaminated sample locations for soil and ground water from 12 Air Force installations across 10 California counties. Background data for 25 inorganic constituents were taken from 3000 borehole and 750 monitoring well locations. Maximum sample sizes for individual chemicals range from 1800 and 7400, depending on the sampling medium. The 95th percentile was used as the best statistic to represent background. Medians and 99th percentiles of background levels are also presented. Since statistical analysis of soil data indicated that background levels differed significantly with depth, separate background calculations for soil are presented for three depths (less than 2.5 feet, between 2.5 and 10 feet, and greater than 10 feet). For ground water, background statistics for each constituent are given without regard to sampling depth. Some inorganic constituents were detected frequently and at levels that exceed important environmental thresholds such as Maximum Contaminant Levels (MCLs) or Action Levels for drinking water. Background 95th percentile levels equal or exceed federal and/or California MCLs for aluminum, antimony, arsenic, beryllium, cadmium, chromium, nickel, and thallium. The 95th percentile level for lead exceeds the U.S. EPA Action Level of 0.015 mg/L for drinking water measured at the tap. This analysis provides background levels that are representative of California installations as a group. These data should not replace local background data, but rather provide important benchmarks by which the adequacy of local data can be judged.

INTRODUCTION

Most contamination at Air Force Bases (AFBs) is organic, typically associated with chlorinated solvents and fuels. The presence of key organic chemicals detected in ground water and soil samples is a good indicator of both inorganic and organic contamination. Even when investigations specifically target contamination by drilling wells and borings into areas of hazardous waste sites, the non-detect (ND) rates for organic chemicals are surprisingly high. The ND rates for trichloroethene, which is highly mobile and the most ubiquitous constituent at AFBs, are about 65% in ground water. Other organic constituents have ND rates around 90% for ground water. ND rates for organic chemicals in soil tend to be even higher. As a result and given the Air Force's extensive monitoring network, an abundance of existing sampling locations are known to be uncontaminated and can be used to estimate background concentrations. Computer algorithms were applied to the Air Force's Environmental Resources Program Information Management System (ERPIMS) to identify background locations. Over 10 years of project data are available for background determinations at California AFBs. This poster presents the automated approach to identify background locations, the statistics used to calculate background concentrations, and background concentrations for both ground water and soil.

METHODS

A computer algorithm was constructed to identify background locations across all California AFBs. The algorithm, using Structured Query Language (SQL), searches out all locations that have been sampled for both inorganic and organic chemicals. Sampling locations with organic contamination are eliminated from the search. High-end outliers, which may represent locations contaminated with inorganic chemicals but not organic chemicals, were also eliminated for each constituent based on "box and whisker" plots. Both upgradient, downgradient, and sidegradient locations could potentially be identified as background sampling locations. Substantially more background locations were identified in soil compared to ground water. On average, at least 25 background well locations and 50 background borehole locations per AFB have been identified using these procedures. A large number of distinct sample locations and large sample sizes easily meet the requirements for the statistical calculations used to determine background levels.

This analysis is complicated by multiple detection limits, diverse hydrogeologic terrains, variability over 3-dimensional space, a variety of types of hazardous waste sites, multiple Air Force bases, and different waste handling practices. All of these issues force one ultimately to discriminate background levels across more than one hydrostratigraphic unit or more than one soil horizon. The 95th percentile was used to best represent background for each analyte for ground water and soil. For small data sets, confidence limits are important but for larger data sets as we have here, the simple percentile of the data is sufficient. In addition, the median (50th percentile) and 99th percentile as well as sample size, number of well locations, number of AFBs, and detection frequency are presented for each chemical. The number of wells and sample sizes of individual AFBs are presented. All statistical analysis used SAS® and Systat® software.

BACKGROUND LEVELS FOR GROUND WATER

The analysis for California ground water is based on 2936 monitoring wells, sampled for both inorganic and organic chemicals, and over 34,000 analytical records. The number of background wells analyzed varied from 94 (chromium-6) to 653 (lead); sample sizes varied from 134 (chromium-6) to 1819 (magnesium); number of AFBs varied from 5 (boron) to 12 for many chemicals. Background level calculations are biased, with more than 50% of data from Vandenberg, Travis, and March AFBs. Detection rates in ground water vary, with chloride, magnesium and sodium detected in 99% of samples, compared to 3% for cyanide and silver. Antimony, arsenic, beryllium, cadmium, chromium-6, cobalt, copper, cyanide, lead, mercury, nickel, selenium, silver, and thallium had median (50th percentile) concentrations less than the median method detection limits (MDLs). The 95th percentile for cyanide and mercury were also below MDL, indicating that they are rarely detected in ground water. Conversely, some inorganic constituents were detected frequently and at levels that exceeded important environmental thresholds such as Maximum Contaminant Levels (MCLs) or Action Levels for drinking water. The 95th percentiles for arsenic, antimony, beryllium, chromium, nickel, and thallium exceed MCLs. The 95th percentile for arsenic is 0.05 mg/L, which is the current MCL. The background level for lead exceeds the U.S. EPA Action Level of 0.015 mg/L for drinking water at the tap. Based on limited analysis, it can be said that chromium-6 is infrequently detected in ground water.

Analyte	n	Percentile in mg/L			Detection	Median Method Detection Limit	Number Wells	Number AF Bases
		50th	95th	99th				
Aluminum	1548	0.16	40	122	56%	0.07	508	11
Antimony	1285	*ND*	0.15	0.2	9%	0.026	556	11
Arsenic	1278	*ND*	0.05	0.15	30%	0.005	498	12
Barium	1619	0.1	0.63	2.1	95%	0.006	482	12
Beryllium	1303	*ND*	0.01	0.01	9%	0.002	570	11
Boron	212	0.07	1.5	2.5	86%	0.03	106	5
Cadmium	1359	*ND*	0.01	0.01	12%	0.004	592	12
Chloride	1099	120	747	2370	99%	0.500	471	10
Chromium	1729	0.01	0.62	5	47%	0.005	578	12
Chromium-6	134	*ND*	0.03	0.06	12%	0.010	94	8
Cobalt	1211	*ND*	0.03	0.12	19%	0.011	521	11
Copper	1438	*ND*	0.07	0.24	27%	0.012	558	12
Cyanide	229	*ND*	*ND*	*ND*	3%	0.01	157	7
Fluoride	606	0.34	1.1	1.89	90%	0.10	335	9
Iron	1762	0.45	48.6	252	80%	0.02	559	11
Lead	1737	*ND*	0.1	0.4	24%	0.004	653	12
Magnesium	1819	24	102	197	99%	0.036	557	12
Manganese	1712	0.06	2	7.35	86%	0.003	544	11
Mercury	786	*ND*	*ND*	0.01	9%	0.0002	468	12
Molybdenum	1271	0.01	0.1	0.11	32%	0.006	487	10
Nickel	1564	*ND*	0.43	1.13	44%	0.022	551	12
Selenium	1237	*ND*	0.03	0.1	13%	0.005	506	12
Silver	1328	*ND*	0.02	0.03	3%	0.006	588	12
Sodium	1810	82	406	1080	99%	0.24	562	12
Thallium	1257	*ND*	0.2	0.5	4%	0.10	526	11
Vanadium	1520	0.02	0.12	0.44	77%	0.007	482	11
Zinc	1800	0.02	0.4	1.31	78%	0.01	554	12

GROUND WATER BACKGROUND BASED ON CALIFORNIA AIR FORCE BASES

BACKGROUND LEVELS FOR SOIL

The analysis for California soils is based on approximately 8500 distinct boreholes, sampled for both inorganic and organic chemicals, and over 133,000 analytical records. The number of background boreholes analyzed varied from 105 (boron) to 2777 (lead); sample sizes varied from 271 (fluoride) to 7429 (lead); number of AFBs varied from 2 (chloride) to 11 (iron and lead). Background levels for soil are biased, with about 50% of the data from Vandenberg, March and Beale AFBs. Detection rates in soil generally exceed those in ground water. This is expected, given the poor solubility of most inorganic chemicals in water. Detection rates in soil vary, with aluminum, barium, iron, magnesium, manganese and vanadium detected in 99% of samples, while antimony, cyanide, mercury, selenium, silver, and thallium had detection frequencies of less than 10%. Antimony, cadmium, chromium-6, cyanide, mercury, molybdenum, selenium, silver, and thallium had median concentrations below MDLs. Except for molybdenum, these same constituents had median concentrations below MDLs for ground water. None of the 95th percentiles for soil fell below MDLs, unlike ground water. Infrequently, background concentrations (arsenic, beryllium, iron) exceed important environmental thresholds (using residential criteria) such as U.S. EPA Region IX's Preliminary Remediation Goals (PRGs). Chromium-6 was detected at about the same frequency in soil and ground water, though the soil sample size was far greater.

SOIL BACKGROUND LEVELS BASED ON CALIFORNIA AIR FORCE BASES

Analyte	n	Percentile (mg/kg)			Detection	Median Method Detection Limit	Number Boreholes	Number AF Bases
		50th	95th	99th				
Aluminum	5032	7980	23000	31300	99%	11.0	2009	10
Antimony	6422	*ND*	12.5	23	9%	6.5	2453	10
Arsenic	6128	2.1	11.1	22.5	60%	0.6	2196	10
Barium	5713	80	357	610	99%	1.0	2148	10
Beryllium	6097	0.3	1.1	10.300001	53%	0.2	2283	9
Boron	327	31	140	190	91%	3.1	105	3
Cadmium	6664	*ND*	2.2	5.6	20%	0.5	2616	10
Chloride	436	8.9	480.0	1600	92%	0.2	206	2
Chromium	7318	11	50.5	99.3	94%	1.0	2721	10
Chromium-6	1770	*ND*	2.5	7.5	12%	0.2	525	8
Cobalt	5188	6.1	22.9	36.9	87%	1.0	1991	10
Copper	6775	10	56.7	153	95%	2.0	2563	10
Cyanide	1005	*ND*	0.6	1.3999997	2%	0.5	441	7
Fluoride	271	1.1	8.9	25	81%	0.5	109	3
Iron	5599	13100	37000	52000	99%	5.5	2120	11
Lead	7429	2.9	31.1	153	65%	1.8	2777	11
Magnesium	5182	3490	9870	16900	99%	20.0	2008	10
Manganese	5530	234	880	1700	99%	1.0	2096	10
Mercury	5167	*ND*	0.2	0.3	9%	0.1	1788	10
Molybdenum	4918	*ND*	20	26	15%	2.1	1876	10
Nickel	6628	6.5	39.3	69	66%	4.0	2507	10
Selenium	5972	*ND*	11.5	26	6%	0.6	2129	10
Silver	6770	*ND*	2.2	6.2	8%	1.0	2595	10
Sodium	4257	228	1720	4220	84%	85.0	1730	10
Thallium	6259	*ND*	25	176	8%	5.5	2415	10
Vanadium	5508	29.7	93	128	99%	1.0	2105	10
Zinc	7125	34	117	356	98%	2.0	2708	10

VARIABILITY OF SOIL BACKGROUND LEVELS WITH DEPTH

A frequency distribution analysis of sampling depths indicated that the data could be clustered into three horizons; each comprising roughly one-third of the data. These horizons are: 1) less than 2.5 feet, 2) 2.5 to 10 feet, and 3) greater than 10 feet. Based on the Kruskal-Wallis nonparametric test, all chemicals except cyanide, fluoride, and silver, showed significant differences (5% level) in background levels across the vertical horizons. Therefore, separate background concentrations by depth were derived for all analytes. There is no consistent pattern relating concentrations and depth. For example, lead concentrations decrease markedly with depth, iron concentrations increase with depth, and thallium concentrations are constant.

SOIL BACKGROUND LEVELS FOR < 2.5 FEET

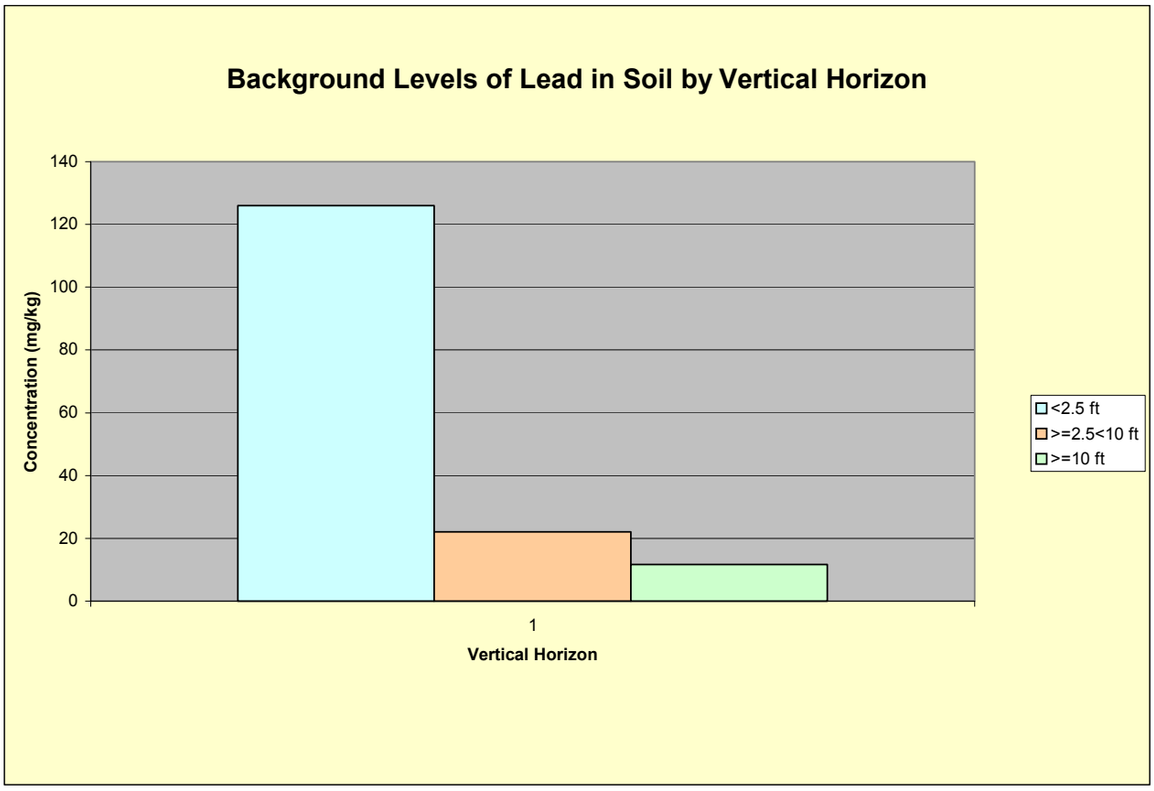
Analyte	n	Percentile (mg/kg)			Detection	Median Method Detection Limit	Number Boreholes	Number AF Bases
		50th	95th	99th				
Aluminum	1820	8070	23000	28900	100%	10.3	1470	9
Antimony	2017	*ND*	12	25	11%	6.2	1618	9
Arsenic	1896	2.3	11	21.3	64%	0.54	1453	9
Barium	1931	87.9	360	643	99%	1	1512	9
Beryllium	1885	0.3	1	5.8	55%	0.2	1515	8
Boron	74	4.6	10	12.9	78%	3.15	67	2
Cadmium	2094	*ND*	3	8.6	25%	0.5	1678	9
Chloride	163	7.3	470	1420	91%	0.2	146	2
Chromium	2242	14.2	53	154	97%	1	1773	9
Chromium-6	468	*ND*	4	14	16%	0.2	385	8
Cobalt	1762	6.7	22	33	88%	1	1365	9
Copper	2073	13	62	180	97%	2	1649	9
Cyanide	311	*ND*	1	0.6	2%	0.51	297	7
Fluoride	98	0.95	9	23	81%	0.5	91	3
Iron	1906	13600	32600	45600	99%	5.4	1516	9
Lead	2255	6.1	126	470	77%	1.7	1732	10
Magnesium	1757	3290	8680	17600	99%	12.3	1418	9
Manganese	1892	248	900	1500	99%	1	1505	9
Mercury	1604	*ND*	0	0.3	14%	0.1	1301	9
Molybdenum	1693	*ND*	21	44	21%	2	1326	7
Nickel	1991	8.2	36	78.3	71%	4	1591	9
Selenium	1945	*ND*	11	33	8%	0.66	1485	9
Silver	2158	*ND*	2	11.2	9%	1	1723	9
Sodium	1447	171	1150	4310	81%	52.0	1178	8
Thallium	1942	*ND*	25	175	6%	6.5	1586	9
Vanadium	1895	30.6	90	131	98%	1	1478	9
Zinc	2196	40	180	625	98%	2	1777	9

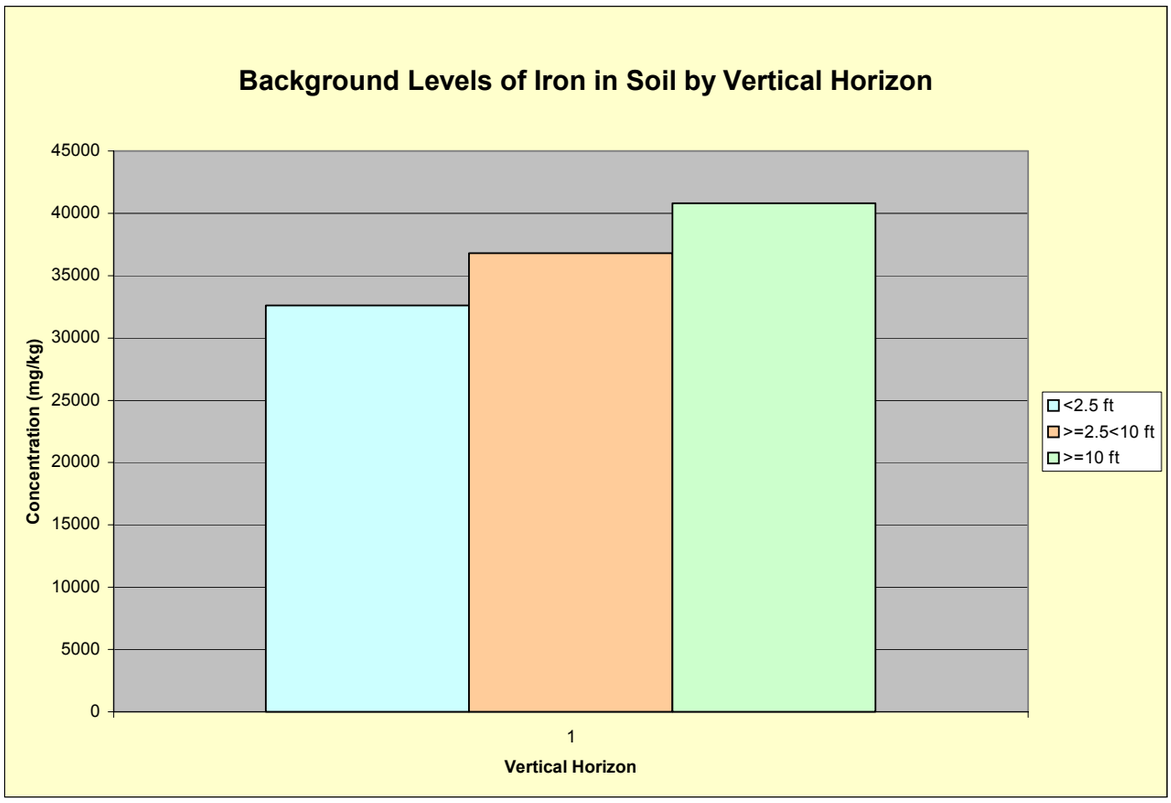
SOIL BACKGROUND LEVELS FOR 2.5 FEET TO 10 FEET

Analyte	n	Percentile (mg/kg)			Detection	Median Method Detection Limit	Number Boreholes	Number AF Bases
		50th	95th	99th				
Aluminum	1259	9150	24200	31100	100%	11	929	9
Antimony	1510	3.4	13	30	11%	6.6	1194	9
Arsenic	1395	2.6	14.7	45.9	72%	0.54	985	9
Barium	1330	97	383	655	99%	1	957	9
Beryllium	1397	0.3	1.1	10.3	59%	0.2	1084	8
Boron	70	40.4	139	141	97%	3.4	52	3
Cadmium	1519	*ND*	2.2	5.2	18%	0.5	1210	9
Chloride	100	6.7	517	2625	93%	0.2	88	2
Chromium	1712	12	48	92.5	96%	1	1288	9
Chromium-6	409	0.3	2.5	7.5	16%	0.2	296	8
Cobalt	1179	7.2	22	36.7	89%	1	866	9
Copper	1614	11	56.1	167	96%	2	1191	9
Cyanide	251	*ND*	*ND*	1.6	2%	0.57	201	6
Fluoride	54	1	5.7	57	78%	0.5	49	1
Iron	1328	15000	36800	49300	99%	5.7	970	9
Lead	1732	2.9	22	71.6	61%	2.1	1308	11
Magnesium	1227	4320	10900	21800	99%	20.3	895	9
Manganese	1318	278	786	1500	99%	1	962	9
Mercury	1136	*ND*	0.3	0.3	10%	0.1	871	9
Molybdenum	1119	*ND*	20	26	16%	2	844	9
Nickel	1602	7.4	39.1	59.8	69%	4	1190	9
Selenium	1352	*ND*	11.5	50	8%	0.6	981	9
Silver	1595	*ND*	2	5	7%	1	1232	9
Sodium	1090	270	2410	5180	90%	52	800	9
Thallium	1465	*ND*	25.000004	166	7%	6.5	1147	9
Vanadium	1317	34	92	130	99%	1	945	9
Zinc	1717	35.1	100	270	98%	2	1281	9

SOIL BACKGROUND LEVELS FOR > 10 FEET

Analyte	n	Percentile (mg/kg)			Detection	Median Method Detection Limit	Number Boreholes	Number AF Bases
		50th	95th	99th				
Aluminum	1953	7180	22200	33500	99%	11	827	10
Antimony	2901	*ND*	13	18.1	6%	6.6	1054	10
Arsenic	2837	1.6	9.4	20	50%	0.6	1006	10
Barium	2452	63	340	583	99%	1	909	10
Beryllium	2815	0.3	1.14	10.3	48%	0.2	1013	9
Boron	169	45.1	157	201	94%	3	67	3
Cadmium	3058	*ND*	1.9	4.9	17%	0.5	1138	10
Chloride	173	15	569	6510	93%	0.2	85	2
Chromium	3364	8.4	50	90	90%	1	1189	10
Chromium-6	893	*ND*	1	4	8%	0.2	204	8
Cobalt	2247	5	25	38.7	85%	1.1	826	9
Copper	3086	7.2	54.7	111	93%	2	1111	10
Cyanide	437	*ND*	0.65	1.1	2%	0.5	174	6
Fluoride	119	1.4	9.4	25	82%	0.5	47	1
Iron	2365	11700	40800	55100	99%	5.5	893	11
Lead	3464	2.6	11.7	28.6	59%	1.5	1266	11
Magnesium	2198	3275	9910	13600	99%	20.6	846	10
Manganese	2320	198	934	1910	99%	1	878	10
Mercury	2401	ND	0.3	0.3	5%	0.1	826	10
Molybdenum	2183	1.1	20	44	9%	2.2	816	10
Nickel	3035	5	41.3	68.5	62%	4	1122	10
Selenium	2656	*ND*	11	13	3%	0.6	964	10
Silver	3016	*ND*	2.5	5.7	8%	1	1117	10
Sodium	1720	248	1500	3340	82%	104	743	10
Thallium	2852	*ND*	26	178	9%	5	1042	10
Vanadium	2296	26.2	95	123	99%	1.1	868	10
Zinc	3209	28.7	100	189	98%	2	1176	10





SUMMARY AND CONCLUSIONS

Computer algorithms were used to automate the identification of background locations for inorganic chemicals in ground water and soil. These procedures identified large numbers of background locations and a more than adequate sample size which was used to determine California-wide background levels for 25 inorganic constituents. These data provide insight on background variability across California Air Force bases. The 95th percentile statistic for an individual constituent is a good representation of background level, given the inherent complexities associated with analyzing these large and diverse samples. Barium, magnesium, and sodium were highly detected in ground water; while aluminum, barium, chromium, copper, iron, magnesium, manganese, vanadium, and zinc were highly detected in background soils. Other constituents were not commonly detected in ground water (antimony, arsenic, beryllium, cadmium, cobalt, copper, cyanide, lead, mercury, nickel, selenium, silver, and thallium) or in background soil (antimony, cadmium, cyanide, mercury, molybdenum, selenium, silver, and thallium). For some analytes (antimony and chromium in ground water and arsenic, beryllium and iron in soil) regulatory limits are placed close to or below background levels.

These results can not replace site-specific background data. They do represent extensive sampling over a significant range of California environments, and should be useful in putting local sampling and analysis outcomes into perspective. The Department of Toxic Substances Control (1997) has guidance for one approach to evaluating site-specific background.

REFERENCES

American Society for Testing Materials (ASTM), 1996, Provisional Standard Guide for Developing Appropriate Statistical Approaches for Ground-Water Detection Monitoring Programs, Designation: PS 64 - 96.

Department of Department of Toxic Substances Control, 1997. Selecting Inorganic Constituents as Chemicals of Potential Concern at Risk Assessments at Hazardous Waste Sites and Permitted Facilities. February, 1997.

EPA, Office of Solid Waste, 1989, Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Interim Final Guidance.

EPA, Office of Solid Waste, 1992, Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance.

Professional affiliations are listed for contact purposes only. Analysis and conclusions contained herein are solely those of the authors, and do not represent official policy of the Department of Toxic Substances Control.