

Elemental Analysis of Aviation Fuel and Aircraft Soot Particles

Hlayiseka M Yingwani^{1,2,3}, Johannes H Potgieter^{3,5}, Sanja Potgieter-Vermaak^{4,5}

¹School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg, hlayiseka.yingwani@gmail.com

²Levego Environmental Services Pty (Ltd), Building R6 Ardeer Road, Modderfontein, 1645

³School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg

⁴Molecular Science institute, School of Chemistry, University of the Witwatersrand, Johannesburg

⁵Ecology and Environment Research Centre, Department of Natural Sciences, Manchester Metropolitan University, Manchester

Aircraft soot emissions contribute significantly towards the state of local air quality. Therefore, the study of the chemical composition of aircraft soot is important in understanding the environmental interactions and human health impacts thereof. In this study, the elemental composition of AVGAS 100LL, Jet A-1 and soot samples collected from various aircraft engine exhausts were investigated using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). The target metals for elemental analysis on both the soot and fuel samples were iron (Fe), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn). These are metals that are normally present in the materials used for constructing aircraft engine parts, in the aircraft fuel and in the engine lubricants. In general, there is a clear difference between the elemental composition of piston engines soot and that of the other engine types investigated in this study. Most noticeable in this study is that the metal concentrations, except for Zn, were at least an order of a magnitude higher in samples collected from the Continental-RH LT-STO-360-E, Lycoming O-320 and Lycoming O-235 piston engines than the soot collected from the other engines (Rolls Royce SPEY 511-8 turbofan engine, PT6A-42 turboprop engine, and the Rolls Royce Allison 250C20B turboshaft engine). Significantly high levels of Pb were measured in soot samples collected from piston engines, with the highest concentration of 6161.11 mg/L measured in the Lycoming O-320 soot sample. The high levels of Pb observed are not unexpected because piston engines are powered by AVGAS 100LL which contains a lead additive. Elemental analysis conducted on the fuel samples yielded metal concentrations that were below the limit of quantification (LOQ) on both fuel samples, except for Pb which yielded a result of 196.9 mg/L in AVGAS 100LL. It is evident from the soot analysis results that a significant concentration of metals is released during landing and take-off (LTO) activities, and that the concentration is highly dependent on the type of the engine and fuel.

Keywords: Aircraft soot, Aircraft Engine, Aviation fuel, AVGAS 100LL, Jet-A1, Elemental analysis, LTO

1. Introduction

Air transportation plays an important role in international mobility. This industry is estimated to have a fast annual growth of approximately 5%, with the developing countries being in the forefront (Masiol & Harrison, 2014). The current and projected growth in the use of air transportation dictates the increase in aviation related air pollution (Masiol & Harrison, 2014; Psanis et al., 2017). Due to this increase, aviation air pollution has gained particular attention in recent years, triggering the need for more stringent industry-wide emission controls to be instituted (Simonetti et al., 2015; Yu et al., 2017).

The efforts to lower impacts of aviation emissions have triggered the venture into synthetic aviation fuel

in recent years. Synthetic aviation fuel is required to comply with ASTM D1655 - "Standard Specification for Aviation Turbine Fuels" and ASTM D7566-19 – "Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons" (ICAO, 2017).

Aircraft soot emissions contain metals, which could potentially be toxic to humans (Kinsey et al., 2011). The source of metals in aircraft engine soot is from fuel additives and impurities, wear and tear of engine components, lubricants, and rust.

Emissions from aircraft engines can be classified through the study of the combustion of the fuel used in the engine (Jasiński, 2019; Vennam et al., 2017). The process of separating and apportioning the local

emissions to aviation is difficult due to several factors. Ambient emissions resulting from other activities such as motor vehicle traffic within and around the airport contribute to some degree towards the state of air quality (Arunachalam et al., 2011; Vennam et al., 2017). Chemistry-transport models have been used in certain studies in the quest to understand “the physics of the aerodynamics of aircraft plumes” (Arunachalam et al., 2011; Cameron et al., 2017; Jasiński, 2019; Vennam et al., 2017). There are limited studies conducted at cruise altitudes due to the complexities of the measurements caused by the nature of the source, the moving aircraft, limiting the data to a few commercial sampling campaigns (Vander Wal et al., 2016).

Landing and Take-Off (LTO) cycle refers to the activities that take place within the airport, up to the altitude of 915 meters (3000 ft) above ground level (Balli, 2022). LTO operations are the biggest contributor to air pollution at airports and the surrounding areas (Levy et al., 2012). According to Zhu et al. (2011), soot emissions are highest during the LTO cycle, and the concentrations are likely to increase at busy airports or during peak-time (Cameron et al., 2017; Phoenix et al., 2019; Vennam et al., 2017). The high concentrations of soot could have an impact on the air quality in the airport surroundings, which in turn could impact on the well-being of ground personnel and the surrounding communities (Yim et al., 2015).

Some metals are necessary for physiological and biochemical functions in the human body. Cr, Cu, Fe, Ni and Zn form part of the metals needed for the normal functioning of the human body at lower concentrations (Briffa et al., 2020). Metals are not biodegradable and cannot be broken down. Consequently, their intake through ingestion or inhalation may result in bioaccumulation, which can have detrimental effects on human health (Briffa et al., 2020).

Zn is involved in wound repair, blood pressure regulation, the normal functioning of the immune system and the synthesis of insulin (Freire et al., 2019; Lin et al., 2017). However, elevated levels of Zn could result in cardiovascular diseases and even cancer (Eide, 2011; Lehvy et al., 2019). Cu, Fe, Cr and Ni can produce reactive radicals which can damage the DNA (Briffa et al., 2020; Islam et al., 2021). Therefore, the monitoring of soot is essential in preventing their negative impacts on the health of airport staff and the surrounding communities.

According to Hudda et al. (2014) the impact of emissions from aircraft exhaust can be distributed over a horizontal range of greater than 16 kilometres, thereby impacting on humans and the environment well beyond the perimeter of the airport. Pb in the air surrounding the airport is likely to be inhaled by

airport staff and people living within a 1 km radius of the airport or ingested once it settles into the soils resulting in lead poisoning.

This study investigates the elemental composition of aviation fuel and soot samples collected from various aircraft exhaust engines. AVGAS 100LL and Jet-A1 are the only types of fuel used at Lanseria International Airport, hence their use in this investigation. The soot samples investigated in this study are regarded as composite samples, therefore the results are applicable on ground level, LTO and at cruise altitudes.

2. Methods

A quantitative approach was employed for the purposes of achieving the aims of this study.

2.1 Soot samples

The soot samples were collected from the following aircraft engines; Continental-RH-LT-STO-360-E piston engine, Lycoming O-320 piston engine, Lycoming O-235 piston engine, Rolls Royce SPEY 511-8 turbofan engine, PT6A-42 turboprop engine, and the Rolls Royce Allison 250C20B turboshaft engine. The choice of the aircraft engines sampled ensured that there is representation for the two types of the fuel (AVGAS 100LL and Jet A-1) investigated in this study. All the piston engines where samples were collected are powered by AVGAS 100LL whereas the turbofan, turboshaft and turboprop engines are powered by Jet-A1. A single sample per engine was collected into petri dishes using clean nylon brushes. The samples were labelled on site and transported to the University of the Witwatersrand for analysis.

The soot samples were prepared by accurately weighing each soot sample on a ST-1508 - Preciso HC5003X Precision Balance. Each weighed sample was digested for 4 hours in a hot water bath at 90°C using a mixture of high purity water (H₂O), 40% hydrofluoric acid (HF), 32% hydrochloric acid (HCl) and 55% nitric acid (HNO₃), prepared according to the following ratio: 10:5:1:1 (H₂O:HNO₃:HCl:HF). The samples were then filtered into Teflon tubes through a whatman filter to remove any solid residue. Aliquots of 20 mL were drawn from each prepared sample using a pipette and transferred into 100 mL volumetric flasks. These were made up to the mark using deionised water.

Calibration standards were prepared by drawing aliquots of the National Institute of Standards and Technology (NIST) traceable stock solution into volumetric flasks. The concentration of the standards used for Fe, Ni, Pb, Cu and Cr were 0 mg/L (blank), 10 mg/L, 50 mg/L and 100 mg/L respectively. The concentrations of the standards used for Zn were 0 mg/L (blank), 0.1 mg/L, 0.5 mg/L and 1 mg/L. Analysis was conducted using the

Agilent 240 FS Atomic Absorption Spectrometer (AAS). The temperature of the laboratory was maintained at 25°C throughout the analysis period.

2.2 Fuel Samples

AVGAS 100LL and Jet A-1 samples (1 litre of each) were also collected in clean glass bottles and taken the University of Johannesburg for analysis. Analysis was conducted using the PerkinElmer NexION 300X ICP-MS. Due to the high volatility of the AVGAS 100LL and Jet-A1 samples, the mass of the samples were used to minimise the measurement error.

Representative aliquots of AVGAS 100LL and Jet-A1 samples of approximately 0.1 g each were drawn and transferred into 10 mL Teflon vials using micropipettes. The vials were closed and accurately weighed. Due to the hydrophobic nature of AVGAS 100LL and Jet-A1, 2-Propanol was added to make the samples more hydrophilic (Trick et al., 2014). This was followed by dilution to volume using MERCK suprapure 2% HNO₃. The PerkinElmer NexION 300X ICP-MS was put on Kinetic energy discrimination (KED) mode during analysis. The KED mode reduces the polyatomic interferences derived from plasma or vacuum interface in the instrument (Yamada, 2015). The instrument was calibrated using NIST traceable calibration stock solutions. The concentrations utilised for Fe, Ni, Cu, Cr, Zn and Pb were 0 µg/L (blank), 0.1 µg/L, 1 µg/L and 10 µg/L.

3. Results and Discussion

All the results in this study are reported at 95% confidence level. The limit of quantification (LOQ) for each metal was determined on the PerkinElmer NexION 300X ICP-MS and the Agilent 240 FS Atomic Absorption Spectrometer. The LOQ values are shown in Table 1.

Table 1: LOQ values for the PerkinElmer NexION 300X ICP-MS & Agilent 240 FS Atomic Absorption Spectrometer

Metal	AAS (mg/L)	ICP-MS (µg/L)
Fe	0.42	0.01
Cr	4.94	0.00
Ni	0.92	0.01
Pb	10.36	0.01
Cu	1.30	0.01
Zn	4.39	0.21

3.1 AVGAS 100LL and Jet-A1 elemental analysis

The regression coefficients of the calibration curves were above 99%, which shows excellent correlation. The relative accuracy and bias of the PerkinElmer NexION 300X ICP-MS was determined by analysing the NIST Standard reference material (SRM) 1640a. The results are presented in Table 2.

Table 2: Relative accuracy and bias for PerkinElmer NexION 300X ICP-MS

	Measured Value	Certified Value	% Accuracy	% Bias
Fe	42.13	36.80 ± 1.80	114.5	+14.5
Cr	42.10	40.54 ± 0.30	103.8	+3.8
Ni	26.89	25.32 ± 0.14	106.2	+6.2
Pb	12.79	12.10 ± 0.05	104.8	+4.8
Cu	90.69	85.75 ± 0.51	105.8	+5.8
Zn	56.55	55.64 ± 0.35	101.6	+1.6

The bias on the SRM measurement results for all the metals are below 15%, which is the acceptable accuracy of the measurements.

None of the target metals were detected in the Jet-A1 sample, confirming that Jet-A1 as a cleaner fuel compared to the AVGS 100LL (Engen, 2011). A similar trend was observed on the elemental analysis results of the AVGAS 100LL fuel for all the other target metals except for Pb, which measured 196.9 mg/L (0.20 g/L). The concentration of Pb measured in the AVGAS 100LL sample is within the 0.56 g/L lead content specified in ASTM D 910.

3.2 Soot samples elemental analysis

A standard reference material was unavailable during the analysis of the soot samples. Therefore, the relative accuracy and bias tests for the Agilent 240 FS Atomic Absorption Spectrometer could not be conducted. However, the regression coefficients for the calibration curves on all the elements were above 99%, indicating a good correlation of the absorbance and concentration of metals. The results obtained from the analysis of soot samples yielded results that are consistent with the elemental composition of the fuel used by each engine. These results also provide some information on the metal composition of the materials used in constructing aircraft engine components. Figure 1 to Figure 6 show the elemental analysis results of soot samples.

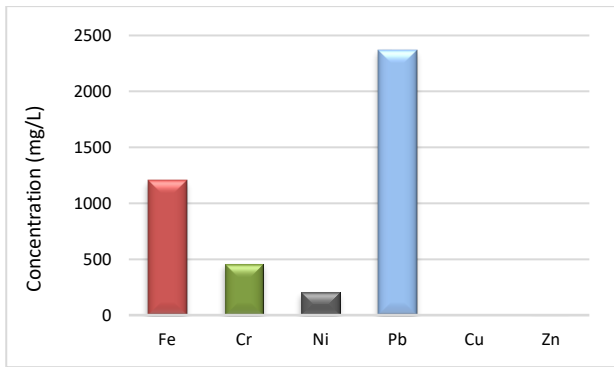


Figure 1: Metal Concentrations, Continental-RH, LT-STO-360-E Piston Engine

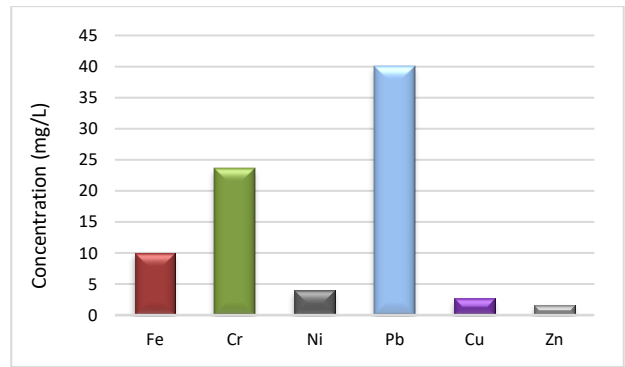


Figure 5: Metal Concentrations, PT6A-42 Turboprop Engine

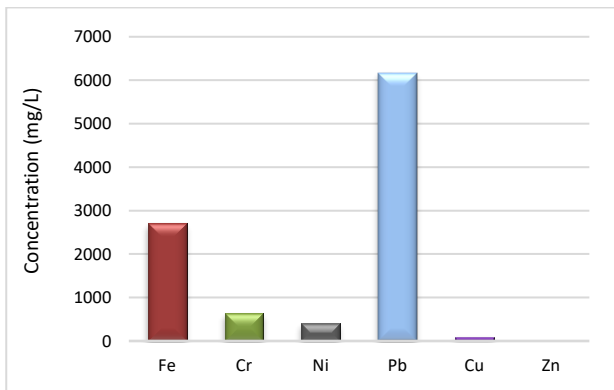


Figure 2: Metal Concentrations, Lycoming O-320 Piston Engine

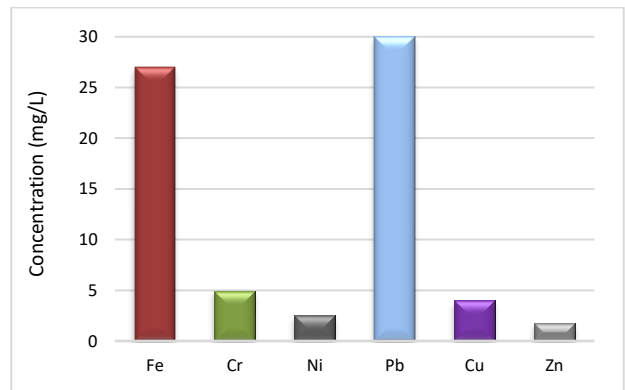


Figure 6: Metal Concentrations, Rolls Royce Allison 250C20B Turboshaft Engine

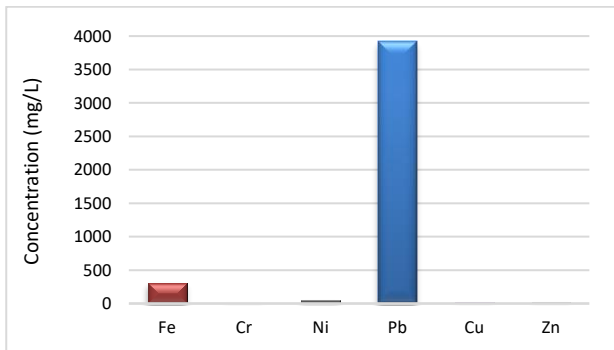


Figure 3: Metal Concentrations, Lycoming O-235 Piston Engine

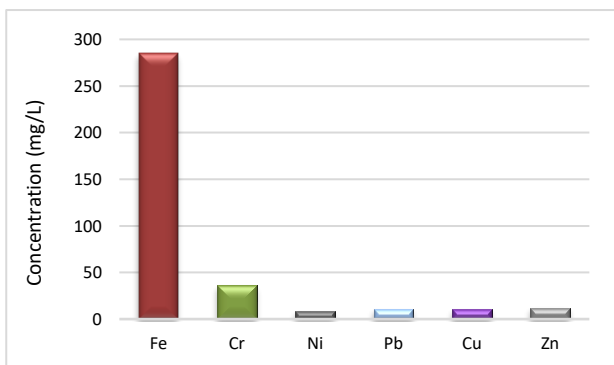


Figure 4: Metal Concentrations, Rolls Royce, SPEY 511-8 Turbofan Engine

In general, there is a clear difference between the elemental composition of soot collected from piston engines (Continental-RH-LT-STO-360-E, Lycoming O-320 and Lycoming O-235) and that of the other engine types (Rolls Royce SPEY 511-8 turbofan engine, PT6A-42 turboprop engine, and the Rolls Royce Allison 250C20B turboshaft engine). Fe, Cr, Ni, Pb, Cu and Zn were detected in all the soot samples except for Cr in the Rolls Royce Allison 250C20B, and Pb in the Rolls Royce SPEY 511-8 engines which were below the LOQ. The range of metals detected in soot samples is consistent with the results obtained by Turgut et al. (2019). Other studies where a similar composition of elements was measured in aircraft soot include Mazaheri et al. (2013), Abegglen et al. (2015), Van der Wal et al. (2016) and Kinsey & Hays (2011).

Most noticeable in this study is that the metal concentrations, except for Zn, were at least an order of a magnitude higher in samples collected from the Continental-RH, LT-STO-360-E, Lycoming O-320 and Lycoming O-235 piston engines than the other soot samples. The soot collected from the Lycoming O-320 piston engine indicated very high concentrations of potentially toxic compounds, as well as elements prone to cause oxidative stress upon inhalation (Bendtsen et al., 2021). Considering the concentrations of metals measured from the soot

samples, it is evident that there will be a potential human health risk upon inhalation and that this risk is dependent on the engine type.

Mechanical fatigue, wear and tear are specific areas of attention in the manufacture of alloys used in aviation (Bernasconi et al., 2020; Maniam & Paul, 2020). This is due the consequences related to structural failure, which may result in multiple fatalities. Addition of 1% Fe or less to alloys used in engine components construction helps in suppressing die soldering and improves high temperature strength of the alloy (Yamasaki et al., 2019). This is seen through the high concentration of Fe in some of the soot samples. The highest concentrations of Fe were measured in samples collected from the Lycoming O-320 and Continental-RH LT-STO-360-E piston engines, measuring 2704.91 mg/L and 1200.15 mg/L respectively. The lower concentrations of Fe measured in the soot collected from the PTA-42 and Rolls Royce Allison 250C20B engines is confirmation of the observations made during sample collection, that the turboprop and turboshaft engines were in a much better condition than the other engines.

Alloys are susceptible to intergranular and pitting corrosion (Hughes et al., 2011; Singh et al., 2016), which exposes the inner layers of the alloy. The reaction of Fe, water and air results in corrosion, which can be carried out through the engine exhaust together with soot emissions (Yamasaki et al., 2019). Cr is added to the alloy to limit intermetallic coarsening by lowering the rate of precipitation in the area where two metals are joined together, which strengthens the grain boundaries (Ribeiro et al., 2020).

To improve the corrosion resistance of an alloy in extreme environments such as aircraft engines, significant efforts have been made to improve the anti-corrosive properties. Cr coating is also applied on the alloy surface to improve corrosion resistance (Boyer et al., 2015). The soot samples collected from the Lycoming O-320 and Continental-RH LT-STO-360-E engines recorded the highest concentrations of Cr, 641.17 mg/L and 457.94 mg/L respectively, while the other engines recorded very low concentrations. The application of Zn alloy coatings such as Zn-Ni, Zn-Cu and Zn-Fe is another way of improving corrosion resistance. These alloy coatings have better corrosion resistance compared to pure Zn coating (Anwar et al., 2018). Cu-Zn coatings are also often used to increase metallic lustre, structure, and surface roughness. Low concentrations of Zn and Cu were measured across the soot samples collected from the different aircraft engines, except for the soot sample collected from the Lycoming O-320 engine, which measured 92.67 mg/L. This could be because of wear tear on the engine components.

Ni is added during the alloy manufacturing process to improve the strength and to increase the oxidation resistance (Esleben et al., 2019; Klein et al., 2013). The highest concentration of Ni was measured in the samples collected from the Lycoming O-320 and Continental-RH LT-STO-360-E engines, measuring at 406.19 mg/L and 205.56 mg/L respectively. The high levels of Ni may be an indication of the age of the engine components, and wear and tear resulting from the multiple moving parts in the piston engines. It is important to indicate that a build-up of rust was observed in the Continental-RH LT-STO-360-E and Lycoming O-320 exhaust systems. These two engines have the highest concentrations of metals measured in their soot samples.

Pb concentrations measured in soot samples provide an indication of the fuel used in each of the engines. Figure 7 shows Pb concentrations measured from the various engine soot samples.

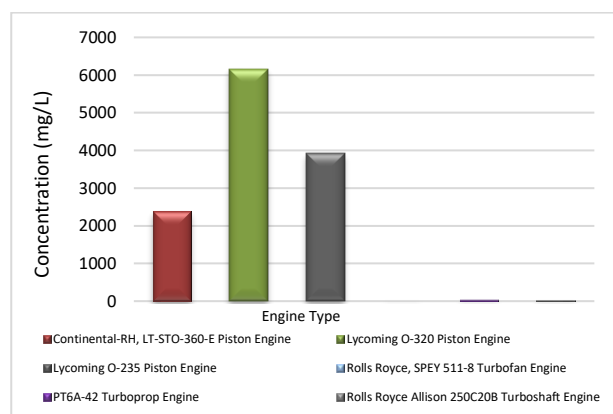


Figure 7: Lead (Pb) Concentrations for the various aircraft engines

The concentrations of Pb measured from the Rolls Royce SPEY 511-8 turboprop, PTA-42 Turboshaft and Rolls Royce Allison 250C20B Turboshaft engines soot samples were <10.36 mg/L, 40.13 mg/L and 30.00 mg/L respectively. These concentrations are significantly lower than those measured in soot samples collected from piston engines. The samples that yielded lower Pb concentrations were collected from the engines that are fueled by Jet-A1, whereas the higher concentrations of Pb were measured in samples collected from piston engines, which are fueled by lead containing AVGAS 100LL.

Pb is an ingredient in the alloys used in the construction of aircraft engine components. Therefore, the presence of Pb in the soot samples could be due to wear and tear from the moving engine parts. The high concentration of Pb detected in the soot samples collected from piston engines is consistent with the results obtained in the analysis of the fuel samples. These Pb results are also

consistent with the findings of Miranda et al. (2011) on lead contamination in the area surrounding the airport in Turkey, which recorded the highest concentrations closer to the highways. Miranda et al. (2011) also measured higher Pb concentrations downwind of the airport than upwind, suggesting a possible influence of prevailing meteorological condition on the dispersion of pollutants.

4. Conclusion and recommendations

Elemental analysis results of AVGAS 100LL and Jet-A1 samples yielded concentrations that were below the LOQ for all the target metals, except for Pb (196.9 mg/L) measured in AVGAS 10LL. This is consistent with the specifications of Pb in AVGAS 10LL and Jet-A1.

A clear distinction between the soot collected from piston engines and that of the other engine types was observed. Generally high concentrations of metals except for Zn, were measured in soot samples collected from piston engines. Significantly high concentrations of Pb were measured in soot samples collected from piston engines. This is not unexpected because piston engines are powered by lead containing AVGAS 100LL. The level of metals measured in the soot samples are concerning. These metals could react with other species in the atmosphere to form potentially toxic compounds which may affect the health of airport staff and the surrounding community.

Studies conducted to investigate the impact of alternative fuels have shown reduced particulate matter emissions when used alone and when blended with conventional fuel (Brem et al., 2016; Pires et al., 2018; Saffaripour et al., 2011; Schripp et al., 2022). The possible use of alternative fuel is therefore recommended to potentially replace AVGAS 100LL so that the emission of lead into the atmosphere is reduced.

Engine oil and lubricant additives contain traces of the metals that may have significant contribution to the composition of aircraft soot emissions. The analysis of these components is also recommended to establish their contribution to the elemental composition of soot emissions.

Studies on dispersion modelling of emissions have shown that the prevailing meteorological conditions have a great influence in the movement of soot particles and other emissions produced from aircrafts. In situ studies to determine the dispersion of pollutants throughout all seasons of the year is recommended. This study could also consider other sources of pollution at the airport. The data obtained could also be integrated into a dispersion model that will predict the movement of airport related emissions in the atmosphere.

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