



October 8, 2021

Kyle Parker
Washington Department of Ecology
Toxic Cleanup Program/Central Regional Office
1250 West Alder Street
Union Gap, Washington 98903

RE: Evaluation of Background Levels of Arsenic and Lead in Soil and Groundwater

Circle K #2706034
7707 West Deschutes Avenue
Kennewick, Washington
Facility Site ID # 5574663
Cleanup Site ID # 12051
VCP # CE0472

Dear Mr. Parker:

Blaes Environmental Management, Inc. (Blaes Environmental), on behalf of Circle K Stores Inc. (Circle K) is submitting this document to present information regarding the concentrations of lead and arsenic in the soil and groundwater at the subject site in Kennewick, Washington as requested by the Washington Department of Ecology (WDOE). The objective of this report is to provide information to support a No Further Action request by Circle K for the subject site. The following sections of this document present Circle K's data and discussion regarding both lead and arsenic based on data from the site.

LEAD IN GROUNDWATER BELOW THE SITE

Naturally occurring concentrations of Lead are found within the near surface soil and the groundwater throughout the State of Washington and within all other States within the United States. The concentrations of naturally occurring Lead in soil and groundwater at any one location within Washington varies based on localized geologic conditions, sedimentation and characteristics of the source rock that produced the sediments, rainfall and precipitation rates, stormwater infiltration, and pH of the soil and groundwater.

The following items provide the information to support the statement that the concentrations of Lead found in the groundwater at the site are consistent with "background" levels of Lead in the Tri-Cities area of Washington.

1. There is No Known Historical Anthropogenic Source of Lead at the Site

Circle K has researched the past operations and processes used at the subject site and has not found a known historical anthropogenic source of the Lead within the soil and groundwater at the property. Circle K has not operated any of the well-known processes that may release Lead into the soil or groundwater at the site. The release of petroleum hydrocarbons into the soil and groundwater at the site was from unleaded fuel.

2. The Concentrations of Lead in Soil and Groundwater at the Site are Consistent with Statewide Lead Levels

Based on data from the WDOE 1994 study of the background levels of Lead in soil around the State of Washington, the median concentration of Lead within soil is 7.9 mg/kg (parts per million – ppm). The 90th percentile Lead concentrations in soil is approximately 17 ppm (Attachment A). The average Lead concentration within the soil at the site is expected to be less than the median lead concentration in the State based on the low levels of lead within the groundwater below the site. If the natural concentration of Lead in soil can be as high as 17 ppm and still be below the Statewide maximum concentration, then it is reasonable that the natural “leached” Lead concentrations through that soil into groundwater can be in the part per billion range.

The current average concentration of Lead in groundwater at the site is approximately <4.0 ug/L (parts per billion – ppb). The highest current concentration of Lead in groundwater at the site is <4.0 ppb. The highest historical lead concentration in groundwater at the site (19 ppb) was found in monitoring well MW-6 in April 2029. Note: Groundwater monitoring well MW-6 is upgradient from the hydrocarbon release at the site and not in the hydrocarbon release source area.

The average concentration of Lead in the groundwater in April 2019 was approximately 6.5 ppb. The overall average of Lead concentrations in groundwater while Circle K has been monitoring the lead in groundwater (December 2017 to September 2021) is approximately 3.02 ppb and below the WDOE action level for Lead in groundwater of 15 ppb.

3. The Concentrations of Lead in Soil and Groundwater are Consistent with Other Sites in the Area

The groundwater below other sites within the Tri-Cities area also contain similar concentrations of Lead. Another site (Circle K #2706032) located at 590 West Gage Boulevard in Kennewick also contains Lead in the soil and groundwater. The average Lead concentration within the soil at the site is 6.6 ppm and the highest concentration in 13 ppm. The groundwater contains an average Lead concentration in groundwater of approximately 9.3 ppb. The high concentration of Lead in groundwater at that site has been 35 ppb.

At Circle K #2706035 located at 2105 West 4th Avenue in Kennewick), the soil contains a Lead concentration at a depth of approximately 10 feet below the ground surface (bgs) of approximately 29 ppm with an average of 9.9 ppm.

4. The Geochemistry of the Site Leaches Lead Concentrations

A. Groundwater is Not Shallow and Not in Contact with Near Surface Soil

Groundwater occurs at this site at a depth most recently averaging 28.08 feet below the ground surface). The groundwater is not in close contact with the near surface soils containing natural positioned Lead.

B. Rainwater and Stormwater Infiltration Can Add to the Lead into the Surficial Soil

Rainwater (known to contain up to 1 ppb Lead) could also be a natural source of Lead in the near surface soils on properties within the Kennewick Washington area in the recent years. However, the asphalt/concrete surface cover and the relatively deeper depth to groundwater at this site provides more of a probability that naturally occurring Lead near the ground surface has attenuated with depth.

C. The pH of the Soil and Groundwater at the Site Increases Leachability

As described in an article from the University of Maine (Attachment B), the pH of the soil and groundwater at any site affects the leachability and mobility of constituents from the soil into the groundwater at a site. At the subject property, and throughout the Tri-Cities area of Washington, the pH of the soil and groundwater is higher than neutral levels. The referenced article documents that a higher pH in the soil increases the leachability and mobility of Arsenic (and likely Lead too) at a site. The historical concentrations of Lead in the groundwater at this site are most likely attributed to downward leached migration of the natural occurring Lead in the soil at the site over time.

Conclusion Regarding Lead in Groundwater at the Site

Circle K has documented that: (1) there was no historical process at the site that would have placed a higher than natural concentration of Lead into the soil or groundwater; (2) the overall average concentrations of Lead in the groundwater is below the Washington statewide allowable maximum concentration; (3) other sites within the Tri-Cities area also contain natural background Lead concentrations in groundwater similar to this site, and (4) the site geochemistry at this site shows that source of the Lead (and mobility) in the groundwater is the natural occurring Lead in the near surface soil leached down into groundwater.

Actions Planned to Address Lead Concentrations in Groundwater at the Site

Circle K plans on maintaining the asphalt/concrete surface cap at the property and leaving the residual background concentrations of Lead in place within soil and groundwater without further remediation action.

ARSENIC IN GROUNDWATER BELOW THE SITE

Similar to Lead (as described above), naturally occurring concentrations of Arsenic are found within the near surface soil and the groundwater throughout the State of Washington and within all other States within the United States. The concentrations of naturally occurring Arsenic in soil and groundwater at any one location within Washington also varies based on localized geologic conditions, sedimentation and characteristics of the source rock that produced the sediments, historical pesticide use (if any), rainfall and precipitation rates, stormwater infiltration, and pH of the soil and groundwater.

The following items provide the information to support the statement that the concentrations of Arsenic found in the groundwater at the site are consistent with “background” levels of Lead in the Tri-Cities area of Washington.

5. There is No Known Historical Anthropogenic Source of Arsenic at the Site

Circle K has researched the past operations and processes used at the subject site and has not found a known historical anthropogenic source of the Arsenic within the soil and groundwater at the property. Circle K has not operated any of the well-known processes that may release Arsenic into the soil or groundwater at the site. Although it is possible that pesticides may have been present in the near surface soils at the site long before development of the property.

6. The Concentrations of Arsenic in Groundwater at the Site are Consistent with Statewide Arsenic Levels

Based on data from the WDOE 1994 study of the background levels of Arsenic in soil around the State of Washington (Attachment C), the median concentration of Arsenic within soil is 2.92 mg/kg (parts per million – ppm). The 90th percentile of Arsenic concentrations in soil is approximately 6.99 ppm. The average Arsenic concentration within the soil at the site is expected to be approximately 8 ppm based on corresponding concentrations of arsenic in the groundwater, and on similar data from other sites in the area. If the natural concentration of Arsenic in soil averages 8 ppm, then it is reasonable that the natural “leached” Arsenic concentrations through that soil into groundwater can be in the part per billion range.

The last recorded average concentration of Arsenic in groundwater at the site in November 2020 was approximately 12.6 ug/L (parts per billion – ppb). The highest current concentration of Arsenic in groundwater at the site during that event was 35 ppb. The average concentration of Arsenic in the groundwater in November 2018 was approximately 17.5 ppb. The average

concentration of Arsenic in groundwater at the site in September 2019 was 10.5 ppb. The overall average of Arsenic concentrations in groundwater while Circle K has been monitoring the groundwater for Arsenic is approximately 15.7 ppb. This overall average at the site (from July 2018 to September 2021) is above the Washington Department of Ecology action level for Arsenic in groundwater of 5 ppb. A general map of the arsenic levels in groundwater within Washington is presented in Attachment D.

7. The Concentrations of Arsenic in Soil Groundwater are Consistent with Other Sites in the Area

The soil and groundwater below other sites within the Tri-Cities area also contain similar concentrations of lead. At another site (Circle K #2706032 mentioned in a previous section of this document), the Arsenic concentration within the soil at the site is 8.33 ppm and the highest concentration in 34 ppm. The most recent average concentration of Arsenic in groundwater at the Circle K #2706032 site is approximately 31.2 ppb. The highest recent concentration of Arsenic in groundwater at the site is 49 ppb. The average concentration of Arsenic in the groundwater in August 2019 was approximately 17.8 ppb. The average concentration of Arsenic in groundwater at the site in November 2020 was 22.7 ppb. The overall average of Arsenic concentrations in groundwater while Circle K has been monitoring the groundwater is approximately 18.7 ppb.

The Arsenic concentrations in the soil at Circle K #2706035 (mentioned in a previous section of this document) were recently detected with a high concentration of 17 ppm at a depth of 10 feet below the ground surface with an average of 5.8 ppm.

8. The Geochemistry of the Site Accounts for the Slightly Higher Apparent Arsenic Concentrations

D. Groundwater is Deeper and Not in Contact with Near Surface Soil

Groundwater occurs at this site at a depth most recently averaging 28.08 feet below the ground surface). The groundwater is not in close contact with the near surface soils containing natural positioned Arsenic.

E. Rainwater and Stormwater Infiltration Likely Adds to the Arsenic into the Surficial Soil

Rainwater (known to contain small concentrations of Arsenic) could also be a smaller natural contributor of Arsenic in the near surface soils on this property. However, the asphalt/concrete surface cover likely helps to retard rainwater from continuing to drive Arsenic downward into the subsurface soils.

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F. The pH of the Soil and Groundwater at the Site Increases Arsenic Leachability

As described in an article from the University of Maine (Attachment B), the pH of the soil and groundwater at a site affects the leachability and mobility of Arsenic from the soil into the groundwater at the site. The referenced article documents that a higher pH values increase the leachability and mobility of Arsenic at any site. The concentrations of Arsenic in the groundwater (similar to Lead) are most likely attributed to downward leached migration of the natural occurring Arsenic in the soil at the site.

Conclusion Regarding Arsenic in Groundwater at the Site

Circle K has documented that: (1) there was no historical process at the site that would have placed a higher than natural concentration of Arsenic into the soil or groundwater; (2) the overall average concentrations of Arsenic in the groundwater is above the Washington statewide allowable maximum concentration; (3) other sites within the Tri-Cities area also contain natural background Arsenic concentrations in groundwater similar to this site, and (4) the site geochemistry at this site shows that source of the Arsenic (and mobility) in the groundwater is most likely attributed to the natural occurring Arsenic in the near surface soil leached down into groundwater.

Actions Planned to Address Arsenic Concentrations in Groundwater at the Site

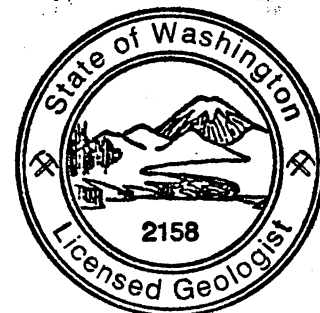
Circle K plans on maintaining the surface pavement at the site and leaving the residual background concentrations of Arsenic in place within soil and groundwater without further remediation action.

Thank you for the opportunity to submit this data to PLIA. If you have any questions, please contact us at 602-728-0707 or on my cell at 602-549-0925.

Sincerely,
Blaes Environmental



Daniel Blaes
Washington Licensed Geologist/Hydrogeologist #2158
President



Daniel Michael Blaes

ATTACHMENT A

Natural Background Soil Metals Concentrations in Washington State

The following table was compiled from information in *Natural Background Soil Metals Concentrations in Washington State* (October 1994), Ecology Publication No. 94-115, available at <https://fortress.wa.gov/ecy/publications/summarypages/94115.html>

Chemical	CAS Number	Region/ County	90th percentile (mg/kg)	50th percentile (mg/kg)	mean (mg/kg)	median (mg/kg)
Aluminum	7429-90-5	Statewide	37206.00	19277.87	21956.00	21956.00
		Puget Sound	32581.00	18376.61	20354.00	17900.00
		Clark County	52276.00	32446.91	34355.00	31192.00
		Yakima Basin	33379.00	20892.85	22263.40	20800.00
		Spokane Basin	21376.00	15380.88	15842.10	15000.00
		West (all)	45735.00	21899.36	25460.15	21760.00
		East (all)	28299.00	67234.76	18190.00	16600.00
		Group "W"	62905.00	18748.95	25392.70	21700.00
		Group "E"	25591.00	13525.62	15003.00	14800.00
Arsenic	7440-38-2	Statewide	6.99	3.10	3.82	2.92
		Puget Sound	7.30	3.24	3.96	2.86
		Clark County	5.81	3.26	3.56	3.045
		Yakima Basin	5.13	2.64	3.73	2.64
		Spokane Basin	9.34	4.39	5.02	4.99
		West (all)	6.37	3.19	3.71	2.91
		East (all)	7.61	3.03	3.90	2.95
		Group "W"	8.47	2.80	3.49	2.80
		Group "E"	5.76	2.14	2.70	2.53

Chemical	CAS Number	Region/ County	90th percentile (mg/kg)	50th percentile (mg/kg)	mean (mg/kg)	median (mg/kg)
Beryllium	7440-41-7	Statewide	1.44	0.59	0.76	0.67
		Puget Sound	0.61	0.35	0.41	0.36
		Clark County	2.07	1.43	1.43	1.48
		Yakima Basin	1.57	0.97	1.03	0.93
		Spokane Basin	0.84	0.64	0.65	0.66
		West (all)	1.51	0.51	0.75	0.53
		East (all)	1.27	0.70	0.77	0.72
		Group "W"	0.75	0.39	0.39	0.40
		Group "E"	0.61	0.35	0.38	0.31
Cadmium	7440-41-9	Statewide	0.99	0.32	0.63	0.49
		Puget Sound	0.77	0.37	0.80	0.49
		Clark County	0.93	0.49	0.55	0.83
		Yakima Basin	0.93	0.49	0.55	0.49
		Spokane Basin	0.72	0.36	0.40	0.40
		West (all)	1.20	0.40	0.83	0.83
		East (all)	0.81	0.30	0.48	0.48
		Group "W"	0.10	0.10	N/A	N/A
		Group "E"	N/A	N/A	N/A	N/A
Chromium	7440-47-3	Statewide	41.88	18.69	23.37	18.42
		Puget Sound	48.15	22.00	30.29	22.00
		Clark County	26.57	21.99	20.64	21.99
		Yakima Basin	38.27	16.43	21.67	16.42
		Spokane Basin	17.81	11.43	11.95	11.78
		West (all)	47.40	22.00	28.67	22.00
		East (all)	31.88	14.51	17.67	13.15
		Group "W"	78.46	28.18	37.74	26.70
		Group "E"	37.80	14.69	18.92	12.60

Supporting material for Cleanup Levels and Risk Calculation (CLARC)
Washington State Department of Ecology – Toxics Cleanup Program

Chemical	CAS Number	Region/ County	90th percentile (mg/kg)	50th percentile (mg/kg)	mean (mg/kg)	median (mg/kg)
Copper	7440-50-8	Statewide	36.01	16.80	20.46	17.07
		Puget Sound	36.36	15.00	24.43	15.00
		Clark County	34.43	20.49	22.04	21.78
		Yakima Basin	26.47	19.23	20.16	19.23
		Spokane Basin	21.61	14.42	14.42	14.14
		West (all)	43.23	17.36	23.15	17.80
		East (all)	28.40	16.22	17.58	16.30
		Group "W"	52.85	12.75	21.24	8.05
		Group "E"	26.42	14.70	17.69	14.70
Iron	Unavailable	Statewide	43106.00	22987.15	25903.72	22033.00
		Puget Sound	36128.00	17050.00	21680.10	17050.00
		Clark County	58665.00	39180.95	40734.60	38508.00
		Yakima Basin	51451.00	27689.82	29780.40	28821.00
		Spokane Basin	25026.00	18278.16	18744.84	18150.00
		West (all)	50125.00	24152.41	28192.00	21433.00
		East (all)	36644.00	21810.59	23471.67	22116.00
		Group "W"	49170.00	21446.18	25557.33	18200.00
		Group "E"	29631.00	19027.40	19935.70	21300.00
Lead	7439-92-1	Statewide	17.09	6.98	10.05	7.90
		Puget Sound	16.83	4.47	15.90	9.80
		Clark County	24.02	9.50	10.65	6.86
		Yakima Basin	11.00	6.56	11.29	6.53
		Spokane Basin	14.91	11.01	7.00	10.80
		West (all)	20.42	5.92	11.90	8.20
		East (all)	13.10	7.84	8.44	7.82
		Group "W"	10.67	4.75	5.63	4.00
		Group "E"	9.85	6.64	6.92	6.40

Supporting material for Cleanup Levels and Risk Calculation (CLARC)
Washington State Department of Ecology – Toxics Cleanup Program

Chemical	CAS Number	Region/ County	90th percentile (mg/kg)	50th percentile (mg/kg)	mean (mg/kg)	median (mg/kg)
Manganese	7439-96-5	Statewide	1094.85	492.82	592.60	509.58
		Puget Sound	1146.00	461.62	592.21	474.00
		Clark County	1511.00	924.17	924.20	915.50
		Yakima Basin	1104.84	611.46	669.00	589.00
		Spokane Basin	663.48	494.78	506.5	470.00
		West (all)	1337.27	494.28	646.71	531.25
		East (all)	836.00	491.30	534.40	490.75
		Group "W"	691.75	257.06	329.30	231.00
		Group "E"	526.59	348.73	364.95	345.00
Mercury	7439-97-6	Statewide	0.07	0.02	NO DATA	0.03
		Puget Sound	0.07	0.04	0.05	0.04
		Clark County	0.04	0.03	0.03	0.03
		Yakima Basin	0.05	0.02	0.03	0.02
		Spokane Basin	0.02	0.01	0.02	0.01
		West (all)	0.08	0.04	0.04	0.04
		East (all)	0.04	0.01	0.02	0.01
		Group "W"	0.13	0.03	0.05	0.04
		Group "E"	0.02	0.01	0.01	0.01
Nickel	7440-02-0	Statewide	38.19	16.92	21.49	16.43
		Puget Sound	38.19	23.00	29.82	23.00
		Clark County	21.04	16.23	17.72	16.23
		Yakima Basin	45.89	16.23	24.83	16.30
		Spokane Basin	16.19	10.49	10.96	10.15
		West (all)	44.20	20.57	25.44	19.20
		East (all)	25.54	12.40	17.25	12.50
		Group "W"	54.19	19.12	25.66	19.10
		Group "E"	22.41	12.54	13.77	11.70

Chemical	CAS Number	Region/ County	90th percentile (mg/kg)	50th percentile (mg/kg)	mean (mg/kg)	median (mg/kg)
Zinc	7440-66-6	Statewide	85.82	51.56	55.53	51.12
		Puget Sound	85.06	46.52	51.45	43.65
		Clark County	95.52	78.5	76.01	78.50
		Yakima Basin	78.71	55.66	57.54	52.90
		Spokane Basin	66.40	50.83	51.77	50.90
		West (all)	98.39	52.50	58.34	54.08
		East (all)	80.91	52.29	55.55	50.64
		Group "W"	85.56	42.85	48.41	44.5
Group "E"	67.47	43.40	45.74	41.00		

Definitions	
State Wide	all statewide sampling locations.
Puget Sound	Snohomish, King, Pierce, Thurston, Mason, Jefferson, Island, San Juan, and Clallam Counties.
Clark County	Clark County.
Yakima Basin	Yakima, Kittitas, Chelan, and Grant Counties.
Spokane Basin	Spokane, Lincoln, Adams, Okanogan, and Whitman Counties.
West (all)	all sampling locations west of the Cascade Mountain Range.
East (all)	all sampling locations east of the Cascade Mountain Range.
Group "W"	Whatcom and Skagit Counties, Pacific Coast (Grays Harbor, Lewis, and Pacific Counties).
Group "E"	Benton, Spokane, Lincoln, Adams, Okanogan, and Whitman Counties.

Source: *Natural Background Soil Metals Concentrations in Washington State* (October 1994), Ecology Publication No. 94-115, available at <https://fortress.wa.gov/ecy/publications/summarypages/94115.html>

ATTACHMENT B

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Arsenic

How Does Arsenic Get into the Groundwater?

The conditions that favour arsenic dissolution (becoming dissolved in the water) and mobilization (movement with the groundwater to your tap) depend on the circumstances. One thing that is certain is that it takes more than just high arsenic concentrations in the soil or rocks of a region. The soil in Bangladesh is much lower in arsenic than soils in many areas that do not share the problem of high arsenic in groundwater, so what is the difference? Well, for one thing, the arsenic needs to be in a soluble form to end up in drinking water.

Of the many known forms of arsenic, only a few are frequently detected in water.

- If the arsenic is not soluble, it will precipitate and remain in the solid phase of the groundwater system as part of the soil.
- If there is a binding site on the soil surface that is available, and the arsenic is in a form that binds strongly, it will also leave the water phase and attach to the soil.

So for most types of arsenic, they'll just stay put. The deciding factor is probably some process that converts those stable, insoluble or stuck-on-surfaces forms of arsenic to a form that is soluble in the water

We have seen that the form of arsenic affects both its toxicity and its mobility. Organic forms of arsenic are rare in groundwater, so we will ignore them in this discussion. Most of the arsenic found in groundwater is either inorganic As(III) mainly as uncharged arsenious acid, or inorganic As(V) in the form of arsenic acid minus one or two of its protons (so with a charge of -1 or -2). That's the case at neutral pH. As discussed in the "[What is arsenic](#)" section, the charge on As(V) allows it to bind to sites on the surface of soil particles, removing it from the water. As in that section we'll assume that the interaction between arsenic compounds and surfaces is due to the charge, even though the real situation is more complicated than that.

As the pH is raised, the compounds will tend to become more and more negatively charged as the arsenic and arsenious acid lose H⁺ groups. So the charge of these arsenic compounds depends on the pH. You might (rightly) guess that as the pH goes up, the charge on the arsenic compounds becomes more negative and they should be better at binding to positively charged sites on the soil surface. The trouble is, the soil binding sites are also affected by the pH. As the pH goes up and the water becomes more basic, OH⁻ groups from the water also associate with the adsorption or ion exchange sites on the soil, neutralizing them. Once they have been neutralized, they are not attractive to the arsenic compounds. The solubility of metals in water is also affected by pH, so if you get to a pH that dissolves the mineral phase, that will result in the release of anything bound to it. So instead of decreasing in concentration, the arsenic concentration in high pH water can actually go up!

In fact, in the southwestern part of the United States, the pH of the groundwater may be high due to the dry, arid conditions. Water evaporates under these conditions, raising the concentration of everything dissolved in it. These waters also tend to have a very long retention time, and older waters usually have higher pH values than water that is flushed through the system more quickly. So high arsenic concentrations in the arid southwest may be high because of (1) concentration by evaporation, and (2) desorption due to the high pH.

There is a general trend between pH and arsenic concentration in groundwater. As the pH increases, the arsenic concentration tends to go up. Unfortunately the correlation is not perfect: the real situation is much more complex than my explanation. Still, if the pH of your well water is high, you are at higher risk of also having high arsenic – so you should test the water.

The other major factor that affects the form of arsenic in solution is something called the redox state of the environment. The word redox is a contraction of "reduction" and "oxidation". A redox reaction is any reaction in which electrons are passed from one atom to another. In a reaction like this, one chemical is reduced (that's the chemical that gains the electron) and one chemical is oxidized (the one that loses the electron).

Sometimes people use the saying "LEO the lion says GER" to remember which is which: Loss of Electron = Oxidation (LEO); Gain of Electron = Reduction (GER).

- Some chemicals, like O₂, are really good at oxidizing other chemicals.
- Some chemicals like hydrogen sulfide (H₂S) are great at reducing other chemicals.
- Many chemicals fall in between.

Since all chemicals are not equal in their ability to be reduced or oxidized, they have been tested and assigned values for their "electron transfer potential". The lower the electron transfer potential, the less likely a compound will accept (gain) electrons or be reduced.

If you take all of the chemicals in a solution and add up the electron transfer potentials of each, you can find out if the environment will have a tendency to reduce chemicals that are added, or a tendency to oxidize them. In general, if the oxygen concentration in the environment is high, the redox potential will be positive and there will be a high likelihood that compounds in the system will be oxidized. This is an oxidizing environment. If, on the other hand, there is no oxygen present, and a high concentration of hydrogen sulfide is present, this is a reducing environment and chemicals that enter the system will tend to be reduced.

OK, so let's get back to arsenic. Under reducing conditions, the most stable soluble form of inorganic arsenic is as arsenious acid (As(III)). Under oxidizing conditions, most of the arsenic will be in the As(V) form, arsenic acid, because it is more stable under oxidizing conditions. Again, remember that the mobility of arsenic may depend on its charge, so at neutral pH, arsenious acid is more mobile than the dissociated forms of arsenic acid. That means arsenic will probably be more mobile under reducing conditions because more of the arsenic will be present as arsenious acid.

Just as the pH of the system affects binding sites on soil particles, the redox potential also affects the binding sites. Many of the binding sites for arsenic are made of oxidized iron, aluminum or manganese species that form a coating on the soil particles or on the rock surface. Sometimes, the metals on the soil surface can also be reduced, releasing them into solution. That means the binding sites are no longer available on the surface and the arsenic that used to be bound is released into solution.

That makes two independent factors that are likely to increase the mobility of arsenic under reducing conditions:

- reduction of As(V) to As(III), which is more mobile
- reduction of binding sites, releasing bound arsenic

One more factor that can affect arsenic mobility under reducing conditions is sulfide. If there is sulfide present in water containing arsenic, the arsenic and sulfide may precipitate, removing both from the water phase. So you get increased mobility of arsenic under reducing conditions only as long as there is no sulfide in the water.

We've discussed all of this as if it were like chemicals in a jar of water with some soil in it. We need to add in another complicating factor. Living things make chemical reactions happen much faster than they would normally go in the absence of life by using proteins called enzymes. Enzymes bring together all the chemicals that are needed for a particular reaction so it can proceed more quickly. When the reaction is complete, the enzyme releases the products and starts over again.

The point of catalyzing reactions, from the organism's point of view, is to trap the energy released from the reaction to fuel movement or growth, or to build new cellular material. Your cells use enzyme systems for respiration. In respiration, the food you eat and oxygen from the air you breathe react together releasing energy, carbon dioxide and water. You trap the energy so you can walk, run, grow, keep your heart beating, and much, much more!

There aren't as many living things in groundwater as there are on the earth's surface, but there are bacteria that survive and grow in this environment.

- Some of them can speed up the reduction of As(V) to As(III). That reaction would increase the mobility of arsenic in water.
- Other bacteria can reduce Fe(III) on soil surfaces to Fe(II), which is released into the water. Again, any arsenic that was attached to the Fe(III) binding site on the soil particle would also be released into the groundwater.

These two examples show how bacteria can affect arsenic mobility directly (by reducing the arsenic) or indirectly (by reducing the binding site). These activities in groundwater are usually limited by the amount of food available to the bacteria.

"Food" to the bacteria in this case is organic carbon – the same as your own food. Normally it is very low in groundwater because the degradable organic carbon is degraded near the surface of the soil column where there are plenty of organisms to use it, or becomes bound to particles near the surface. Less and less is available as the water moves downward toward the water table. In places where the organic carbon in the water is enriched – say by applying manure to soil just before a rain, or where a landfill releases organic carbon – more can reach depths in the groundwater

to feed the bacteria that live there. Organic carbon in this system acts as a reductant, reducing the redox potential and fueling the reduction of As(V) to As(III) and Fe(III) to Fe(II). Again, both reactions increase the mobility of arsenic in water.

In groundwater environments with plenty of oxygen, oxidation reactions can also potentially release arsenic. In these situations, arsenic has to be associated with a reduced chemical, like sulfide. Many arsenic-containing minerals also contain sulfide.

In the presence of oxygen, bacteria can oxidize sulfides instead of organic carbon to generate energy (for these bacteria, reduced sulfur is "food"). Once the sulfide is oxidized to sulfate, it is soluble in water, and releases the arsenic. This is the same process as the one that releases acid and metals into water at mining sites, and it is the way that bacteria contribute to acid mine drainage.

Note that these reactions can occur without bacteria present, but they will proceed more slowly.

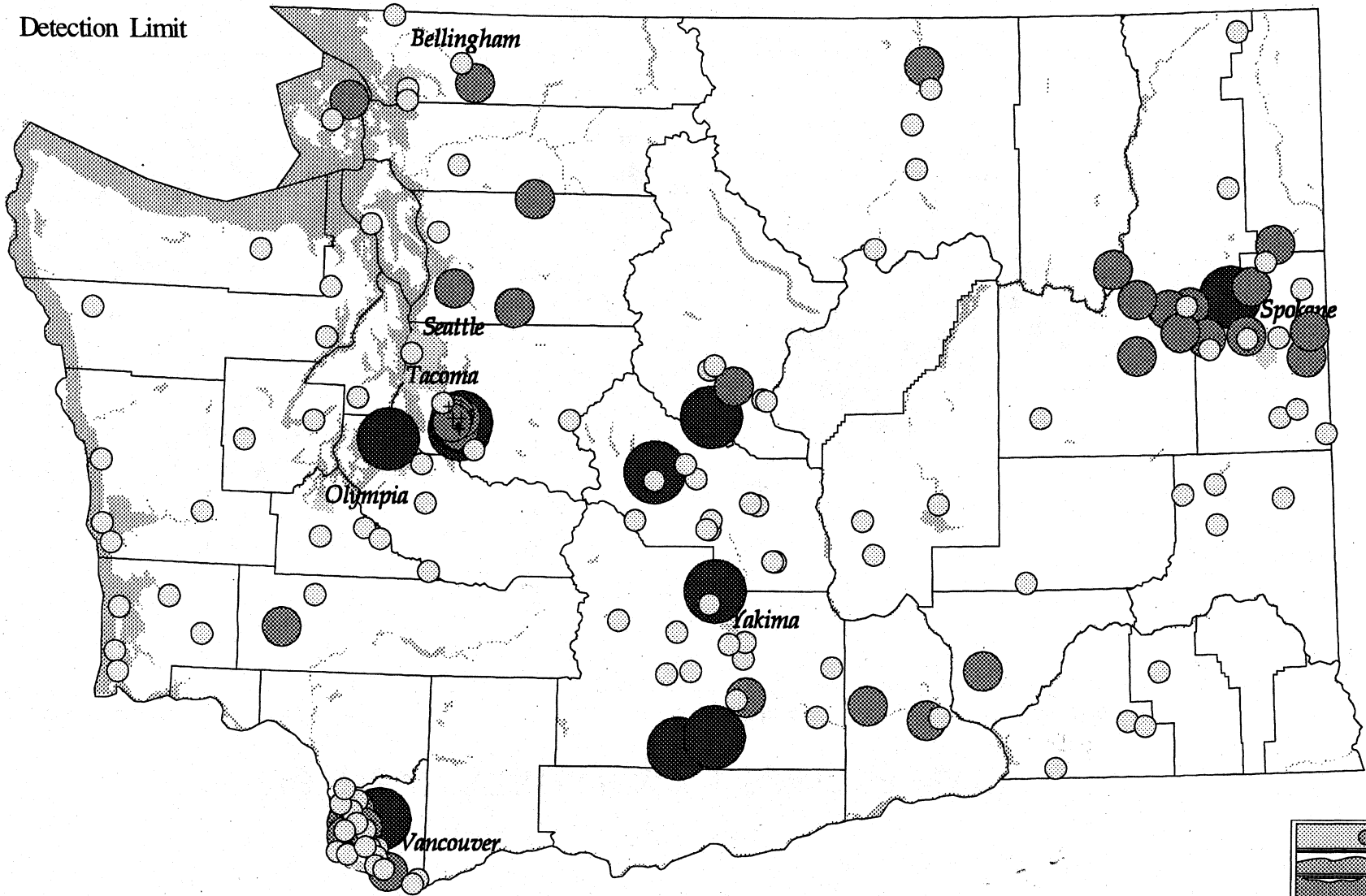
So to sum up, we have seen three ways that arsenic can get in to water.

1. In situations where the pH is high, arsenic may be released from surface binding sites that lose their positive charge.
2. When organic carbon is present in the groundwater, it can feed bacteria that release arsenic either by (a) directly reducing As(V) to As(III), which is more soluble, or (b) by reducing the element at the binding site which releases the arsenic that was attached there (for example, Fe(III) is converted to Fe(II) which dissolves in the water, freeing the arsenic).
3. Finally, arsenic trapped in sulfide minerals can be released when the minerals are exposed to oxygen. This can happen when the water level drops and the minerals are exposed to air.

ATTACHMENT C

Figure 26: Arsenic Concentrations

- > 10 mg/kg
- $\geq 5 < 10$ mg/kg
- < 5 mg/kg
- + Detection Limit



Map Prepared by EILS Program



