

Measurement of Regulated and Unregulated Exhaust Emissions from a Lawn Mower with and without an Oxidizing Catalyst: A Comparison of Two Different Fuels

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Relatively few emission characterization studies have been made on small engines used in garden equipment. The present investigation focuses on exhaust characterization from a lawn mower engine fueled with two different fuels in combination with and without an oxidizing catalyst. The compounds measured in the exhaust are carbon monoxide, hydrocarbons, nitrogen oxides, particulates, polycyclic aromatic hydrocarbons, methane, ethane, ethene, ethanol, and nitrous oxide. A significant reduction can be achieved by the use of a catalyst. By selection of the fuel, a significant reduction of certain carcinogenic compounds ("probably carcinogenic to humans" according to the IARC; benzo[a]pyrene and benzo[a]anthracene) may be achieved. The highest reduction improvement is achieved through the combination of an environmentally improved fuel, i.e., alkylate fuel, and a catalyst system. The data presented show that emissions from lawn mower engines are still relatively large although there is the potential for further improvements.

Introduction

Air pollution in urban environments is of great concern, especially in densely populated areas. A major source contributing to urban air pollution is automobile traffic (1). Furthermore, old cars, i.e., cars older than 10 yr, are significant contributors to air pollution (2). An important way in which exhaust pollution from gasoline-fueled vehicles was reduced was through the introduction of three-way catalyst (TWC) exhaust after-treatment devices. TWC gasoline cars were first introduced in California in 1976. TWC gasoline-fueled vehicles are however widely available today and are required to fulfill exhaust regulations around the world.

When discussing exhaust emissions from vehicles, the distinction is generally made between regulated and unregulated constituents. Carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x), and, for diesel-fueled cars, particulates are regulated exhaust constituents from vehicles (3). Unregulated exhaust constituents are defined as emitted compounds that are not specified by law, a group that consists of several thousands of compounds. These compounds may

well belong to the group of hydrocarbons, although not as individuals. In general, exhaust emissions from vehicles have been greatly reduced and are expected to be further reduced in the future. Therefore, there is an increased need to investigate and evaluate other sources that contribute to air pollution.

In this investigation, emission factors are presented that emanate from a lawn mower engine. Furthermore, fuel impact and exhaust emission reduction using an oxidizing catalyst were investigated and compared to exhaust emissions emanating from gasoline-fueled vehicles. There are relatively few emission data available in the scientific literature for small engines (4–6), although CO and HC emissions in the Newcastle region of Australia were estimated in a recent publication (7). The contributions from in-use lawn mowers were 5.2% for CO and 11.6% for HC, respectively, when compared to the mobile sources. In an attempt to regulate emissions, the California Air Resources Board (CARB) (8) has proposed an exhaust emission standard for small internal combustion engines, i.e., engines with effects less than 25 kW, employed in garden appliances and small industrial appliances. The importance of exhaust emissions from these unregulated mobile sources must not be underestimated, especially not during the months of the year when recreational activities and lawn manicuring peak. With widespread affluence in the present world's population and with the advent of newly industrialized countries, emissions from these small internal combustion engines as well as engines used in working machinery are expected to be of interest for future regulation standards of emissions. This study was made on a lawn mower engine both with and without a catalyst in order to gain a better understanding of the exhaust emissions from lawn mowers. Two different types of fuel were also tested; a reference (gasoline) fuel and a commercial alkylate fuel.

Experimental Section

Lawn Mower. A Klippo Comet lawn mower (Dahlmans Klippo AB, Sweden), equipped with a Briggs & Stratton Quantum 40 Power engine (4-stroke, 1 cylinder, cylinder volume of 0.19 L, model year 1997) was used in this study. The new engine was run in for 10 h prior testing with the reference fuel. This engine exhibited 2.9 kW at 3060 rpm. Studies were performed with and without a catalyst. The catalyst was a commercially available oxidizing catalyst manufactured by Dahlmans Klippo AB (Sweden) with the dimensions of 130 × 90 × 50 mm.

Test Fuels. Two test fuels were used for the investigation. The reference fuel was purchased from Haltermann GmbH, Germany (CEC legislative fuel RF-08-A-85 batch 27), and the other fuel was a pure alkylate produced by Neste Oy, Finland, imported to Sweden by OK Petroleum and sold as OK Ultima for use in 4-stroke lawn mowers and other utility 4-stroke engines. In Table 1, the general fuel parameters for both fuels are shown.

Sampling and Analysis. All exhaust sampling was carried out on diluted exhausts in a dilution tunnel (average dilution ratio approximately 100), designed to fulfill the specifications in the U.S. Federal Test Procedure (9). During the investigation, the lawn mower was operated on an in-house-made electrical engine dynamometer according to the six-step steady-state testing procedure of the CARB regulation (8), Table 2. In the present investigation, the test cycle was performed for 10 min, and each mode was run in accordance with the weighting factors and torque shown in Table 2. The average power produced in one test cycle by the engine was

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TABLE 1. Fuel Parameters

parameter	method	unit	ref fuel	alkylate fuel
research octane no., RON	ASTM D 2699-86		95	95
density	ASTM D 4052	g/L	756	690
olefins	ASTM D 1319	vol %	6	<0.5
aromatics	ASTM D 1319	vol %	38	<0.5
saturates	ASTM D 1319	vol %	56	>99
benzene	ASTM D 5580	vol %	1.5	<0.1
heating value	ASTM D 3338	MJ/kg	42.57	44.00
calculated heating value		MJ/L	32.2	30.4

TABLE 2. Six-Step Steady-State Engine Test Cycle (California Air Resources Board)

mode no.	1	2	3	4	5	6
weighting factor	0.09	0.2	0.29	0.3	0.07	0.05
torque % of full load	100	75	50	25	10	idling

1.36 kW. Fuel consumption was measured by the carbon balance method (9).

Measurements of CO, HC and NO_x. Regulated emissions were measured using a Horiba 9000 system in accordance with a test procedure described in the literature (8). The regulated emissions were measured as follows: carbon monoxide (CO) with a nondispersive infrared (NDIR) analyzer, total unburned hydrocarbons (HC) with a flame ionization detector (FID), and oxides of nitrogen (NO_x) with a chemiluminescence analyzer (CLA) using a NO₂ to NO converter.

Measurements of Volatile Components. The measurements of volatile unregulated components were carried out using Fourier transformation infrared (FTIR) spectrometry technique. The FTIR analyzer is based on an infrared spectrometer technique for simultaneous realtime concentration measurements of exhaust gas components. The instrument consists of an infrared radiation source, an interferometer sample cell, and a detector. The signal obtained from the IR absorption is converted into an infrared spectrum using a Fourier transformation procedure so that the exhaust spectra could be compared to spectra in the computer library. Thus, identification of individual compounds may be performed and their respective concentrations calculated. These methods have been described in detail elsewhere (10).

Particulate-Associated Compounds. Teflon-coated glass fiber filters (Pallflex T60A20; Pallflex Inc., USA) with a diameter of 150 mm was used for particulate emission measurements. The filters were weighed before and after sampling according to specifications in the literature (9). Before sampling, the filters were washed with ethanol, acetone, and dichloromethane and then dried at 200 °C; a cleaning procedure that is described elsewhere (11). After being sampled, the filters were stored at -20 °C until extraction. The filters were Soxhlet extracted with dichloromethane for 18 h (170 mL during a 20-min refluxing time). Each dichloromethane raw extract was evaporated under reduced pressure to just dryness, diluted with acetone, and then stored at -20 °C until chemical analysis. Blank samples were run in parallel.

Semivolatile-Associated Compounds. An anodized aluminum sampling device containing polyurethane foam (PUF) plugs was used. Before sampling, the PUF plugs were washed with 8 × 250 mL portions of distilled water, squeezed between portions, followed by 4 × 250-mL portions of 99% ethanol, squeezed between portions, and 4 × 250 mL portions of acetone. In addition, the PUF plugs were extracted, two at

TABLE 3. Fuel Consumption (in L/h)^a

	reference fuel				alkylate fuel			
	without cat.		with cat.		without cat.		with cat.	
	MV	SD	MV	SD	MV	SD	MV	SD
fuel consumption	0.79	0.02	0.82	0.02	0.89	<0.01	0.89	0.02

^a Given as mean value (MV), standard deviation (SD), and catalyst (cat.) (N = 3 in each engine combination).

a time, in a Soxhlet extractor (1.5 L) with toluene for 12 h (30-min refluxing time), acetone for 12 h (60-min refluxing time), and finally with acetone for 12 h. The latter extract was used as a blank sample. The purified PUF plugs were stored separately in sealed glass jars until sampling. After being sampled, the PUF plug was transferred to a sealed glass jar and stored at -20 °C until extraction. The samples were Soxhlet extracted with acetone for 12 h, and the raw extracts were then evaporated under reduced pressure and treated in the same way as the particulate extract.

Chemical Analysis of Particulate- and Semivolatile-Associated Compounds. The particulate and semivolatile crude extracts were fractionated into two fractions. However, prior to the chemical fractionation procedure, an internal standard mixture consisting of phenanthrene-*d*₁₀ and 2,2'-binaphthyl was added, where both compounds elute in the PAH fraction. Two different fractions were collected: fraction I containing "light" aliphatic hydrocarbons (not analyzed further in the present investigation) and fraction II, which included the "heavy" aliphatic hydrocarbons and PAH. This fractionation followed the one described by Alsberg and co-workers (12), except that solvent elution volumes were modified to fit the column size used.

Analysis of fraction II, containing the PAH (and dibenzothiophene), was performed by gas chromatography/mass spectrometry (GC/MS). The gas chromatograph, a Hewlett-Packard 5890 series II, was equipped with a split-splitless injector and a fused silica capillary column (30 m × 0.25 mm i.d., DB5-MS, J&W Scientific, USA), and the temperature program was as follows: Initial temperature, 110 °C for 1 min; rate, 7 °C/min; final temperature, 300 °C for 20 min. The mass selective detector (Hewlett-Packard 5971A) interface temperature was set to 300 °C. The mass spectrometer was operated in the electron impact ionization (70 eV) mode. The quantitative analysis was carried out by integrating the areas of the molecular ions (M⁺) of the internal standards and the PAH. A standard mixture containing known amounts of internal standard and all determined compounds was used for response factor calculations and for determination of retention times.

Results and Discussion

Fuel Consumption. The average values determined for the consumption of the fuels tested are shown in Table 3. The fuel consumption originating from the alkylate fuel was increased approximately 10% as compared to the reference fuel. This may be explained by the fact that the energy content, expressed in terms of MJ/L of the alkylate fuel, is less (approximately 6%) than for the reference fuel (Table 3). From Table 3, it can further be seen that for neither of the fuels tested, the fuel consumption was significantly affected by the use of an oxidizing catalyst. The average fuel consumption reported by Priest and co-workers (7) from 4-stroke lawn mower engines was 0.76 L/h, a value that is similar to that reported in the present investigation.

Regulated Components. From the results of the determinations of the regulated components presented in Table

TABLE 4. Emission of Regulated Compounds (in g/h)^a

	reference fuel				alkylate fuel			
	without cat.		with cat.		without cat.		with cat.	
	MV	SD	MV	SD	MV	SD	MV	SD
CO	583	45	401	27	562	16	318	12
HC	22	2	16	3	26	4	17	3
NO _x	2.6	0.5	1.4	0.1	2.0	0.2	1.2	0.2
particulate	0.8	0.1	0.5	0.04	0.8	0.3	0.4	0.03

^a Given as mean value (MV), standard deviation (SD), catalyst (cat.) (N = 3 in each engine combination).

TABLE 5. Emission of Volatile Compounds (in g/h)^a

	reference fuel				alkylate fuel			
	without cat.		with cat.		without cat.		with cat.	
	MV	SD	MV	SD	MV	SD	MV	SD
methane	2.1	0.16	2.58	0.26	3.85	0.26	3.86	0.43
ethane	0.21	0.07	0.11	0.09	0.44	0.11	0.26	0.08
ethene	1.56	0.1	1.61	0.05	2.27	0.24	2.08	0.27
ethanol	1.16	0.25	3.3	0.56	1.63	0.65	3.4	0.3
nitrous oxide	0.31	0.19	0.48	0.19	0.45	0.08	0.38	0.15

^a Given as mean value (MV), standard deviation (SD), catalyst (cat.) (N = 3 in each engine combination).

4, it can be seen that the emissions of CO, HC, NO_x, and particulates do not differ significantly when the two fuels investigated are compared without a catalyst present. The use of a catalyst however caused a reduction of approximately 30–50% for each fuel in such emissions. Comparing both fuels (with a catalyst), the HC and NO_x emissions were not

statistically different. The CO and particulate emissions were however reduced by 20% when using the alkylate fuel. It can be noted that the catalyst reduced the emission of NO_x by 40–50% for both fuels. This may be due to the fact that the engine runs rich; however, no calculation of the air/fuel ratio was carried out.

Emissions of CO, HC, and NO_x (g/kWh) reported by Zinger and Hecker (6) from 4-stroke engines without catalyst are recalculated to grams per hour revealing values of 630, 43, and 9.3, respectively. These numbers originate from 1974 and are obviously higher as compared to emissions presently reported (Table 4). Emissions (in g/h) of CO, 489; HC, 44.2; and NO_x, 4.85 were however reported recently (7). These data indicate that emission levels from lawn mower engines is still relatively large. As shown in Table 4, a significant reduction can be achieved by the use of a catalyst.

Unregulated Components. The levels of the emissions of methane, ethane, ethene, ethanol, and nitrous oxide are shown in Table 5. When the two fuels are compared (without catalyst) with respect to emissions, only the methane and ethene emissions from the alkylate fuel are significantly higher, while other emissions are not significantly different. Using the reference fuel, the addition of a catalyst led to an increase of the emissions of methane and ethanol, while other emissions are relatively unaffected considering the large standard deviations shown in the table. The corresponding values for the alkylate fuel show that only the ethanol emission was increased, while for the other emissions an increase could not be statistically ascertained. With the catalyst, statistically increased emissions of methane and ethene were determined from the alkylate fuel as compared to the reference. In addition to the components shown in Table 5, ammonia, hydrogen cyanide, methanol, propene, and 1,3-butadiene were also measured. The values for these compounds were

TABLE 6. Emission of Particulate-Associated PAH (in µg/h)^a

	particulate-associated PAH							
	reference fuel				alkylate fuel			
	without cat.		with cat.		without cat.		with cat.	
	MV	SD	MV	SD	MV	SD	MV	SD
2-methylfluorene	13.0	1.7	0.2	<0.1	3.8	2.0	0.2	<0.1
dibenzothiophene ^b	1.0	0.1	0.1	<0.1	0.8	0.3	0.1	<0.1
phenanthrene	91.2	8.3	6.7	1.6	24.9	12.4	2.1	0.8
anthracene	29.2	2.8	<0.1		6.3	4.2	<0.1	
2-methyl phenanthrene	55.7	3.9	2.8	1.1	22.6	11.1	1.6	0.6
2-methyl anthracene	24.8	1.7	0.5	0.3	8.8	4.6	0.5	0.2
1-methyl phenanthrene	31.7	4.9	1.1	0.6	13.0	6.6	0.6	0.3
fluoranthene	154	14	19.2	9.3	63.8	26.2	9.0	2.5
pyrene	274	26	34.2	17.4	108	39	15.8	3.7
retene	1.6	0.3	<0.1		1.4	0.6	<0.1	
2-methyl pyrene	27.8	1.1	3.1	1.0	8.7	1.8	2.4	0.5
1-methyl pyrene	18.4	0.9	2.4	0.6	6.2	1.1	2.1	0.3
benzo[ghi]fluoranthene	59.1	13.0	13.5	3.9	20.3	7.0	7.9	1.5
cyclopenta[cd]pyrene	532	115	10.7	3.3	121	44	5.5	2.8
benz[a]anthracene	80.5	5.5	10.0	2.5	21.6	7.5	5.7	1.4
chrysene+triphenylene	45.1	2.3	11.8	2.6	14.5	3.6	7.0	1.3
benzo[b]fluoranthene	60.3	7.6	13.1	3.9	20.9	7.2	5.1	1.7
benzo[k]fluoranthene	16.9	2.7	3.1	0.9	6.9	2.1	1.3	0.5
benzo[e]pyrene	48.8	4.6	10.2	3.5	14.5	6.2	2.4	1.2
benzo[a]pyrene	92.7	14.5	6.4	2.4	30.6	12.7	2.8	0.5
perylene	13.5	2.0	1.2	0.4	4.3	1.9	0.9	0.4
indeno[1,2,3-cd]fluoranthene	2.5	0.8	0.2	<0.1	1.1	0.7	0.6	0.4
indeno[1,2,3-cd]pyrene	73.8	17.4	8.7	2.8	28.7	13.0	3.3	0.8
dibenz[a,h]anthracene	2.4	0.8	0.1	<0.1	1.9	<0.1	1.1	<0.1
benzo[ghi]perylene	218	27	27.5	8.1	63.3	29.4	6.9	1.6
coronene	244	52	20.2	5.3	67.0	32.3	5.4	1.6
sum of PAH	2212	293	207	60	683	189	90	20

^a Given as mean value (MV), standard deviation (SD), catalyst (cat.) (N = 3 in each engine combination). ^b A polycyclic aromatic heterocyclic containing one sulfur atom.

TABLE 7. Emission of Semivolatile Associated PAH (in $\mu\text{g/h}$)^a

	semivolatile associated pah							
	reference fuel				alkylate fuel			
	without cat.		with cat.		without cat.		with cat.	
	MV	SD	MV	SD	MV	SD	MV	SD
2-methylfluorene	211	29	18.2	1.7	58.0	14.6	9.9	6.2
dibenzothiophene ^b	17.5	1.4	7.4	0.6	16.9	2.1	8.2	1.8
phenanthrene	725	59	275	41	247	35	112	37
anthracene	266.4	16.2	63.1	8.1	79.3	15.8	24.0	9.0
2-methyl phenanthrene	162	10	51.0	8.0	62.0	8.0	40.4	7.1
2-methyl anthracene	68.8	3.2	13.5	2.1	24.1	4.2	11.3	2.2
1-methyl phenanthrene	74.5	1.6	25.7	4.5	29.8	4.5	24.7	4.0
fluoranthene	112	13	72.0	27.5	53.3	12.6	67.5	17.7
pyrene	118	23	81	34	60.7	19.8	83.2	19.7
retene	1.5	0.4	2.7	0.8	0.9	0.2	0.9	0.1
2-methyl pyrene	8.1	0.7	5.9	1.3	2.9	1.0	5.0	0.3
1-methyl pyrene	3.8	0.4	2.7	1.4	1.1	0.7	2.1	0.4
benzo[ghi]fluoranthene	5.5	2.1	3.7	1.6	2.8	2.2	2.9	0.3
cyclopenta[cd]pyrene	26.9	6.4	1.7	0.7	10.6	5.9	1.9	0.2
benz[a]anthracene	<0.1		<0.1		<0.1		<0.1	
chrysene+triphenylene	2.4	1.7	4.4	<0.1	<0.1		0.7	<0.1
benzo[b]fluoranthene	1.4	0.8	0.7	<0.1	0.2	0.2	0.5	0.1
benzo[k]fluoranthene	1.1	0.9	0.6	<0.1	0.2	<0.1	0.5	0.1
benzo[e]pyrene	1.5	0.9	0.3	0.3	0.2	0.3	0.7	0.1
benzo[a]pyrene	1.9	0.8	0.3	<0.1	0.4	0.2	0.5	<0.1
perylene	1.0	0.8	0.4	<0.1	0.2	0.2	0.4	<0.1
indeno[1,2,3-cd]fluoranthene	<0.1		<0.1		<0.1		<0.1	
indeno[1,2,3-cd]pyrene	<0.1		<0.1		<0.1		<0.1	
dibenz[a,h]anthracene	<0.1		<0.1		<0.1		<0.1	
benzo[ghi]perylene	<0.1		<0.1		<0.1		<0.1	
coronene	<0.1		<0.1		<0.1		<0.1	
sum of PAH	1809	124	626	129	650	59	396	86

^a Given as mean value (MV), standard deviation (SD), catalyst (cat.) ($N = 3$ in each engine combination). ^b A polycyclic aromatic heterocyclic containing one sulfur atom.

however below the detection limit of 0.1 g/h. The emissions of methane determined from the lawn mower (mean value) is higher as compared to those reported by Priest et al. (7) of 4.46 g/h. The contribution of the methane to the total hydrocarbon emission (HC) is however about 10% in both studies. As shown in Table 5, the levels of the methane emissions are not affected by the use of a catalyst.

Polycyclic Aromatic Hydrocarbons (PAH). The particulate- and semivolatile-associated emissions of PAH are shown in Tables 6 and 7, respectively.

When a catalyst was not used, the emissions from both fuels of particulate-associated PAH were dominated by fluoranthene, pyrene, cyclopenta[cd]pyrene, benzo[ghi]perylene, and coronene. These PAH contribute to approximately 61% (reference fuel) and 64% (alkylate fuel) of the total emissions of PAH determined in Table 6. The corresponding values when the catalyst was used were approximately 54% (reference fuel) and 48% (alkylate fuel). As can be seen in Table 6, the use of a catalyst reduces PAH emissions by approximately 90%. However, the lowest emissions of particulate-associated PAH were determined when the alkylate fuel was used in conjunction with the catalyst investigated. This may be explained by the fact that the PAH base emissions were lower from the combustion of the alkylate fuel prior to exposure to the catalytic device. A substantial PAH reduction was achieved by the use of the catalyst, when the reference fuel was used. This value was lower than that generated by the combustion of the alkylate fuel without a catalyst.

The PAH benzo[a]pyrene is classified by the International Agency for Research on Cancer (IARC) (13) as "probably carcinogenic to humans". In the emissions from the reference fuel, the level of benzo[a]pyrene was reduced by the catalyst with more than 90% (Table 6). The benzo[a]pyrene reduction

using the alkylate fuel was also more than 90% due to the catalyst. By fuel selection only (reference versus alkylate fuel), a reduction of approximately 65% may be obtained in the absence of catalyst. Another PAH classified as probably carcinogenic to humans by the IARC is benz[a]anthracene. A similar comparison as that made for benzo[a]pyrene reveals that the catalyst causes a reduction of more than 85% for the reference fuel and more than 70% for the alkylate fuel, respectively. By fuel selection only (reference versus alkylate fuel and no catalyst), a reduction of approximately 70% may be obtained. In summary, by the selection of fuel, a significant reduction of the carcinogenic compounds (probably carcinogenic to humans) discussed may be achieved. The most reduction of benz[a]anthracene and benzo[a]pyrene is however achieved through the combination of the environmentally improved fuel, i.e., alkylate fuel, with a catalyst exhaust after-treatment system. Furthermore, by calculating the benzo[a]pyrene particle load (μg of benzo[a]pyrene/g of particle mass), the following numbers are obtained: reference fuel without catalyst, 117 ppm; reference fuel with catalyst, 13 ppm; alkylate fuel without catalyst, 60 ppm; alkylate fuel with catalyst, 6.5 ppm (or in relative numbers 1.0, 0.11, 0.51, and 0.08, respectively). It is evident from this that from the point of view of human health particles emitted from alkylate fuel combined with a catalyst are preferable as compared to the other fuel/catalyst combinations tested.

Emissions of semivolatile associated PAH are shown in Table 7. As expected, the PAH allocated to the semivolatile associated fraction include smaller compounds, which have relatively high vapor pressures. The PAH dominating in this fraction are 2-methylfluorene, phenanthrene, anthracene, 2-methylphenanthrene, fluoranthene, and pyrene. These PAH contribute to approximately 88% (reference fuel) and 86% (alkylate fuel) of the summed emissions of PAH presented

in Table 7. The corresponding values when the catalyst was used were approximately 85% for both fuels.

Taking both particle-associated and semivolatile PAH (Tables 6 and 7) into account, it seems that the worst case is presented by the reference fuel without a catalyst (4021 $\mu\text{g/h}$) and the best case is presented by the alkylate fuel combined with a catalyst (486 $\mu\text{g/h}$). The latter gives a reduction of approximately 90% of the emissions determined. As shown, it is however favorable to use the catalyst on standard commercial lead-free fuels. Using the reference fuel, a PAH reduction of approximately 80% was determined in the present investigation. Obviously, if catalysts will become mandatory on lawn mover engines (and, possibly, other small engines as well) a significant reduction of exhaust components will be achieved.

The PAH emission factors (for particulate- and semi-volatile-associated PAH) reported previously (14) from TWC light-duty vehicles have a mean value of 24 $\mu\text{g/km}$. The emissions produced from a lawn mover engine during 1 h of operation in the present investigation were around 4000 $\mu\text{g/h}$, which is comparable to driving a distance of more than 150 km with a TWC car.

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