Kamloops Air Pollution: Sampling and Characterization of Metals in $PM_{2.5}$

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Fall 19 -Winter 20

Background


Mt. Paul Industrial Park


Sunrivers


TRU Weather Station

Air Sampling

Air samples and particulate matter

- Air quality is affected by weather conditions like temperature, **precipitation**, and **wind speed**, **topography** and **air pollutants**[1].
- Atmospheric particulate matter (PM) is small solid or liquid particles suspended in the air.
- Particulate matter **< 2.5 µm in diameter** ($PM_{2.5}$) can move deep in the respiratory system[1].
- Ambient $PM_{2.5}$ air pollution is attributed to causing *4.2 million deaths globally in 2016*, including strokes, heart disease, lung cancer, respiratory infections (pneumonia) and chronic obstructive pulmonary disease[2].
- Industry, fossil fuel combustion, residential wood-burning and transport are the main anthropogenic sources of primary particulates and gaseous precursors of secondary particles
- Chemical characteristics of air samples can vary greatly depending on emission sources, dispersion conditions, atmospheric reactions and air masses transported from nearby areas[3]. Trace metals can bind to PM, such as As, Cd, Cu, Pb, and Zn, which will be analyzed further

Air sampling locations

- Residential (Sunrivers) and industrial (Mt. Paul) locations on the KIB reserve were selected. TRU location was chosen for comparison.
- Nearby industries in Mt. Paul include Ecopave Systems, M3 Steel Structures Absorbent Products, Van Kam Freightways LTD, King Transport, Kamloops Glass, Mansini Steel Manufacturing and Trick Transport

Table 1: Sampling locations and dates

Sample	Location	Date
1	Mt. Paul	30-Jan-20
2	Sunrivers	11-Dec-19
3	TRU	14-Feb-20
4	Sunrivers	28-Jan-20
5	Mt. Paul	03-Feb-20
6	Sunrivers	02-Jan-20
7	TRU	03-Feb-20
8	Sunrivers	29-Jan-20
9	Sunrivers	12-Dec-19
10	TRU	20-Feb-20
11	Sunrivers	13-Feb-20
12	Mt. Paul	31-Jan-20
13	Sunrivers	14-Feb-20
14	Sunrivers	23-Jan-20
15	Mt. Paul	27-Jan-20
16	Sunrivers	15-Jan-20

Chemical Characterization

Flame atomic absorption spectroscopy (FAAS) analyzes elements using the absorption of optical radiation by free metallic ions and can determine the concentration of **individual elements** in a sample by using the **Beer-Lambert Law:**

Absorbance = ε ℓ c

Where **ε =** molar attenuation coefficient ≈ 1, ℓ = optical path length = 1 and **c = analyte concentration in solution**

Flame atomizes the sample, which is irradiated by a light source. The radiation passes through a monochromator, separating the radiation at a specific wavelength and is measured with a detector.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) can analyze multiple elements sequentially with high sensitivity, stability and low interference[4]. Electromagnetic induction produces currents of energy for the plasma to excite atoms. Emission rays are released when atoms return to low energy state, and their intensity corresponds to the concentration of each atom (element). OES uses grating for diffracting emission rays through a prism to the CCD detector.

Methodology

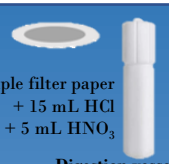
Sampling

1) The initial masses of the filter papers were weighed on a 5-decimal balance.

2) $PM_{2.5}$ air samples were collected through a 2.5 µm screen for **~24 hours** onto cellulose filter papers. Final mass was recorded.

MiniVol Tactical Air Sampler provided by **Tk'emlups Indian Band**

Sample preparation

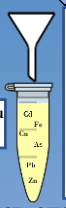


Digestion vessel

Anton Paar Multiwave GO

3) Aqua regia was used to carry out the digestion. A **reagent blank** and **filter paper blank** were used. A custom microwave program was used, ramping the digestion up to **170°C** and holding for **15 minutes.**

4) Samples are filtered with a Whatman 40 qualitative paper. The digestion destroyed organic matter, allowing the metal ions exist freely in solution. Venting has occurred in this exothermic reaction, causing volumes to evaporate out—exact volumes were recorded.

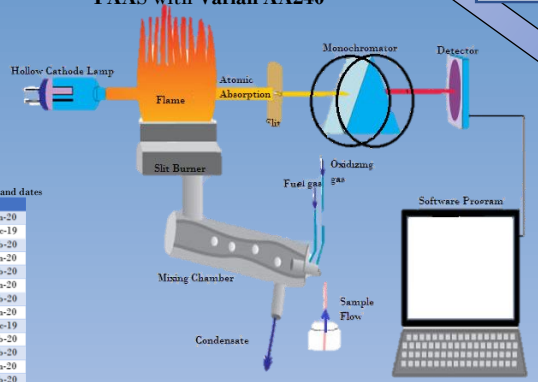


Chemical Characterization

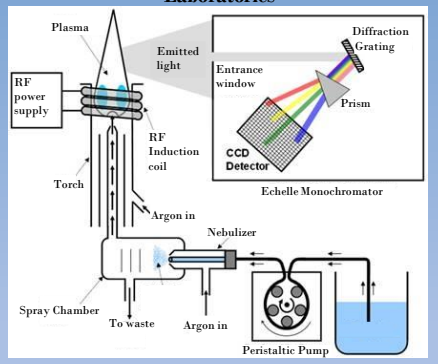
Cd

***Pb*, *As*,** Zn, Fe, Cu
Diluted 5x

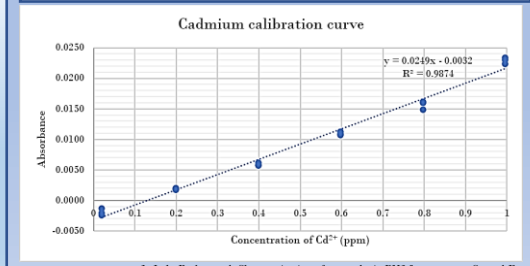
FAAS with Varian AA240



ICP-OES with **Thermo Scientific iCAP 6000 series** provided by **Base Metallurgical Laboratories**



5) Samples 14-16 were analyzed for **Cd** using **FAAS**. Cadmium (II) standards were made from $Cd(NO_3)_2$, and sample results were calculated from the slope of the calibration curve. All standards and samples were read in triplicate. Further analysis is needed.



6) Samples 1-13 were transported to **Base Metallurgical Laboratories,** where they were **diluted 5x** and analyzed sequentially for **Pb, As,** Zn, **Fe** and **Cu** using **ICP-OES**. Calibration standards and quality checks were used, and rinses between high standards and samples were used to reduce memory effects. Concentrations of *Fe* and *Cu* were *below* the known *detection limit*, and *Zn* values were unusable; all were *omitted from the results*. The instrument reported concentrations in ppm in solution, which was calculated back to g [Element] / g sample.

References:

1. Juda-Rezler et. al. Characterization of atmospheric PM2.5 sources at a Central European urban background site. 2020. *Sci. Tot. Enviro.* 713. DOI: 10.1016/j.scitotenv.2020.136729
2. Osserein, N. 9 out of 10 people worldwide breathe polluted air, but more countries are taking action. 2018. WHO, PHE. https://www.who.int/news-room/detail/02-05-2018-9-out-of-10-people-worldwide-breathe-polluted-air-but-more-countries-are-taking-action
3. Holnicki et. al. Air quality modeling for Warsaw agglomeration. 2018. *Arch. Environ. Prot.*, 43 (48-64) DOI: 10.1515/aep-2017-0005.
4. Principle of ICP Optical Emission Spectrometry (ICP-OES). Hitachi High-Tech GLOBAL. Retrieved Feb 14, 2020 at: https://www.hitachi-hightech.com/global/products/science/tech/ana/icp/descriptions/icp-oes.html#top

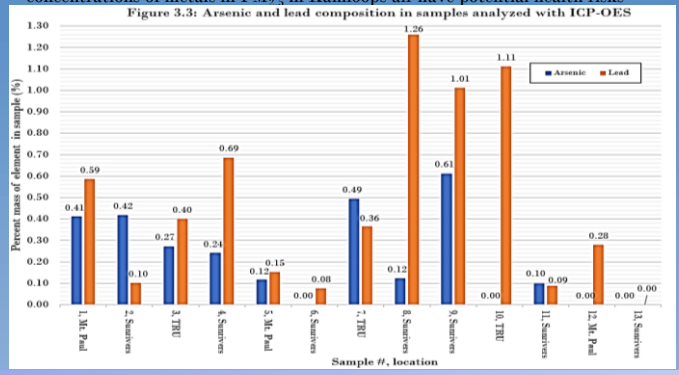
Results

Table 2: Percent of arsenic, lead, copper, iron and cadmium in samples

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	Average
Mass (10^{-4} g)	2.8	4.1	6.2	1.8	8.0	1.8	3.9	1.4	0.1	1.6	1.8	4.1	3.1	**3.13**
Arsenic %	0.41	0.42	0.27	0.24	0.12	<LOQ	0.49	0.12	0.61	<LOQ	0.10	<LOQ	<LOQ	**0.31**
Lead %	0.59	0.10	0.40	0.69	0.15	0.08	0.36	1.26	1.01	1.11	0.09	0.28	<LOQ	**0.51**
Copper %	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**<LOQ**
Iron %	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**<LOQ**

Sample	14	15	16	Average
Mass (10^{-4} g)	4.3	2.9	1.5	**2.90**
Cadmium %	<LOQ	<LOQ	<LOQ	**<LOQ**

- The absorbances for cadmium (FAAS), copper and iron (ICP-OES) were **below the probable (LOQ).**
- Contamination caused zinc results to be discarded.
- Percent mass of sample for arsenic and lead were calculated and plotted below, with 0-values given for those that were below the probable LOQ.
- The highest concentration of metals were 1.26% lead (sample 8) and 0.61% arsenic (sample 9), and the samples averaged **0.51% lead** and **0.31% arsenic.**
- **Development of a robust method for trace metal determination is needed** to show concentrations of metals in $PM_{2.5}$ in Kamloops air have potential health risks



Discussion and recommendations for future work

More samples from each location are needed to determine if air quality varies by location—not enough data is present to distinguish industrial and residential locations. Furthermore, samples taken at the same time, in the same weather conditions would produce more comparable results; these samples, however, should be looked at individually, as isolated events. Windy, rainy and snowy days should be avoided in the future because they affect the air intake. To have a more accurate estimation of missing masses, a larger sample number would allow the inverse-distance-weighting method to be used. Missing masses occurred when the sample paper would stick to the inside of the sampling tube, leaving pieces behind when removed, skewing the actual sample mass. An improved technique for paper-collection would reduce loss of mass, giving an accurate final sample mass. In the future, flow rate calibration should be included to estimate the volume of air being sampled over 24 hours. Filter papers should be removed and weighed immediately, and it may be advisable to standardize their moisture contents.

Great care was taken to avoid contamination during sample preparation. Samples were digested and had to be filtered to remove remaining filter paper. An optimized sample digestion should be developed, because upon visual inspection, there appeared to be sample left on the discarded filter papers. This may have produced low results.

Detection limit was an issue in reporting results: FAAS results for cadmium were too close to the LOD and used a lot of sample, whereas the ICP-OES would have been more ideal, but it is new and needed more time to develop methods for these trace results. If zinc contamination on the samples persists, investigation into the causes would be valuable.

Acknowledgements

I would like to thank **Kingsley Donkor** and **Marten Lettinga** for all their guidance in this research project; **Johanna Hales** and the **T'kemlups Indian Band** for permitting the use of their air sensors and; **Jessica Marten** and **Base Metallurgical Laboratories** for the training and use of their ICP-OES.