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Chemical Characterization of Water-soluble Ions and Metals in Particulate Matter Generated by a Portable Two-stroke Gasoline Engine

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ABSTRACT

To examine the characteristics of water-soluble ions and metals on the particulate matter (PM) in the exhausts, a P2SGE (portable two-stroke gasoline engine) was fueled by unleaded gasoline #92 blended with different two-stroke engine oil brands (*CPC Super Low Smoke Two-Stork Engine Oil* (SLS), *CPC Low Smoke Two-Stroke Engine Oil* (LS), and *MERCURY STAR* (MS)) and operated under idling, mid-load (1.5 kW), and high-load (1.9 kW), respectively. Experimental results reveal that the PM mass concentrations in the exhausts were in the order MS (avg. 1,934 mg Nm^{-3}) > SLS (avg. 1,543 mg Nm^{-3}) > LS (avg. 1,167 mg Nm^{-3}) in all test conditions. The mass concentrations and emission factors (EFs) of PM decreased as the P2SGE load increased by adding each tested lubricant. Based on fuel consumption, EFs of ΣIons were the lowest when utilizing the LS additive (avg. 89.7 mg L-fuel^{-1}), followed by the MS and SLS (165 and 168 mg L-fuel^{-1}, in average, respectively); whereas the lowest levels of ΣMetals were observed by using MS additive (avg. 61.3 mg L^{-1}), followed by using the LS (avg. 83.8 mg L^{-1}) and SLS (avg. 85.2 mg L^{-1}). The soluble ions on the PM were mostly Na^+, Ca^{2+}, NO_3^-, and SO_4^{2-} among eight tested species, which accounted for only 0.05–0.19% (avg. 0.1%) of PM mass. The 21 analyzed metal components represented only 0.05% of the mass of the PM, and were dominated by Na, Mg, Al, K, Ca, Fe, and Zn, which represented 98.7% by mass of ΣMetals. Our finding for portable engine emission has been rarely considered in the literature but it is unneglectable for labors who are usually exposed to the ions and metals. Further health risk assessment research is suggested to include temporarily real-life exposures with high pollutant levels.

Keywords: Portable two-stroke gasoline engine, Particulate matter, Water-soluble ions, Metals, Environmental pollution

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1 INTRODUCTION

The internal combustion engine (ICE) is one of the greatest inventions in history. It has a high thermal efficiency and high power output and enables vehicles to travel at high speed (with good maneuverability). Since the mid-19th century, ICEs have been used around the world. Almost all motor vehicles, agricultural machinery, engineering machinery, and even power generation equipment, use internal combustion engines to generate power. The working principle of the ICE is that burning fossil fuels (including gasoline, diesel, kerosene, and natural gas) inside the machine releases chemical energy, which is converted to mechanical kinetic energy. This process can provide huge amounts of energy for various activities, but it generates many harmful air pollutants (such as fine particulate matter ($PM_{2.5}$), traditional pollutants, organic/inorganic component species, and even toxic compounds) (Lin *et al.*, 2008; Tsai *et al.*, 2018; Lin *et al.*, 2020). Furthermore, when the high-temperature exhaust from an ICE have been discharged into the lower-temperature atmosphere, the low-volatility substances (such as H_2SO_4) therein may undergo gas-to-particle conversion (nucleation and coagulation reactions); thus, many ultrafine particles with aerodynamic diameters of 10–50 nm are generated (Schneider *et al.*, 2005; Beddows and Harrison, 2008), harming human health, affecting the environment, and contributing to climate change (Ramanathan and Carmichael, 2008; Hao *et al.*, 2010; Ramana *et al.*, 2010).

Generally, the particulate pollutants emitted by gasoline engines consist of mainly: (1) carbon particles after combustion, (2) solvable organic fraction (SOF), mainly from incompletely burned engine oil or fuel, and (3) combustion oxides, including sulfates, nitrates, and phosphates. A study by Sodeman *et al.* (2005) also revealed that the water-soluble ions on the PM in the exhaust might be contributed by lubricating oil. Vehicle exhaust particles have been proven to harm human health and affect the environment, such as entering a human body through breathing, polluting various environmental media with toxic substances, affecting visibility, and even accelerating global climate change (Maricq, 2007). Once those gasoline-engine exhausts containing water-soluble ions enter the human lungs through respiration, they will readily dissolve in the body fluids on the surface of the trachea due to their hydrophilicity, and thereby cause inflammation or toxicological reactions. Our earlier work showed that the particle-induced cytotoxicity [as CEC (cumene-hydroperoxide equivalent concentration)] correlated more significantly with NO_3^-, SO_4^{2-}, NH_4^+, and Cl^-, while the contents of sulfate ion (SO_4^{2-}) and nitrate ion (NO_3^-) were positively correlated with the cytotoxicity of PM_{10} in the atmosphere (Chen *et al.*, 2006). Therefore, the water-soluble ions on the PM that is emitted from two-stroke gasoline engines must be studied to reduce the hazard to operators of exposure to such emissions.

The metal content of the PM in exhausts has always been a critical issue in relation to air pollution (Lin *et al.*, 2005, 2020). Several works have suggested that the main metallic elements in lubricating oil are Ca, Zn, and Mg, while the primary non-metallic elements are P and B (Hu *et al.*, 2009; Liati *et al.*, 2015). Most of the Fe, Ni, Cu, Cr, and Sb on PM in exhausts come from the wear and tear of engine parts (Lim *et al.*, 2007; Sappok *et al.*, 2012). These trace metals are mainly associated with the compositions of lubricating oils, fossil fuels, additives, and detergents. Consequently, a higher metal content of the fuel corresponds to a higher metal content in the exhaust (Wang *et al.*, 2016). Although the non-road two-stroke gasoline engine emits fewer trace metals, metallic elements are usually tricky to decompose and accumulate in the human body and result in various toxic effects harmful to human health. A study by Chen and Lippmann (2009) found that Ni, V, Pb, and Zn were positively associated with acute cardiac function changes and high short-term mortality. Järup and Åkesson (2009) pointed out that Cd might raise the incidence of kidney disease and was detrimental to bone growth, whereas prolonged exposure to high levels of Cd even directly damaged bones. Furthermore, epidemiological and toxicological research reports have confirmed that metallic elements on PM may contribute to carcinogenesis (Lippmann *et al.*, 2006; Kawata *et al.*, 2007; Calvo *et al.*, 2013).

Studies have noted that ultrafine particles that are derived from traffic sources can cause serious oxidative pressure in human cell tissues and cause DNA damage (Bräuner *et al.*, 2007; Møller *et al.*, 2008). The International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) announced as long ago as 1989 that "gasoline engine exhaust" is a level 2 human carcinogenic factor (possibly carcinogenic to humans, Group 2B). Although many countries have set relevant emission standards for the exhausts of on-road gasoline-powered equipment (o-RGE, such as motorcycles, four-wheeled vehicles, and buses, and trucks), the emission of air pollutants from non-road gasoline-powered equipment (n-RGE, such as brush cutters, sprayers, and leaf blowers) has attracted relatively little concern. People have long been accustomed to the use of all kinds of equipment that is powered by gasoline engines to perform various economic or non-economic activities to improve work efficiency and to reduce human labor. In particular, emissions from n-RGE that is used in agricultural activities may pollute crops and fruits, increasing the risk associated with their ingestion. Therefore, attention should be paid to the potential risks to human health and the environment of emissions from n-RGE. In order to examine the emission characteristics of P2SGE, a small commonly used sprayer (*KAWAGOE*, C12E) was used herein as a testing engine. To prepare fuels for testing, unleaded gasoline #92 was used as the base oil and blended (4 vol.% two-cycle engine oil + 96 vol.% gasoline) with one of three two-cycle engine oil brands: *CPC Super Low Smoke Two-Stroke Engine Oil* (CPC-SLS), *CPC Low Smoke Two-Stroke Engine Oil* (CPC-LS), and *MERCURY STAR Two-Stroke Engine Oil* (MS). The three lubricants used in this study were the lubricating oils that are commonly available in Taiwan and are relatively inexpensive. The characteristics of water-soluble ions and metal components on PM were measured at various engine loads.

2 MATERIALS AND METHODS

2.1 Instruments and Sampling Methods

The tested small portable gasoline-powered sprayer (*KAWAGOE*, Model: C12E) was equipped with a single-cylinder, naturally aspirated, and air-cooled two-stroke gasoline engine (Model: G45H; manufactured by *Chaang Cherng* Co., Ltd., TAIWAN). The fuel oil mixing ratio (gasoline: two-stroke engine oil), set by its manufacturer, was 25: 1; the cylinder displacement was 41.5 c.c.; and the maximum horsepower was 2.2 ps.

The base oil, unleaded gasoline #92, was purchased from the CPC (Chinese Petroleum Corporation) in Taiwan. Table 1 presents the physicochemical properties of two-stroke engine oils (SLS, LS, and MS) used in this study.

The flue sampling equipment that was used in this study was consistent with US EPA Method 5. Before sampling was begun, an S type Pitot tube was used to measure the flow velocity of the exhaust gas from the engine. After calculating the flow rate, a constant-flow sampling system that was equipped with a 47 mm dia. quartz fiber filter (Pallflex Tissuqartz 2500QAT-UP) was installed downstream of the P2SGE's exhaust to gather the particle-phase samples. PM emissions were tested at P2SGE rotation speeds of 3,800 rpm (idling), 5,000 rpm, and 7,000 rpm with three fuels. For each combination of parameters, the experiment was performed three times (each sampling time = 15 min). Sampling data were collected after the engine had been run for at least 10 min. Fig. 1 shows the schematic diagram of the experimental system.

The quartz filters were pretreated before sampling by heating them in a muffle furnace in air for 2.5 h at 900°C. The filters were dried for 24 h in a desiccator at 25 ± 1°C and a relative humidity of 40 ± 5% before and after each sampling. They were then weighed on an electronic seven-digit balance (UMX2, *Mettler Toledo*) with a resolution of 0.1 µg.

2.2 Water-soluble Ion Analysis

Before water-soluble ions were analyzed, collected particles were extracted for 120 minutes from quarter sections of each quartz filter in an ultrasonic bath using 10 mL of *n*-hexane. Then, 10 mL of deionized water (specific resistance ≥ 18.3 MΩm) was added and ultrasonic extraction was conducted for another 120 minutes. Next, the n-hexane was removed by purging with ultra-pure nitrogen. Finally, each extraction solution was filtered using a C18 pretreatment column and a cellulose acetate filter in that order, and then stored in a plastic vial in a refrigerator at 4°C before chemical analysis by ion chromatography (IC) (DIONEX ICS-3000).

Table 1. The physicochemical properties of two-stroke engine oils.

Test Item	Unit	two-stroke engine oils			Method
		SLS	LS	MS	
Kinematic Viscosity @40°C	cSt	52.73	48.46	62.47	ASTM D445-17a
Kinematic Viscosity @100°C	cSt	8.20	7.83	8.90	ASTM D445-17a
Viscosity Index	–	127	129	118	ASTM D2270-10(2016)
Specific Gravity @15.6°C	–	0.8645	0.8680	0.8682	ASTM D4052-18a
Sulfate Ash	wt%	0.13	0.15	0.01	ASTM D874-13a(2018)
Total Acid Number	mg(KOH) g^{-1}	0.43	0.46	0.22	ASTM D664A-18
Total Base Number	mg(KOH) g^{-1}	2.7	2.8	0.46	ASTM D2896B-15
Carbon Residue, Rams	wt%	0.28	0.27	0.05	ASTM D524-15
Flash Point	°C	94	98	136	ASTM D92-18
Pour Point	°C	−27	−15	−24	ASTM D97-17b

Data from Tsai *et al.* (2020).

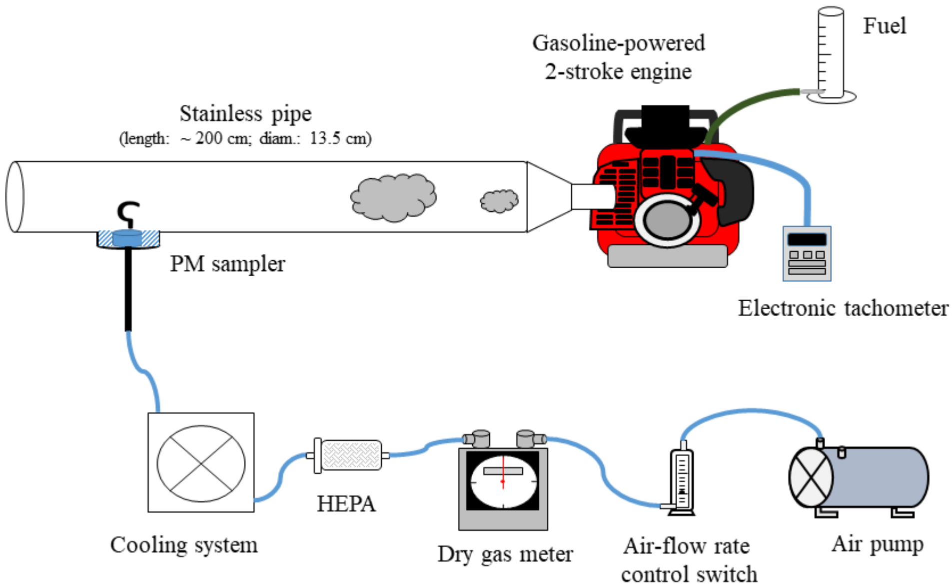

Fig. 1. Scheme of the sampling system and the P2SGE.

The method detection limits were as follows; Na^+, 0.038 ppm; K^+, 0.041 ppm; NH_4^+, 0.076 ppm; Mg^{2+}, 0.027 ppm; Ca^{2+}, 0.077 ppm; Cl^-, 0.046 ppm; NO_3^-, 0.060 ppm, and, SO_4^{2-}, 0.021 ppm. The recovery efficiencies of these ions were 92.3–114.3% based on the IC measurements. Both field and laboratory blank samples were prepared and analyzed for each sampling and analysis. All data were corrected using filter blanks.

2.3 Metal Analysis

Before the particle-bound metals had been chemically analyzed, extraction was performed on one-quarter of each quartz filter for 120 minutes using an ultrasonic bath of 20 mL 10% (v/v) HNO_3 solution. Then, each sample was heated to 85°C for 30 minutes for digestion. The digested solution was diluted to a volume of 25 mL using ultra-pure water (specific resistance ≥ 18.3 MΩcm) to identify 21 metals (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba, and Pb) by inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent, 7500 series). Calibration was conducted using multi-element (metal) standards (certified reference materials (CRMs); Spex, Metuchen, USA) in a 1% (v/v) HNO_3 solution. Every tenth sample was spiked using the liquid standards that contained known amounts of the metal elements that were analyzed. The CRMs were also used as quality control standards.

In the analyses of elements from ICP-MS measurements, the method detection limits for Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba, and Pb were 6.12, 5.22, 3.16, 19.3, 24.3, 0.36, 0.04, 0.14, 0.03, 2.22, 0.03, 0.31, 5.27, 0.31, 0.20, 0.99, 0.02, 3.15, 0.12, 0.51, and 0.06 ppb, respectively. The recovery efficiencies of 21 metals were 91.2–108.4%. Both field and laboratory blank samples were prepared and analyzed for each sampling and analysis. All data were corrected using filter blanks.

3 RESULTS AND DISCUSSION

3.1 PM Concentrations and Emission Factors in the Exhaust

Fig. 2 presents the mass concentrations and emission factors (based on fuel consumption (EF_{FC}) and output energy (EF_{OE})) of PM in the exhausts emitted from P2SGE that was operated at idling (0 kW), mid-load (~1.5 kW), and high-load (~1.9 kW) with 4 vol.% of SLS, LS, or MS as the additive in 92-gasoline. Experimental results show that the mass concentration of the PM from P2SGE was the lowest when LS was used (947–1,331 mg Nm^{-3}, with an average of 1,167 mg Nm^{-3}), followed by SLS (1,020–1,913 mg Nm^{-3}, with an average of 1,543 mg Nm^{-3}) and MS (1,289–2,405 mg Nm^{-3}, with an average of 1,934 mg Nm^{-3}) at all engine loads. Accordingly, the PM concentration

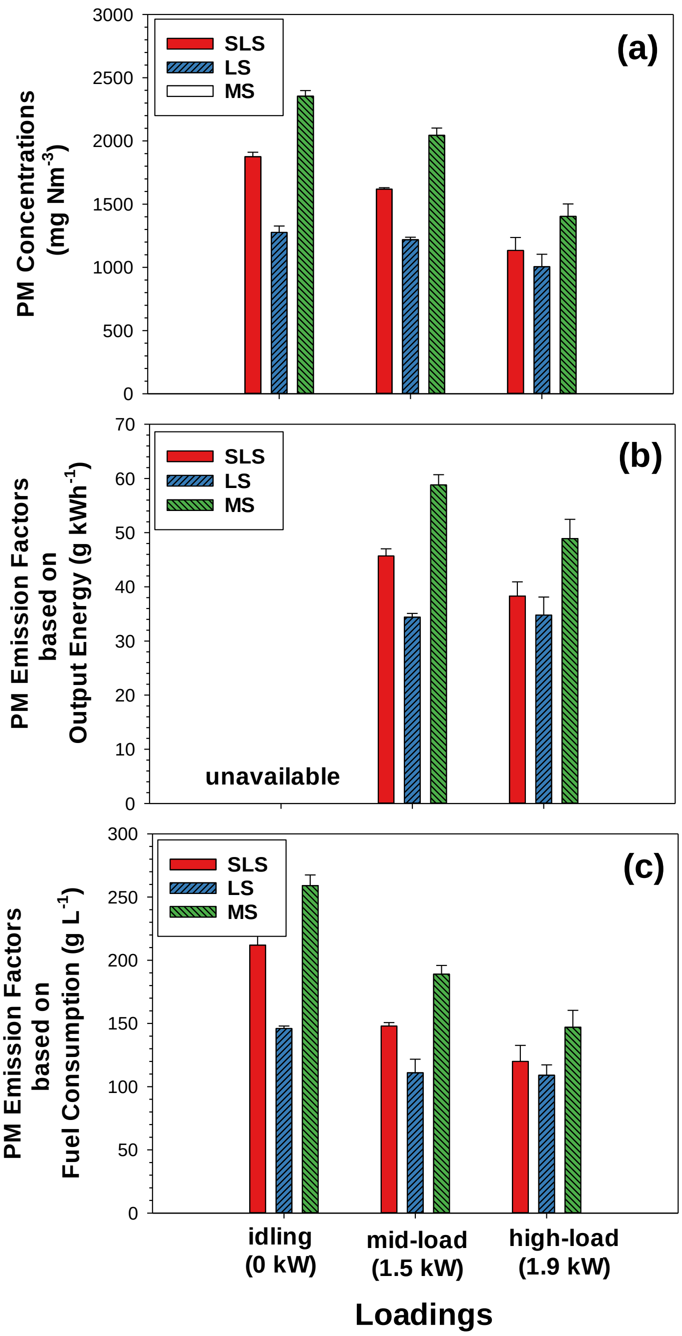

Fig. 2. Mass concentrations (a) and emission factors ((b) and (c)) of PM from a P2SGE by using SLS, LS, and MS operated at various loads.

decreased as the P2SGE load increased regardless of the lubricant used (as shown in Fig. 2(a)). Moreover, this trend was also observed for EF_{FC} and EF_{OE} (as shown in Figs. 2(b) and 2(c)). This phenomenon may be related to the sampling temperature was higher at the high-load (85–90°C) than at idling (40–45°C) and mid-load (50–55°C), and thus the P2SGE had a better combustion efficiency when operated at high-load and helped to inhibit PM formation.

Adding SLS or LS reduced the PM concentration below that obtained when MS was added at a given engine load; adding LS reduced the PM concentration (38.2%) by almost twice as much as adding SLS (20.1%), perhaps because higher flash point of MS (136°C) (as shown in Table 1) leads to less complete combustion and higher PM emission than with the other two lubricant oils, which have lower flash points (LS = 98°C and SLS = 94°C), at the same engine load (Tsai *et al.*, 2020). Generally, the flash point of oil is the lowest temperature of oil at which the application of defined test flames leads the vapors above the surface to ignition and the release of vapors at this temperature is not sufficiently rapid to sustain combustion (Ljubas *et al.*, 2010). Once the flash point of two-stroke engine oil was getting higher, it was less likely to be burned entirely (in order to protect the engine cylinder) and remained in the exhausts during the combustion process, resulting in more significant amounts of emission (as displayed in Fig. 3). On the other hand, although the flash points of SLS and LS were similar, the PM emissions of using these two fuels differed by about 30%, which was possibly associated with their different viscosities. As is well known, the higher the viscosity of the oil, the less favorable it is to be atomized, eventually leading to more PM generation during the combustion process.

3.2 Concentrations and Emission Factors of PM-bound Water-soluble Ions

The mass concentrations of ΣIons (sum of 8 ions, namely Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) on PM from the P2SGE's exhausts by using 4 vol.% of SLS, LS, or MS as the additive in 92-gasoline were 1,213–2,115 (average 1,627 μg Nm^{-3}), 660–1,047 (average 858 μg Nm^{-3}), and 1,359–1,850 μg Nm^{-3} (average 1,614 μg Nm^{-3}), respectively (Table 2). Additionally, based on fuel consumption, emission factors of ΣIons were the lowest when utilizing the LS additive (average 89.7 mg L-fuel^{-1}), followed by the MS and SLS (165 and 168 mg L-fuel^{-1}, in average, respectively) (Fig. 4). Similarly, based on output energy, the order of ΣIons magnitude was also LS (average 30.4 mg kWh^{-1}) < MS (average 55.7 mg kWh^{-1}) < SLS (average 57.7 mg kWh^{-1}). The dominant water-soluble ions among eight considered (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) on PM that emitted from the P2SGE that was fueled with different lubricants and operated at various loads were Ca^{2+}, Na^+, and SO_4^{2-}, with 20.5%, 31.4%, and 13.6%, in average, respectively, as displayed in Fig. 5. Our results are consistent with the findings of the preceding study by Yang *et al.* (2019), who found that Ca^{2+} and SO_4^{2-} dominated the $PM_{2.5}$-bound ions (K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}). Related studies have demonstrated that Na^+ and Ca^{2+} are generated by the incomplete combustion of lubricant oils (Jaiprakash and Habib, 2017), while NO_3^- and SO_4^{2-} were generated mainly by an atmospheric photochemical reaction of compounds in fossil fuel emissions (NO_x and SO_x) (Chiang *et al.*, 2012; Alves *et al.*, 2015). Moreover, Hao *et al.* (2019) identified that the primary water-soluble ion species on $PM_{2.5}$ were NO_3^-, Cl^-, Na^+, and Ca^{2+} from light-duty diesel vehicles, NO_3^-, Ca^{2+}, SO_4^{2-}, and Na^+ from heavy-duty diesel vehicles, and NO_3^-, Ca^{2+}, Na^+, and Cl^- from light-duty gasoline vehicles. In another related study conducted by Yu *et al.* (2020), they reported that the primary water-soluble ions on $PM_{2.5}$ in the exhausts from non-road construction equipment (including excavators, bulldozers, wheel loaders, stackers, road rollers, graders, and rotary drills) were NO_3^-, SO_4^{2-}, NH_4^+, and Ca^{2+}, regardless of operational load.

Our analysis demonstrated that the A/C (summation of equivalent concentrations of anions to that of cations) ratio increased with the engine load but were all less than 0.5 as presented in Table 2. Nevertheless, the A/C ratios that were calculated from the data in several previous gasoline exhausts studies were all less than 0.2 (Table 3), supporting our finding. This phenomenon may be related to the fact that lubricant oil usually contains a certain amount of $CaCO_3$ which

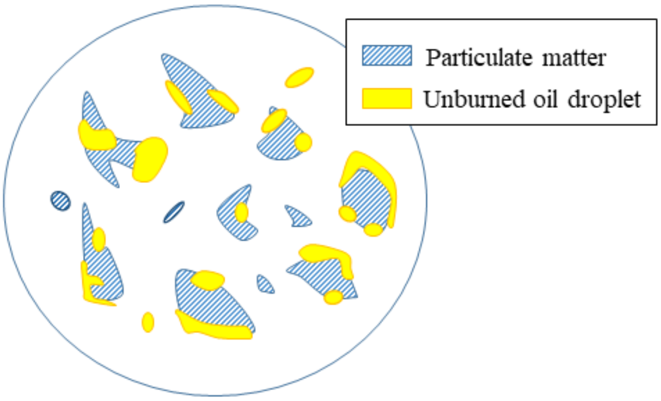

Fig. 3. Schematic diagram of particulate matter and unburned lubricating oil in gasoline engine exhaust.

Table 2. Mass concentrations of particle-bound water-soluble ions and A/C ratios.

	idling (0 kW)			mid-load (1.5 kW)			high-load (1.9 kW)		
	SLS	LS	MS	SLS	LS	MS	SLS	LS	MS
Concentrations (μg Nm^{-3}) (N = 3)									
Na^+	**619** (±79.2)	**219** (±16.0)	**847** (±72.8)	**346** (±53.5)	**117** (±7.14)	**804** (±97.8)	**264** (±85.3)	**72.4** (±5.57)	**593** (±77.0)
NH_4^+	**29.3** (±3.72)	**61.1** (±13.6)	**50.8** (±18.3)	**87.2** (±37.8)	**81.1** (±7.54)	**108** (±21.7)	**274** (±53.8)	**102** (±0.89)	**245** (±82.1)
K^+	**48.2** (±6.64)	**23.9** (±18.3)	**46.5** (±4.44)	**57.9** (±18.6)	**24.0** (±11.4)	**59.1** (±11.0)	**64.1** (±19.9)	**28.0** (±3.19)	**78.3** (±8.59)
Mg^{2+}	**22.0** (±9.02)	**19.8** (±6.70)	**16.2** (±4.25)	**27.1** (±12.4)	**53.8** (±16.5)	**28.0** (±7.68)	**24.0** (±6.86)	**47.5** (±9.04)	**14.9** (±5.50)
Ca^{2+}	**250** (±47.1)	**200** (±35.9)	**145** (±29.0)	**364** (±25.3)	**229** (±22.7)	**190** (±35.3)	**413** (±37.8)	**309** (±14.6)	**229** (±13.9)
Cl^-	**39.1** (±3.36)	**29.0** (±11.7)	**38.3** (±3.87)	**111** (±21.3)	**46.9** (±15.4)	**113** (±24.1)	**494** (±79.0)	**115** (±2.04)	**320** (±38.0)
NO_3^-	**72.1** (±12.6)	**53.0** (±17.7)	**95.9** (±29.5)	**244** (±45.8)	**143** (±39.4)	**151** (±40.4)	**306** (±65.3)	**173** (±21.4)	**162** (±17.5)
SO_4^{2-}	**132** (±14.7)	**54.1** (±37.2)	**119** (±15.3)	**316** (±16.6)	**173** (±67.7)	**182** (±7.37)	**275** (±14.6)	**200** (±32.8)	**208** (±27.5)
ΣIons	**1213** (±57.8)	**660** (±67.9)	**1359** (±115)	**1555** (±96.3)	**867** (±144)	**1633** (±78.8)	**2115** (±209)	**1047** (±42.1)	**1850** (±83.8)
Ratio (N = 3)									
A/C	**0.11** (±0.01)	**0.11** (±0.05)	**0.10** (±0.02)	**0.33** (±0.02)	**0.27** (±0.08)	**0.17** (±0.02)	**0.48** (±0.06)	**0.35** (±0.03)	**0.30** (±0.01)

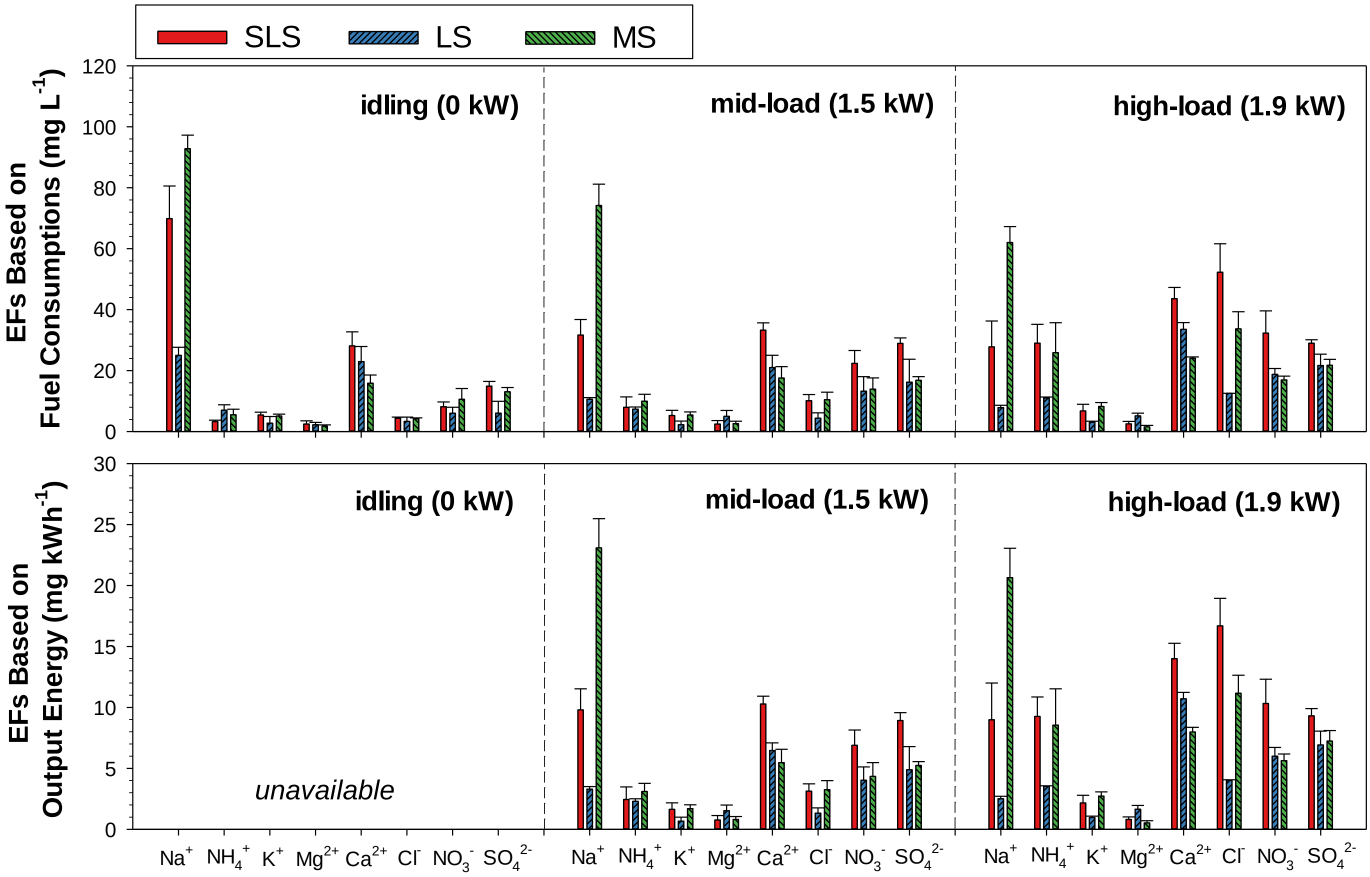

Fig. 4. Emission factors of water-soluble ions on PM from a P2SGE by using SLS, LS, and MS operated at various loads.

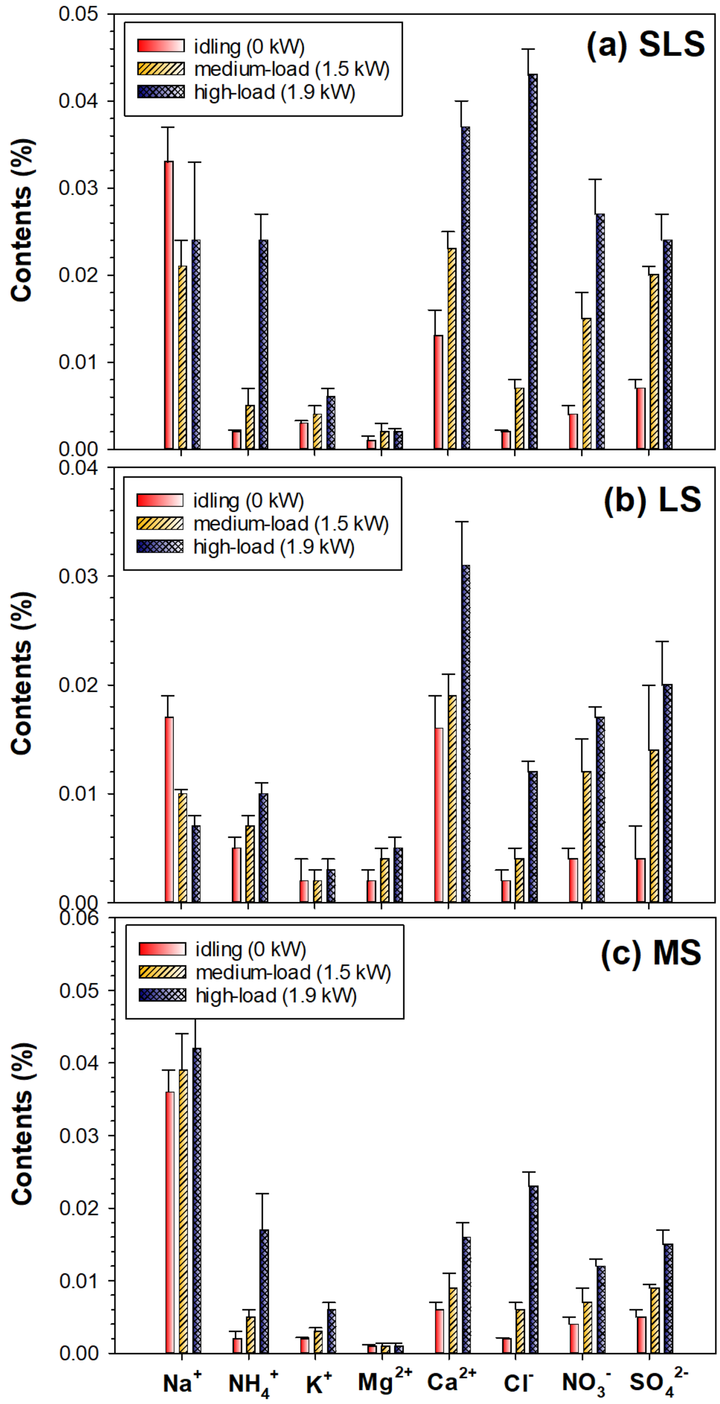

Fig. 5. Contents of water-soluble ions on PM from a P2SGE by using (a) SLS, (b) LS, and (c) MS operated at various loads.

Table 3. Summary of the relative gasoline engine researches.

Types	Water-soluble ions	A/C ratios	Reference
2-stroke gasoline engine (non-road)	Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}	0.10–0.48	this study
light duty gasoline engine (2 and 4 wheel vehicles)	Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}	0.10–0.16	Jaiprakash and Habib (2017)
4-stroke gasoline engine (4 wheel vehicles)	K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}	0.05	Yang *et al.* (2019)

could maintain the lubrication of a piston during engine operation (Eastwood, 2008; Raza *et al.*, 2018). The $CaCO_3$ is a typical alkaline additive for preventing the deterioration of lubricant oil by oxidation and extending operational lifetime. Moreover, to prevent wear and tear on the two-stroke engine, inevitably some unburned lubricant oil-droplets might be present in the exhausts (as shown in Fig. 3). At this situation, the unburned lubricant oil-droplets would be collected on the PM samples that were obtained by the filtering method. Furthermore, a mixture of deionized water and n-hexane was used herein to extract the water-soluble ions on PM, which might also cause the extraction of $CaCO_3$ in the unburned oil-droplets. Thus, the Ca^{2+} content was increased and became one of the major ions on the PM, whereas CO_3^{2-} was not analyzed in this study, leading to lower A/C ratios.

3.3 Concentrations and Emission Factors of PM-bound Metals

Table 4 and Fig. 6 illustrate the mass concentrations and EFs of 21 PM-bound metals (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba, and Pb) from the exhaust of the P2SGE with 4 vol.% of LS, MS, and SLS lubricants in 92-gasoline. The results showed that the three metallic elements of As, Mo, and Sn were not detected in all test conditions. On average, the mass concentrations of ΣMetals on PM from the P2SGE's exhausts by using 4 vol.% of SLS, LS, or MS as the additive in 92-gasoline were 677–923 (average 824 μg Nm^{-3}), 690–800 (average 810 μg Nm^{-3}), and 576–687 μg Nm^{-3} (average 603 μg Nm^{-3}), respectively. In terms of emission factors, the lowest levels of ΣMetals in the exhausts were observed by using 4% MS additive (average 61.3 mg L^{-1}), followed by LS (average 83.8 mg L^{-1}) and SLS (average 85.2 mg L^{-1}). According to the mass concentration or emission factor data, the amount of each metallic element from the P2SGE almost decreased with increasing loading no matter what kinds of lubricants were used.

The metallic components were divided (based on their average levels in ΣMetals) into three groups — major metals (Na, Mg, Al, K, Ca, Fe, and Zn, $\geq \sim$1%), sub-major metals (Cr, Mn, Ni, Cu, Sr, Ba, and Pb, ~1 to 0.1%), and minor metals (Ti, V, As, Mo, Cd, Sn, and Sb, $<$ 0.1%). According to Fig. 7, the major metals represented 96.5–99.4% by mass of ΣMetals, while the sub-major and minor metals accounted for only 0.47–3.44% and 0.04–0.14%, respectively. Previous studies have identified the major PM-bound metals in gasoline engine exhaust as Ca, Fe, Al, and Zn (Cheung *et al.*, 2010; Hao *et al.*, 2019); Yang *et al.* (2019) identified the major metal components on $PM_{2.5}$ as Na, Ca, Fe, Zn, and Al. These observations were consistent with those herein, supporting our finding of the main metal components on PM from the P2SGE.

In addition, the most abundant metals by mass were Ca, Na, K, and Al, which accounted for 93.8% by mass of ΣMetals when 4-vol% SLS was added to the fuel in the P2SGE at various loads, as reported in Table 4. The dominant four metals were Ca, Mg, Na, and K (79.9% by mass of ΣMetals) and Ca, Na, K, and Al (85.3% by mass of ΣMetals) when LS and MS were used, respectively. Consequently, the dominant metals among the 21 analyzed metals in PM were Ca, Na, K, Al, Fe, Mg, and Zn. Those dominant metals together accounted for 98.7% by mass of ΣMetals. At first glance, Fe and Zn (only about 4% each) had relatively low contents among seven primary metals. However, previous researches have confirmed that extended exposure to Fe may cause the generation of free radicals in cells and result in respiratory diseases (Kadiiska *et al.*, 1997), whereas prolonged exposure to Zn leads to acute heart diseases (Chen and Lippmann, 2009). Therefore, it is necessary to regulate the limits of the hazardous metal contents in P2SGE exhausts to reduce the risk of inhaling such harmful ingredients for P2SGE operators (such as farmers).

4 CONCLUSIONS

Portable two-stroke gasoline engines (P2SGEs), commonly fueled by lubricant oil-gasoline mixtures, may emit more pollutants than regular gasoline engines in on-road vehicles because they are not equipped with exhaust gas control devices and typically lack maintenance. This study explored the concentrations of chemical components and metallic elements in PM emissions from the exhaust of a P2SGE. The results showed that the PM mass concentrations in the exhausts were in the order MS (average 1,934 mg Nm^{-3}) $>$ SLS (average 1,543 mg Nm^{-3}) $>$ LS (average 1,167 mg Nm^{-3}) in all test conditions. The mass concentrations and EFs of PM using #92-gasoline

Table 4. Mass concentrations of particle-bound metals from a P2SGE by using SLS, LS, and MS operated at various loads.

	Concentrations (µg Nm^{-3}) (N = 3)								
	idling (0 kW)			mid-load (1.5 kW)			high-load (1.9 kW)		
	SLS	LS	MS	SLS	LS	MS	SLS	LS	MS
Na	**182**	**141**	**150**	**168**	**179**	**237**	**126**	**112**	**172**
	(±45.8)	(±49.5)	(±84.5)	(±16.2)	(±68.8)	(±102)	(±71.2)	(±126)	(±56.8)
Mg	**27.8**	**125**	**21.3**	**16.7**	**179**	**35.1**	**11.3**	**159**	**44.8**
	(±5.75)	(±7.63)	(±10.5)	(±3.55)	(±17.7)	(±11.1)	(±1.37)	(±8.02)	(±29.3)
Al	**66.8**	**96.9**	**72.7**	**31.2**	**42.5**	**54.4**	**40.3**	**58.7**	**41.6**
	(±36.2)	(±86.7)	(±45.6)	(±8.92)	(±11.5)	(±16.7)	(±20.3)	(±51.1)	(±23.5)
K	**148**	**109**	**102**	**159**	**176**	**127**	**109**	**65.1**	**89.3**
	(±34.1)	(±27.4)	(±40.0)	(±11.4)	(±38.4)	(±47.2)	(±43.7)	(±73.0)	(±23.2)
Ca	**448**	**230**	**145**	**467**	**260**	**177**	**369**	**209**	**177**
	(±66.0)	(±11.4)	(±6.90)	(±25.8)	(±7.65)	(±21.3)	(±45.3)	(±13.6)	(±90.4)
Ti	**0.78**	**0.84**	**0.30**	**0.75**	**0.22**	**0.59**	**0.73**	**0.42**	**0.22**
	(±0.12)	(±0.82)	(±0.33)	(±0.11)	(±0.13)	(±0.40)	(±0.11)	(±0.46)	(±0.21)
V	**0.09**	**0.09**	**0.06**	**0.03**	**0.08**	**0.06**	**0.02**	**0.04**	**0.05**
	(±0.06)	(±0.06)	(±0.03)	(±0.02)	(±0.04)	(±0.03)	(±0.02)	(±0.01)	(±0.03)
Cr	**1.08**	**0.88**	**0.70**	**0.65**	**0.86**	**1.81**	**0.35**	**0.35**	**2.11**
	(±0.23)	(±0.37)	(±0.64)	(±0.45)	(±0.12)	(±0.70)	(±0.33)	(±0.03)	(±1.86)
Mn	**0.20**	**0.64**	**0.13**	**0.29**	**0.34**	**0.82**	**0.31**	**0.10**	**3.56**
	(±0.11)	(±0.24)	(±0.12)	(±0.12)	(±0.25)	(±0.63)	(±0.35)	(±0.07)	(±5.39)
Fe	**33.0**	**31.2**	**39.0**	**13.1**	**17.6**	**35.7**	**11.4**	**13.8**	**19.0**
	(±4.28)	(±5.14)	(±19.5)	(±2.03)	(±5.65)	(±23.3)	(±6.59)	(±2.94)	(±7.45)
Ni	**1.73**	**1.50**	**1.83**	**0.62**	**0.37**	**0.33**	**0.51**	**0.30**	**12.1**
	(±0.47)	(±0.50)	(±1.65)	(±0.09)	(±0.12)	(±0.15)	(±0.11)	(±0.16)	(±20.5)
Cu	**1.85**	**1.79**	**1.69**	**1.14**	**1.26**	**1.90**	**0.76**	**0.83**	**1.66**
	(±0.04)	(±0.47)	(±0.37)	(±0.36)	(±0.35)	(±0.60)	(±0.36)	(±0.13)	(±0.99)
Zn	**8.45**	**56.7**	**6.95**	**12.1**	**80.1**	**9.65**	**5.27**	**68.4**	**10.1**
	(±2.91)	(±14.6)	(±1.55)	(±1.22)	(±5.21)	(±1.71)	(±2.39)	(±2.11)	(±1.71)
As	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Sr	**1.04**	**1.11**	**0.58**	**0.74**	**0.77**	**0.84**	**0.51**	**0.42**	**0.73**
	(±0.21)	(±0.55)	(±0.04)	(±0.15)	(±0.09)	(±0.20	(±0.05)	(±0.05)	(±0.52)
Mo	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Cd	**0.07**	**0.03**	**0.03**	**0.06**	**0.03**	**0.11**	**0.02**	**0.03**	**0.04**
	(±0.06)	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.04	(±0.01)	(±0.01)	(±0.01)
Sn	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Sb	**0.26**	**0.12**	**0.09**	**0.11**	**0.06**	**0.11**	**0.06**	**0.06**	**0.07**
	(±0.10)	(±0.04)	(±0.05)	(±0.03)	(±0.01)	(±0.06)	(±0.02)	(±0.002)	(±0.04)
Ba	**1.07**	**1.98**	**1.05**	**0.64**	**1.49**	**1.55**	**1.07**	**1.44**	**0.58**
	(±0.66)	(±0.56)	(±1.39)	(±0.68)	(±0.79)	(±0.86)	(±0.69)	(±0.65)	(±0.21)
Pb	**0.27**	**0.94**	**0.48**	**0.06**	**0.54**	**2.95**	**0.15**	**0.31**	**0.69**
	(±0.26)	(±1.00)	(±0.46)	(±0.04)	(±0.22)	(±1.68)	(±0.21)	(±0.27)	(±0.58)
ΣMetals	**923**	**800**	**544**	**873**	**941**	**687**	**677**	**690**	**576**
	(±99.6)	(±130)	(±158)	(±60.9)	(±83.1)	(±136)	(±90.6)	(±243)	(±163)

N.D.: Not Detected.

with 4% engine oil (either SLS or LS or MS has been added) decreased as the engine load increased. Adding SLS or LS to gasoline reduced the PM emission levels by 38.2% or 20.1%, respectively, below that achieved by adding MS. Based on fuel consumption, emission factors of ΣIons were the lowest when utilizing the LS additive (average 89.7 mg L-fuel^{-1}), followed by the MS and SLS (165 and 168 mg L-fuel^{-1}, in average, respectively). The dominant water-soluble ion species on the PM were Ca^{2+} (20.5%), Na^{+} (31.4%), and SO_4^{2-} (13.6%). The ratios of the sum of

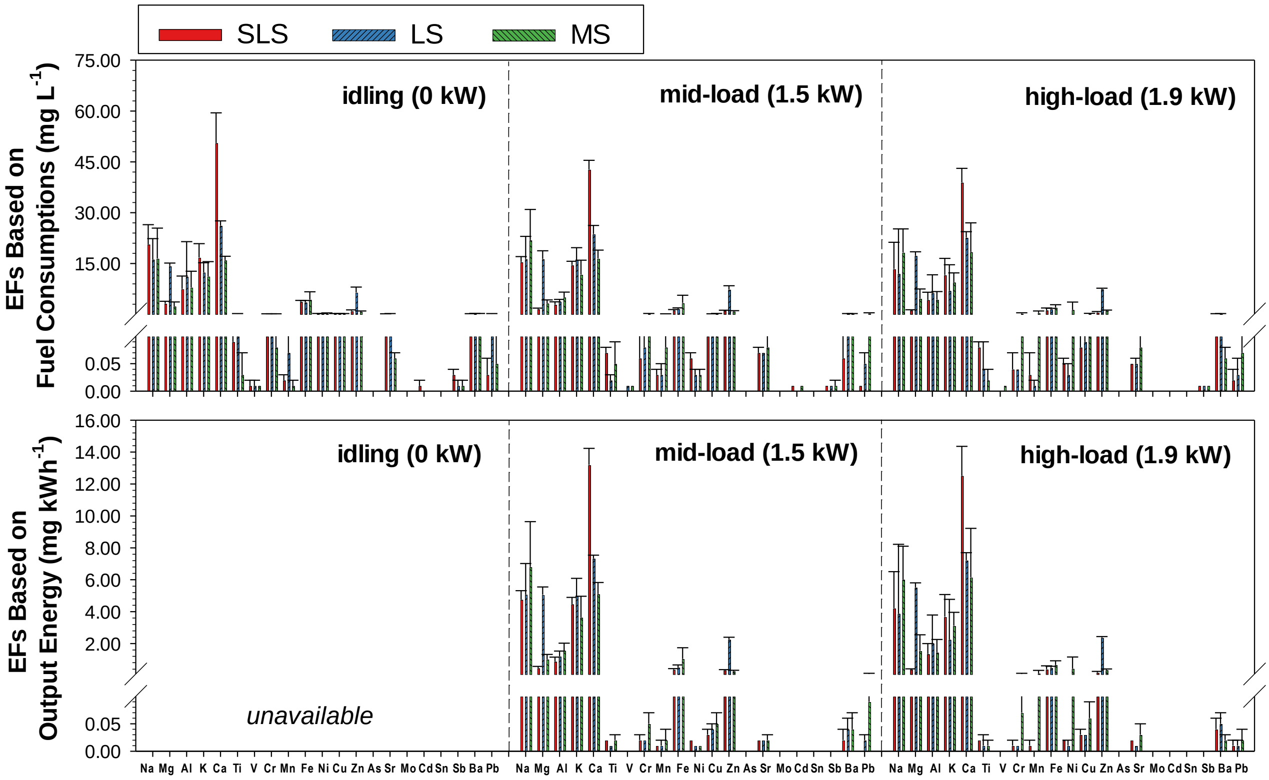

Fig. 6. Emission factors of metals on PM from a P2SGE by using SLS, LS, and MS operated at various loads.

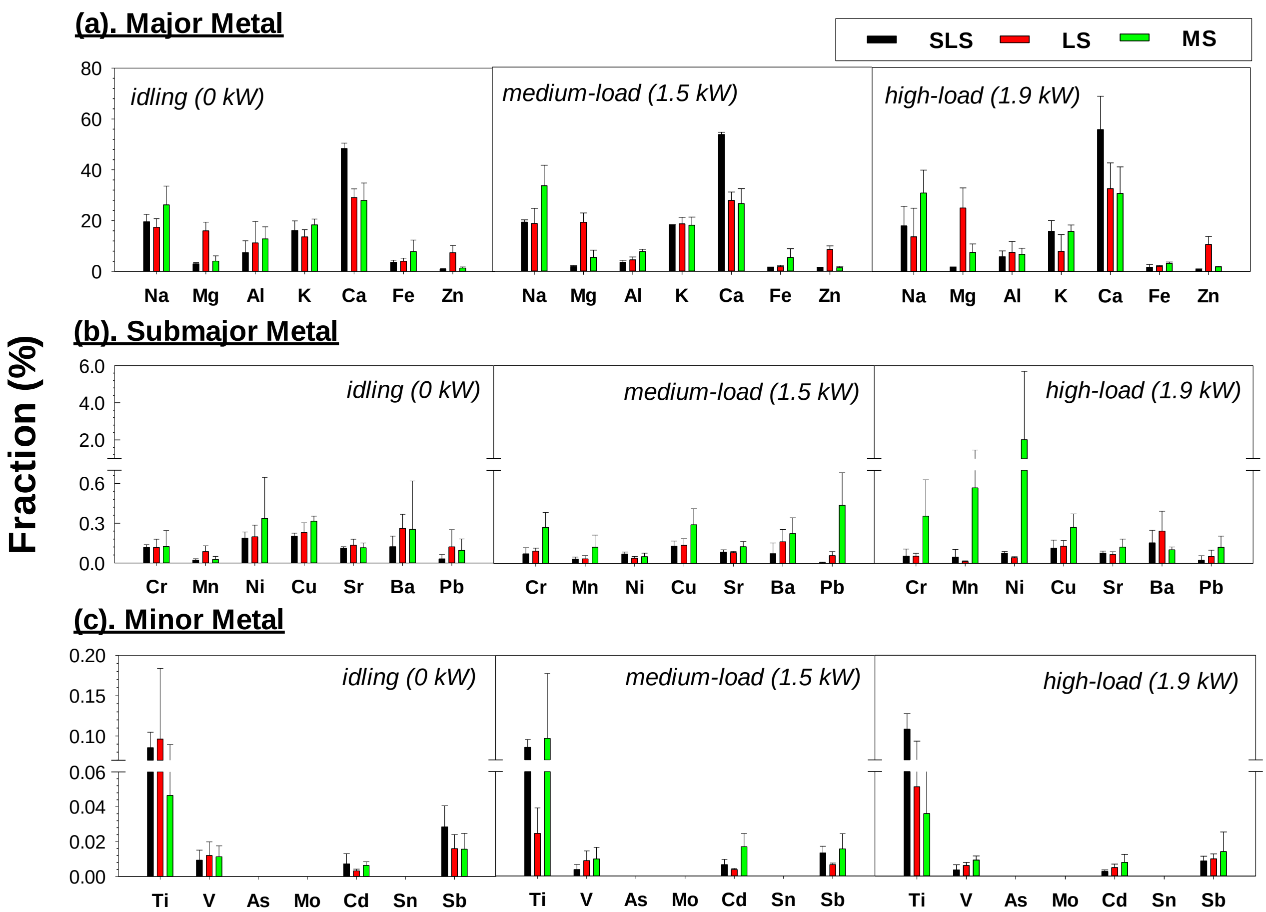

Fig. 7. Fractions of (a) major, (b) submajor, and (c) minor metals from a P2SGE by using SLS, LS, and MS operated at various loads.

equivalent concentrations of anions to that of cations (A/C) increased with the increase of engine load, although all the A/C ratios were lower than 0.5. In terms of emission factors, the lowest levels of ΣMetals in the exhausts were observed by using MS additive (average 61.3 mg L^{-1}), followed by LS (average 83.8 mg L^{-1}) and SLS (average 85.2 mg L^{-1}). Despite the difference in blended fuels, the dominant metallic elements on PM were Ca, Na, K, Al, Fe, Mg, and Zn (over 90% from ΣMetals) at all tested conditions. The subdominant metals (Cr, Mn, Ni, Cu, Sr, Ba, and Pb) accounted for 0.5–3.5% of the PM by mass, while the trace metals (Ti, V, As, Mo, Cd, Sn, and Sb) accounted for only 0.1% PM mass.

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