Lead and Halogen Contamination from Aviation Fuel Additives at Brackett Airfield

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Compounds containing lead, chlorine, and bromine are used as anti-knock fuel additives in aviation gasoline. Their presence in elevated amounts indicates fuel runoff or particle settlement from combusted fuel. This study aims to measure the concentration of these elements in the soil around Brackett Airfield in LaVerne, California. X-ray fluorescence measurements reveal lead content at 22.1 – 152.2 ppm with an average of 48.0 ± 7.4 ppm; bromine at 2.1 – 42.6 ppm, averaging at 10.0 ± 2.1 ppm; and chlorine at 315.5 – 2567.3 ppm, averaging at 605.2 ± 110 ppm. Atomic absorption spectroscopy measured lead at 5.9 – 94.8 ppm, averaging at 20.6 ± 5.0 ppm. None of the results obtained exceed allowable EPA standards and therefore should not pose a health risk to surrounding communities. Further studies are recommended on soils collected within the airport fence line—contamination is likely higher due to closer proximity to the runway, fueling stations, and airplane hangars.

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Introduction

Brackett Airfield in LaVerne, California is a small, publicly owned airfield open to Los Angeles County. The airport is in continuous operation and provides services to helicopters, military, and jet aircraft; however, general aviation aircraft make up the majority of operations based in the field.[1] General aviation planes are of interest because they run on aviation gasoline, or avgas, a leaded, high-octane fuel. Avgas is used by piston-driven engines while the larger turbine engines of jet planes run off of a non-leaded, kerosene-based fuel.

Lead is added to avgas in the form of tetraethyl lead (TEL) in order to increase the octane rating, a measure of the "knock" inside engines. Knock describes the tendency for gasoline to spontaneously ignite, which can cause dangerous pressure and stress on an engine. Piston engines need a high-octane fuel to withstand the high power and pressure required of them, especially during takeoff.[2] There is currently no suitable, cost-effective unleaded fuel option available—thus leaded avgas has remained standard[3] despite the negative health effects of exposure to lead.

Lead is a toxin that targets the nervous system, renal function, and vascular system. It is responsible for decreased physical and mental development and capacity, especially in children who are still maturing. It can also cause high blood pressure, hearing loss, attention deficit, and more extreme neurological damage, including short-term memory loss and lowered IQ.[4,5] Lead typically enters the body through digestion or inhalation, and in some cases, skin contact. Inorganic lead, like the type found in paint, food, plastics, etc., is not absorbed by the skin. However, tetraethyl lead, which is still legal for aircraft, watercraft, and farm machinery, may be absorbed through the skin.[4] Once absorbed, lead enters the bloodstream and circulates throughout the body, making its way into soft tissue and eventually to bone, where it replaces calcium. The ability of lead to mimic the role of calcium is a major reason for its neurological effects: as lead reacts similarly to calcium, it can compete for binding sites in the cerebellum, ultimately leading to flaws in neurotransmission.[6]

The body is able to purge the bloodstream relatively quickly, the half-life of lead in blood being 35 days. Thus, a blood lead test is a good indicator of recent exposure. However, bone samples must be analyzed to evaluate long-term exposure. Although symptoms may not be recognized, it is established that no toxic threshold for lead exists; bodily lead contamination at any level has the potential to interfere with normal activity.[7]

The Environmental Protection Agency (EPA) estimates that almost half of all lead emissions in the United States comes from small aviation aircraft fuel.[8] In April 2010, the EPA issued the Advanced Notice of Proposed Rulemaking (ANPR) on Lead Emissions from Piston-Engine Aircraft Using Leaded Aviation Gasoline,[5] which was open to public comment until August 28, 2010.[9] If the EPA finds in the future that lead emissions from aircraft contribute to pollution and therefore endanger public health, the Federal Aviation Administration (FAA) would be required to establish standards to control lead emissions from piston-engine aircraft.[5] This would place pressure on the development of an unleaded aviation gasoline.

General aviation aircraft currently runs off of Avgas 100LL. This gas contains TEL, which acts to form a protective layer on the soft valve seat of engines to prevent it from fusing to the valve and being taken from the surface of the seat.[2] This, along with other surface damage, is known as Valve Seat Recession (VSR). The only way to prevent VSR is to produce harder metal valve seats, a costly modification for old aircraft, or use VSR additives, which do not up octane ratings and thus cannot be used for aviation.[2] Unleaded fuels are in development, including 82UL in the U.S., which is only approved for use on a few engine types. Even so, it is estimated that only 60% of aircraft world-wide would be able to use this fuel grade; the rest would need system modifications prior to approval.[2] It is obvious that the transition to unleaded gasoline will be slow and arduous given current conditions, but there is little doubt that the unleaded fuel transition will occur at some point in the future.

Effort to redirect the path of aviation fuel is due in large to the Clean Air Act. Current National Ambient Air Quality

Standards (NAAQS) for lead are set to 0.15 μg/m3 over a rolling 3-month average,[10] while soil concentration is set to a standard of 1200 ppm in non-play areas and 400 ppm in play areas.[11]

Lead emitted from internal combustion engines is usually in the form of lead halides due to the presence of ethylene dibromide and ethylene dichloride (EDC), added as scavenging agents[12] to prevent lead deposition inside an engine. EDC is reasonably anticipated to be a human carcinogen. However, experimental trials on animals have been inconclusive.[13] Chlorine and bromine in their elemental forms are highly toxic, but these gases would not remain in soil. It was expected that only the typically harmless chlorides and bromides would be found. However, a positive correlation of halogen to lead concentration would support the hypothesis that contamination is in large part due to leaded gasoline.

We used X-ray fluorescence (XRF) to measure lead and halogen content, and graphite furnace atomic absorption (AA) spectroscopy for lead analysis. Employing two different techniques enabled us to determine the percent extractability of lead in soil and provide a measure of reproducibility. X-rays penetrate but do not destroy the entire sample, and the emitted rays analyzed by the detector are representative of all present elements regardless of their chemical form. However, the AA method requires the sample to be digested first by an acid. While hydrofluoric acid would dissolve the silicates and metal oxides that are present in environmental samples, safety concerns necessitate the use of nitric acid instead: thus, some of the lead that remains bound in complexes will be filtered out and will not contribute to the concentration measured by AA.

Materials and Methods

Sample collection: A coring sampler was bored into the ground to a depth of about six inches in order to collect the soil packed inside. In areas covered with freshly turned dirt or heavy organic debris, only the lower four to five inches was collected. A total of 48 samples were taken from the playground near the main parking lot, areas near hangars, and along the eastern perimeter of the fence around the field (latitudinal and longitudinal locations were recorded on a Trimble® Juno™ ST handheld GPS unit).

Sample preparation: All samples were filtered in sieves to eliminate larger rocks and organic material to be dried for up to 12 hours in a 100 °C oven. The dried soil was then powdered using a steel ball mill.

For analysis by atomic absorption (AA) spectrometry, three replicates of 0.5 g each per soil sample were digested with 10 mL of 70% HNO_3 and microwaved with recommended EPA settings.[14] The remaining soil was filtered out and the remaining solution was diluted to 25 mL of deionized water. Further dilutions were carried out using deionized water as needed.

For analysis by X-ray fluorescence (XRF), three replicates of 5 g each per soil sample were mixed with 1 g of cellulose binder. These were then pressed into 32 mm pellets using SPEX 3630 X-Press for five minutes of 30 tons and one minute of release.

Sample analysis by AA spectrometry: All samples were analyzed for lead content with the graphite furnace method in PerkinElmer AAnalyst 800 after a 1:10 dilution. Three injections of each sample replicate were measured against a calibration curve using lead standards of 5, 10, 25, 50, and 100 ppb.

Sample analysis by XRF: Each pressed pellet was analyzed for lead, chlorine, and bromine using a PANalytical Axios X-Ray Fluorescence Spectrometer. Lead and bromine levels were measured based on pre-programmed calibrations on PANalytical's ProTrace program. A separate chlorine calibration was created using standards from U.S. Geological Survey (USGS) BHVO-2 (ultra-pure quartz dilutions of 70%, 50%, 30%, and 10% of a given 150 ppm chlorine concentration), Geological Survey of Japan JMS-1 (a 10% dilution of 26,900 ppm chlorine), and undiluted USGS GSP-2 (400 ppm chlorine). A blank of 5 g ultra-pure quartz and 1 g binder was also incorporated in the calibration.

Statistical and data analysis: Outliers among replicates were subjected to Dixon's Q test and rejected accordingly. Remaining replicates were then averaged and 95% confidence intervals determined.

All maps were created using ArcGIS software with data points taken from the handheld GPS unit.

Results and Discussion

Table 1. Lead Concentration (XRF)

Sample	Lead Concentration (ppm)	95% C.I. (ppm)
1	152.2	1.1
2	37.2	1.6
3	29.8	0.91
4	42.4	1.0
5	55.0	1.1
6	22.1	1.9
7	32.5	6.9
8	79.3	1.5
9	116.4	5.7
10	85.8	2.2
11	36.4	2.0
12	42.0	1.1
13	54.6	10.6
14	53.7	5.3
15	26.0	0.95
16	70.4	1.3
17	62.8	0.53
18	86.9	6.4
19	115.7	6.5
20	33.3	1.5
21	27.2	0.65
22	27.6	1.4
23	35.4	3.3
24	36.23	2.1
25	37.1	2.5
26	37.2	2.4
27	26.3	1.9
28	25.2	1.8
29	47.0	1.9
30	52.3	2.7
31	44.4	2.6
32	36.6	5.5
33	47.5	3.5
34	26.3	0.75
35	28.4	1.4
36	45.5	0.71
37	55.0	1.5
38	52.5	4.7
39	41.3	0.64
40	36.1	1.9
41	42.2	2.6
42	39.3	0.79
43	40.7	3.5
44	48.3	1.1
45	33.2	3.4
46	37.3	2.8
47	29.1	0.17
48	34	0.52

Average lead concentration: 48.0 ± 7.4 ppm

Table 2. Lead Concentration (AA)

Sample	Lead Concentration (ppm)	95% C.I. (ppm)
1	29.1	1.8
2	12.7	0.72
3	8.9	1.1
4	13.3	1.0
5	19.1	4.6
6	8.9	1.1
7	14.7	3.0
8	38.5	0.59
9	95.0	10.
10	40.8	1.9
11	15.0	0.38
12	22.8	0.61
13	28.9	4.0
14	27.4	3.3
15	13.8	2.0
16	39.7	4.0
17	36.7	1.6
18	46.1	0.72
19	21.0	2.7
20	14.9	0.57
21	12.5	1.6
22	15.3	2.8
23	16.3	0.54
24	17.1	1.4
25	14.0	0.31
26	13.8	0.010
27	9.0	0.41
28	7.9	0.31
29	21.7	8.8
30	17.9	0.74
31	14.4	0.41
32	9.7	0.22
33	18.3	4.5
34	5.9	0.20
35	7.5	0.69
36	12.7	0.79
37	14.6	1.6
38	87.6	130*
39	10.9	0.55
40	8.7	0.92
41	12.5	0.12
42	9.9	0.35
43	12.2	0.15
44	15.6	1.3
45	9.9	0.34
46	10.1	0.010
47	9.0	0.060
48	9.8	0.34

*possible contamination
Average lead concentration: 20.6 ± 5.0 ppm

Table 3. Extractability (Lead)

Sample	ppm (AA)	ppm (XRF)	% Extraction
1	29.1	152.2	19.1%
2	12.7	37.2	34.0%
3	8.9	29.8	29.8%
4	13.3	42.4	31.4%
5	19.1	55.0	34.8%
6	8.9	22.1	40.1%
7	14.7	32.5	45.4%
8	38.5	79.3	48.6%
9	95.0	116.4	81.6%
10	40.8	85.8	47.6%
11	15.0	36.4	41.3%
12	22.8	42.0	54.3%
13	28.9	54.6	52.9%
14	27.4	53.7	51.0%
15	13.8	26.0	53.3%
16	39.7	70.4	56.3%
17	36.7	62.8	58.4%
18	46.1	86.9	53.0%
19	21.0	115.7	18.2%
20	14.9	33.3	44.7%
21	12.5	27.2	45.7%
22	15.3	27.6	55.4%
23	16.3	35.4	46.0%
24	17.1	36.2	47.2%
25	14.0	37.1	37.7%
26	13.8	37.2	37.1%
27	9.0	26.3	34.4%
28	7.9	25.2	31.4%
29	21.7	47.0	46.1%
30	17.9	52.3	34.3%
31	14.4	44.4	32.5%
32	9.7	36.6	26.5%
33	18.3	47.5	38.4%
34	5.9	26.3	22.4%
35	7.5	28.4	26.5%
36	12.7	45.5	27.9%
37	14.6	55.0	26.6%
38	87.6	52.5	167.0%*
39	10.9	41.3	26.5%
40	8.7	36.1	24.1%
41	12.5	42.2	29.6%
42	9.9	39.3	25.2%
43	12.2	40.7	29.9%
44	15.6	48.3	32.3%
45	9.9	33.2	29.7%
46	10.1	37.3	27.0%
47	9.0	29.1	30.8%
48	9.8	34.0	28.7%

*possible contamination
Average extractability: 40.9% ± 6.3%

Table 4. Bromine Concentration (XRF)

Sample	Bromine Concentration (ppm)	95% C.I. (ppm)
1	22.0	1.2
2	24.6	0.49
3	42.6	0.35
4	16.7	0.24
5	16.4	0.41
6	3.8	0.13
7	2.1	1.4
8	8.8	0.57
9	6.5	1.1
10	9.7	0.20
11	23.8	0.75
12	2.2	1.6
13	6.0	1.3
14	4.9	0.73
15	2.4	1.1
16	9.7	0.63
17	6.2	0.17
18	6.5	0.070
19	7.6	0.52
20	14.2	0.26
21	6.2	0.11
22	6.5	0.77
23	7.3	0.41
24	8.0	0.69
25	5.2	0.35
26	3.3	0.36
27	14.4	1.1
28	4.9	0.33
29	5.7	0.59
30	5.4	0.73
31	7.1	0.34
32	17.2	0.35
33	7.4	0.60
34	15.8	0.40
35	10.6	0.23
36	14.9	0.56
37	19.8	0.74
38	10.8	0.24
39	14.5	0.75
40	9.8	0.41
41	7.7	0.00
42	8.0	0.35
43	6.3	1.4
44	5.5	1.3
45	4.9	0.13
46	7.5	0.57
47	4.0	1.3
48	6.6	0.33

Average bromine concentration: 10.0 ± 2.1 ppm

Table 5. Chlorine Concentration (XRF)

Sample	Chlorine Concentration (ppm)	95% C.I. (ppm)
1	525.7	26
2	532.9	2.9
3	650.3	12
4	430.9	30.
5	428.4	21
6	392.1	14
7	645.4	12
8	365.9	2.9
9	653.7	8.6
10	523.2	17
11	1312.6	43
12	447.0	83
13	527.7	45
14	548.6	8.1
15	363.8	21
16	340.8	5.3
17	346.7	22
18	509.2	48
19	534.1	11
20	2567.3	28
21	315.5	24
22	388.8	20
23	408.6	6.8
24	344.3	18
25	362.3	16
26	372.4	8.6
27	360.5	15
28	433.8	36
29	579.0	9.5
30	467.0	17
31	572.5	6.7
32	1028.0	40
33	451.3	11
34	460.4	29
35	652.0	15
36	491.1	13
37	1094.5	19
38	488.3	6.3
39	1078.3	30
40	710.9	12
41	483.4	9.7
42	903.5	24
43	477.8	29
44	597.6	11
45	462.8	29
46	1262.6	38
47	416.4	18
48	741.0	29

Average chlorine concentration: 610 ± 110 ppm

Figure 1. Spatial distribution of lead concentrations in ppm given by XRF analysis.

Figure 2. Spatial distribution of lead concentrations in ppm given by AA spectroscopy.

Figure 3. Spatial distribution of bromine concentrations in ppm given by XRF analysis.

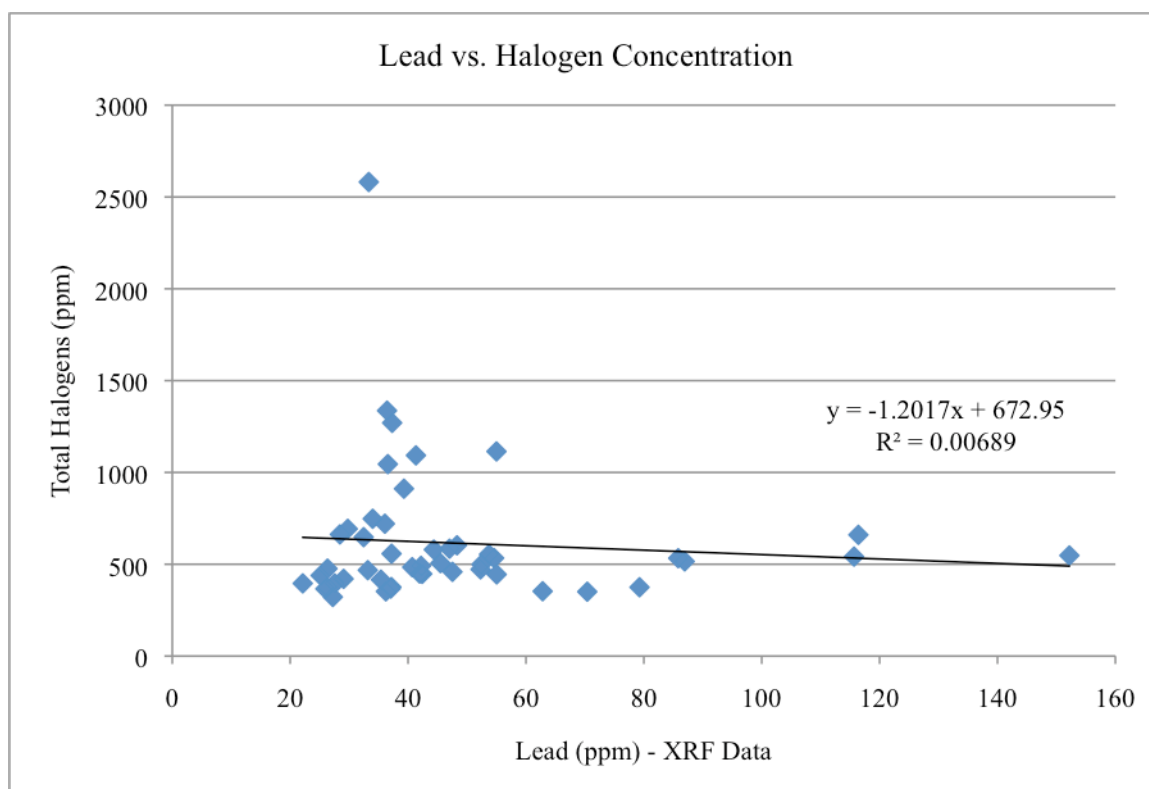Figure 4. Spatial distribution of chlorine concentrations in ppm given by XRF analysis.

Figure 5. Regression of lead concentration vs. total halogen concentration. Lead XRF data was used to avoid differences in concentration due to different extractabilities of the lead compounds. Total halogen concentration was obtained by adding chlorine and bromine concentrations.

Soil samples were analyzed for lead using X-ray fluorescence (XRF) and atomic absorption spectroscopy (AA). XRF results showed lead concentrations ranging from 22.1 – 152.2 ppm with an average of 48.0 ± 7.4 ppm (Table 1, Fig. 1). AA results showed lead concentrations ranging from 5.9 – 94.8 ppm, averaging at 20.6 ± 5.0 ppm (Table 2, Figure 2). While XRF is able to measure the total lead concentration in each sample, AA is only able to measure the portion of lead that is extractable. On average, 40.9% ± 6.3% of the lead in the samples is extractable under the given sample preparation conditions (Table 3). There was one sample (Sample 38) in which AA yielded a higher concentration than XRF, giving a value of >100% extractability. The lead concentration given by AA for this sample had a very large confidence interval, which included zero. This is likely due to contamination of replicates.

XRF analysis was used to measure both the chlorine and bromine concentrations in the soil samples. Bromine levels ranged from 2.1 – 42.6 ppm, averaging at 10.0 ± 2.1 ppm (Table 4, Fig. 3). Chlorine levels ranged from 315.5 – 2567.3 ppm, averaging at 605.2 ± 110 ppm (Table 5, Fig. 4). There is no correlation between lead concentration and total halogen concentration in the soil samples (R^2 = .0069, Fig. 5).

Conclusions

None of the soil samples had concentrations of lead exceeding EPA standards and therefore should not pose a health risk to the surrounding community. This sample set, however, is limited to the southeast perimeter and public parking lot of the airport. Contamination is likely to be higher inside the airport fence line and closer to the runway, fueling stations, and airplane hangars. While the surrounding community may not be at risk, the people who work at and use the airport may be.

The samples with the highest observed lead concentrations

tend to be from the west side of the airport, where the fueling station and many airplane hangars are located. This can be accounted for by pilots checking or emptying fuel tanks as well as by actual fueling. The eastern fence line, located behind the runway, carries moderate levels of lead content. Engine power, and therefore pollutant emissions, is highest during takeoff and climbout, explaining the elevated lead concentrations behind the runway.[15] The southeast corner at the bottom of the map presents the smallest amount of lead contamination. This area is relatively distant from the runway, fueling station, and hangars, thus providing little opportunity for contamination.

While there is no correlation between the lead concentration and total halogen concentration between each sample, roughly similar deposition patterns may be observed by looking at the maps, particularly in the chlorine map. The bottom southeast corner of the airport has very little contamination, while the west and east sides have higher concentrations, which suggests that the source of these halogens is, in fact, the avgas. Differences in lead and halogen concentrations in the soil may be due to differences in mobility and reactivity of the species in this environment: when lead halides are exposed to sunlight, photolysis occurs and releases free halogens into the air, while the lead remains in the soil.[16] If certain areas of the airport receive more sunlight than others, such as the open field, halogens will be more readily released and their concentrations in the soil will differ.

It is recommended that further research be conducted inside the perimeter of the airfield. In addition, soil contamination is only one facet of the impact of avgas emission; studies performed on air quality around airports indicate elevated levels of harmful pollutants such as ultrafine particles,[17] while combustion of aviation fuel contributes to rising levels of greenhouse gases.[18]

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