

PM Speciation Profiles for Off-road Diesel Military Generators

—PM1110~1112

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I. Introduction

In CARB's inventory, the particulate matter (PM) emissions from military tactical support equipment are currently mapped to off-road diesel vehicle exhaust PM profiles, which were developed based on the on-road diesel vehicles speciation profiles and off-road diesel regulations [1]. There are about 60% elemental carbon (EC), and about 20% organic carbon (OC) in the off-road diesel PM profiles.

In 2008, the DRI researchers performed source tests to characterize the emissions from military diesel engines by using methods that are more efficient and more realistically representative of actual operations than engine dynamometer certification tests [2]. The following three PM speciation profiles were developed for military diesel engines based on that study. These profiles will replace the currently in-use off-road diesel PM profiles associated with the military tactical support equipment emission inventory categories (Table 1).

- PM1110: Off-road diesel military generator using warm start
- PM1111: Off-road diesel military generator using cold start
- PM1112: Off-road diesel military generator (composite)

II. Methodology

The DRI researchers performed In-Plume Emission Test Stand (IPETS) measurements in Camp Pendleton, CA in 2008. The IPETS offered a movable platform that can be used in field situations. The tests were conducted on 13 military diesel generators [2]. The engine power of the test generators varied from 10kW, 30kW, 60kW to 100kW. The test fuels were mixtures of military JP-8 fuels with sulfur content ranging between 311 and 349 ppmw and California No. 2 diesel fuels with sulfur content between 139 and 148 ppmw.

After passing through the cyclone, PM samples were collected on Teflon filters for mass measurement by gravimetric method. Samples for elements were collected on Teflon filters and analyzed using X-Ray Fluorescence (XRF). Samples for water-soluble sodium and potassium were collected on quartz filters and analyzed using Atomic Absorption Spectroscopy (AAS). Samples for chloride, nitrate, and sulfate were collected on quartz filters and analyzed using Ion Chromatography (IC). Samples for EC/OC were collected on quartz filters and analyzed using the IMPROVE_A Thermal/Optical Protocol.

The DRI report provides two PM_{2.5} source profiles, one for warm start and another for cold start, by normalizing the emission of each species by PM_{2.5} mass [2]. The profiles contain anions, cations, elements, and all types of OC and EC. To transform these two profiles to the format for CARB PM profiles, the following steps are implemented:

- NCOM (non-carbon organic matter): a factor of 1.4 was used to convert OC to OM (organic matter) for combustion [3]. NCOM is calculated by subtracting OC from OM, i.e.,

$$[\text{NCOM}] = [\text{OM}] - [\text{OC}] = 1.4 \times [\text{OC}] - [\text{OC}] = 0.4 \times [\text{OC}]$$

- 'others': this species group is created to capture the metal-bound oxygen by multiplying the five geological elements (i.e., Al, Si, Ca, Fe and Ti) by their oxygen-to-metal ratios. These ratios were based on the expected oxidation state of the metals in the atmosphere (i.e., Al₂O₃, SiO₂, CaO, Fe₂O₃ and TiO₂). The following equation is used to calculate 'others' [4]:

$$[\text{others}] = 0.89 \times [\text{Al}] + 1.14 \times [\text{Si}] + 0.40 \times [\text{Ca}] + 0.43 \times [\text{Fe}] + 0.67 \times [\text{Ti}]$$

- Double-counting species: because different analytical methods are performed on PM samples to determine more complete speciation information for multiple purposes, some species are reported twice in the report, such as, sulfur (S) and sulfate (SO₄²⁻), chlorine (Cl) and chloride (Cl⁻), sodium (Na) and water-soluble sodium (Na⁺), and potassium (K) and water-soluble potassium (K⁺). To avoid double counting of these species contained in the profiles, non-sulfate sulfur, insoluble chlorine, insoluble sodium, and insoluble potassium fractions are calculated to replace sulfur (S), chlorine (Cl), sodium (Na), and potassium (K). Any negative values are set to zero [4].
- Normalization: the emissions of all the chemical species, including EC/OC, metals, elements, ions, NCOM and 'others', are summed to get an emission total for the profile species; and then the emission of each species is divided by the total emission to determine its weight percentage in the speciation profile.

Details of the new CARB format PM profiles PM1110 (for warm start) and PM1111 (for cold start) are listed in Appendix Table 2 to Table 3. A composite profile for diesel generator without specific start information, PM1112, is created by averaging profiles PM1110 and PM1111. The detailed information of PM1112 is shown in Appendix Table 4.

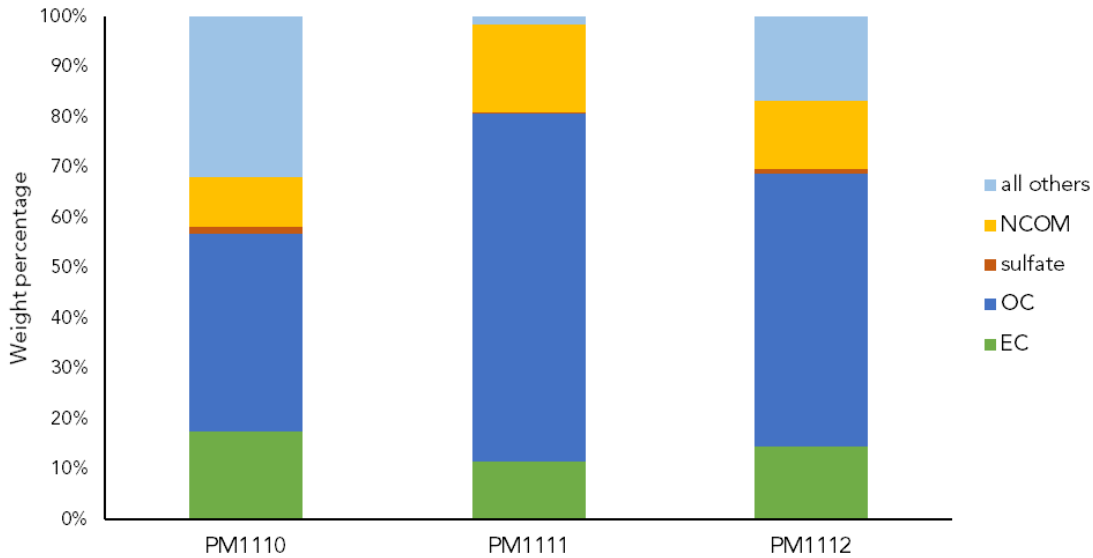
Due to the lack of size fraction data in the DRI report, the size profile of the currently in-use off-road diesel profiles is applied to the three new profiles, i.e., PM₁₀/TPM (total particulate matter) is 0.994 and PM_{2.5}/TPM is 0.951 [1]. Since particle-size-specific chemical composition data are not available, a homogeneous chemical composition is assumed for all PM size ranges. That is, the chemical speciation profiles of TPM, PM₁₀ and PM_{2.5} are assumed to be the same.

III. Results and Discussion

The key PM modeling components, such as EC, OC, and sulfate, are plotted for the new profiles PM1110, PM1111 and PM1112 in Figure 1. Overall, OC is the most abundant species in all three profiles, followed by EC. The weight percentage of OC ranges from 39% for warm start, 69% for cold start, and 54% for the composite profile. EC weights less than 20% for all profiles: 17%, 11% and 14% of the PM mass for warm start, cold start and the composite profile, respectively.

Sulfate accounts for a small percent in all three profiles, varying from a high of 1.3% in PM1110 for warm start to a low of 0.4% in PM1111 for cold start. Levels of trace elements were low with elevated iron (0.13-0.19%), phosphorous (0.07-0.13%), and calcium (0.07-0.10%).

Figure 1. Major species in off-road diesel military generator profiles



CARB has 46 Emission Inventory Codes (EICs) for off-road diesel military tactical support equipment categories (Table 5). Since there is no specific description of the start conditions for these EICs (i.e., warm vs. cold start), the composite profile PM1112 will be assigned to them to replace the existing general off-road diesel vehicle profile.

Compared to the existing off-road diesel PM profile PM6179, the new profile PM1112 has much higher OC (54% vs. 23%) but lower EC (14% vs. 62%) and sulfate (0.9% vs. 1.7%). Thus, the application of PM1112 will increase OC emissions but reduce EC and sulfate emissions.

The emissions for year 2017 were chosen as an example to evaluate the impacts of the profile update on some of the PM_{2.5} species for military tactical support equipment. Based on CEPAM: California 2019 Ozone SIP Baseline Emission Projection Planning Inventory (version 1.02) [5], the 2017 statewide annual average PM emissions from military diesel equipment are 0.027 tons/day. The emissions of certain PM_{2.5} species are calculated by multiplying the PM emissions by the PM_{2.5}/TPM fraction and its weight percentage in the profile. Compared with the estimates using PM6179, the OC emissions will increase from 0.006 to 0.014 tons/day, and the emissions of EC and sulfate estimated by the new profiles will be reduced by about 75.0% and 50.0%, respectively (Table 1).

Table 1: Impacts on emissions of PM_{2.5} species for off-road diesel military tactical support equipment using updated profile (2017)

Statewide annual average emissions	Using current profile PM6179 (tons/day)	Using new profiles PM1112 (tons/day)	Change of Emissions (tons/day)	Percentage of Change
OC	0.006	0.014	0.008	133.3%
EC	0.016	0.004	-0.012	-75.0%
sulfate	0.0004	0.0002	-0.0002	-50.0%

References:

1. Yang, W., *PM Speciation Profiles for Gas- and Oil-Fired Stationary Combustion - PM1101, PM1102, PM1103, PM1104 and PM1105*, 2015, California Air Resources Board: Sacramento, CA.
2. Watson, J.G., et al., *Characterization of Off-Road Diesel Emissions of Criteria Pollutants*, 2008.
3. Reff, A., et al., *Emissions Inventory of PM_{2.5} Trace Elements across the United States*. Environmental Science & Technology, 2009. **43**(15): p. 5790-5796.
4. Allen, P., *Developing PM Species Profiles for Emission Inventory*, 2008.
5. CEPAM, 2021, California Air Resources Board, Accessed: November 2, 2021.

V. Appendix

Table 2. Profile PM1110: Off-road diesel military generators using warm start

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
elemental carbon (EC)	12116	17.4722	17.4722	17.4722
organic carbon (OC)	11102	39.4552	39.4552	39.4552
non-carbon organic matter (NCOM)	11103	9.8638	9.8638	9.8638
sulfate	12403	1.3311	1.3311	1.3311
non-sulfate sulfur	12404	0.3130	0.3130	0.3130
nitrate	12306	0.0429	0.0429	0.0429
chloride	12203	0.0223	0.0223	0.0223
chlorine insoluble	12202	0.0064	0.0064	0.0064
aluminum	12101	0.0256	0.0256	0.0256
ammonium	12301	0.6158	0.6158	0.6158
antimony	12102	0.0011	0.0011	0.0011
barium	12107	0.0088	0.0088	0.0088
bromine	12109	0.0013	0.0013	0.0013
cadmium	12110	0.0027	0.0027	0.0027
calcium	12111	0.0650	0.0650	0.0650
chromium	12112	0.0010	0.0010	0.0010
copper	12114	0.0059	0.0059	0.0059
gallium	12124	0.0014	0.0014	0.0014
gold	12143	0.0030	0.0030	0.0030
indium	12131	0.0006	0.0006	0.0006
iron	12126	0.1341	0.1341	0.1341
lanthanum	12146	0.0031	0.0031	0.0031
lead	12128	0.0055	0.0055	0.0055
magnesium	12140	0.0056	0.0056	0.0056
manganese	12132	0.0021	0.0021	0.0021
molybdenum	12134	0.0004	0.0004	0.0004
nickel	12136	0.0006	0.0006	0.0006
palladium	12151	0.0026	0.0026	0.0026
phosphorus	12152	0.1301	0.1301	0.1301
potassium ion	65312	0.0036	0.0036	0.0036
potassium insoluble	12182	0.0072	0.0072	0.0072
rubidium	12176	0.0004	0.0004	0.0004
silicon	12165	0.0708	0.0708	0.0708
silver	12166	0.0002	0.0002	0.0002
sodium ion	12181	0.0088	0.0088	0.0088
sodium insoluble	12186	0.0160	0.0160	0.0160
strontium	12168	0.0007	0.0007	0.0007

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
thallium	12173	0.0002	0.0002	0.0002
tin	12160	0.0010	0.0010	0.0010
titanium	12161	0.0023	0.0023	0.0023
uranium	12179	0.0006	0.0006	0.0006
vanadium	12164	0.0006	0.0006	0.0006
yttrium	12183	0.0003	0.0003	0.0003
zinc	12167	0.0522	0.0522	0.0522
zirconium	12185	0.0014	0.0014	0.0014
others	12999	0.1887	0.1887	0.1887
unknown	12000	30.1218	30.1218	30.1218
Total		100.0000	100.0000	100.0000

Table 3. Profile PM1111: Off-road diesel military generators using cold start

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
elemental carbon (EC)	12116	11.4820	11.4820	11.4820
organic carbon (OC)	11102	69.1784	69.1784	69.1784
non-carbon organic matter (NCOM)	11103	17.2946	17.2946	17.2946
sulfate	12403	0.4323	0.4323	0.4323
non-sulfate sulfur	12404	0.2340	0.2340	0.2340
chlorine	12115	0.0096	0.0096	0.0096
aluminum	12101	0.0436	0.0436	0.0436
ammonium	12301	0.2859	0.2859	0.2859
antimony	12102	0.0019	0.0019	0.0019
barium	12107	0.0104	0.0104	0.0104
bromine	12109	0.0032	0.0032	0.0032
cadmium	12110	0.0008	0.0008	0.0008
calcium	12111	0.0984	0.0984	0.0984
chromium	12112	0.0008	0.0008	0.0008
cobalt	12113	0.0004	0.0004	0.0004
copper	12114	0.0098	0.0098	0.0098
gallium	12124	0.0170	0.0170	0.0170
gold	12143	0.0137	0.0137	0.0137
indium	12131	0.0233	0.0233	0.0233
iron	12126	0.1856	0.1856	0.1856
lanthanum	12146	0.0126	0.0126	0.0126
lead	12128	0.0105	0.0105	0.0105
magnesium	12140	0.0006	0.0006	0.0006
manganese	12132	0.0058	0.0058	0.0058
molybdenum	12134	0.0064	0.0064	0.0064
nickel	12136	0.0031	0.0031	0.0031
phosphorus	12152	0.0663	0.0663	0.0663

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
potassium ion	65312	0.0003	0.0003	0.0003
potassium insoluble	12182	0.0116	0.0116	0.0116
rubidium	12176	0.0043	0.0043	0.0043
silicon	12165	0.0983	0.0983	0.0983
silver	12166	0.0044	0.0044	0.0044
sodium	12184	0.0888	0.0888	0.0888
strontium	12168	0.0004	0.0004	0.0004
thallium	12173	0.0041	0.0041	0.0041
tin	12160	0.0038	0.0038	0.0038
titanium	12161	0.0017	0.0017	0.0017
uranium	12179	0.0029	0.0029	0.0029
vanadium	12164	0.0001	0.0001	0.0001
yttrium	12183	0.0037	0.0037	0.0037
zinc	12167	0.0712	0.0712	0.0712
zirconium	12185	0.0023	0.0023	0.0023
others	12999	0.2711	0.2711	0.2711
Total		100.0000	100.0000	100.0000

Table 4. Profile PM1112: Off-road diesel military generators (composite)

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
elemental carbon (EC)	12116	14.4771	14.4771	14.4771
organic carbon (OC)	11102	54.3168	54.3168	54.3168
non-carbon organic matter (NCOM)	11103	13.5792	13.5792	13.5792
sulfate	12403	0.8817	0.8817	0.8817
non-sulfate sulfur	12404	0.2735	0.2735	0.2735
nitrate	12306	0.0215	0.0215	0.0215
chloride	12203	0.0112	0.0112	0.0112
chlorine	12115	0.0048	0.0048	0.0048
chlorine insoluble	12202	0.0032	0.0032	0.0032
aluminum	12101	0.0346	0.0346	0.0346
ammonium	12301	0.4508	0.4508	0.4508
antimony	12102	0.0015	0.0015	0.0015
barium	12107	0.0096	0.0096	0.0096
bromine	12109	0.0022	0.0022	0.0022
cadmium	12110	0.0018	0.0018	0.0018
calcium	12111	0.0817	0.0817	0.0817
chromium	12112	0.0009	0.0009	0.0009
cobalt	12113	0.0002	0.0002	0.0002
copper	12114	0.0078	0.0078	0.0078
gallium	12124	0.0092	0.0092	0.0092
gold	12143	0.0084	0.0084	0.0084

Species Name	ARB-SAROAD	TPM Weight Percentage (%)	PM ₁₀ Weight Percentage (%)	PM _{2.5} Weight Percentage (%)
indium	12131	0.0120	0.0120	0.0120
iron	12126	0.1598	0.1598	0.1598
lanthanum	12146	0.0078	0.0078	0.0078
lead	12128	0.0080	0.0080	0.0080
magnesium	12140	0.0031	0.0031	0.0031
manganese	12132	0.0040	0.0040	0.0040
molybdenum	12134	0.0034	0.0034	0.0034
nickel	12136	0.0018	0.0018	0.0018
palladium	12151	0.0013	0.0013	0.0013
phosphorus	12152	0.0982	0.0982	0.0982
potassium ion	65312	0.0020	0.0020	0.0020
potassium insoluble	12182	0.0094	0.0094	0.0094
rubidium	12176	0.0024	0.0024	0.0024
silicon	12165	0.0846	0.0846	0.0846
silver	12166	0.0023	0.0023	0.0023
sodium	12184	0.0444	0.0444	0.0444
sodium ion	12181	0.0044	0.0044	0.0044
sodium insoluble	12186	0.0080	0.0080	0.0080
strontium	12168	0.0006	0.0006	0.0006
thallium	12173	0.0022	0.0022	0.0022
tin	12160	0.0024	0.0024	0.0024
titanium	12161	0.0020	0.0020	0.0020
uranium	12179	0.0018	0.0018	0.0018
vanadium	12164	0.0004	0.0004	0.0004
yttrium	12183	0.0020	0.0020	0.0020
zinc	12167	0.0617	0.0617	0.0617
zirconium	12185	0.0018	0.0018	0.0018
others	12999	0.2299	0.2299	0.2299
unknown	12000	15.0606	15.0606	15.0606
Total		100.0000	100.0000	100.0000

Table 5. Mapping of new PM profiles to off-road diesel military tactical support equipment EICs

EIC	EIC Name	PM Profile
86089212100000	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Sub-Category Unspecified	PM1112
86089212100100	Off-Road Equipment – Military Tactical Support Equipment – Diesel – A/C unit-D-120-Exhaust	PM1112
86089212100120	Off-Road Equipment – Military Tactical Support Equipment – Diesel – A/C unit-D-250-Exhaust	PM1112
86089212100130	Off-Road Equipment – Military Tactical Support Equipment – Diesel – A/C unit-D-500-Exhaust	PM1112
86089212100630	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Aircraft Support-D-120-Exhaust	PM1112
86089212100640	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Aircraft Support-D-175-Exhaust	PM1112
86089212101040	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Cart-D-120-Exhaust	PM1112
86089212101050	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Cart-D-175-Exhaust	PM1112
86089212101060	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Cart-D-250-Exhaust	PM1112
86089212101410	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Communications-D-50-Exhaust	PM1112
86089212101420	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Communications-D-120-Exhaust	PM1112
86089212101540	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Compressor (Military)-D-50-Exhaust	PM1112
86089212101550	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Compressor (Military)-D-120-Exhaust	PM1112
86089212101560	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Compressor (Military)-D-175-Exhaust	PM1112
86089212101570	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Compressor (Military)-D-250-Exhaust	PM1112
86089212101580	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Compressor (Military)-D-500-Exhaust	PM1112
86089212101790	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Crane-D-120-Exhaust	PM1112
86089212101800	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Crane-D-175-Exhaust	PM1112
86089212101810	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Crane-D-250-Exhaust	PM1112
86089212102290	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Deicer-D-120-Exhaust	PM1112
86089212103340	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-50-Exhaust	PM1112
86089212103350	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-120-Exhaust	PM1112
86089212103360	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-175-Exhaust	PM1112
86089212103370	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-250-Exhaust	PM1112
86089212103380	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-500-Exhaust	PM1112
86089212103390	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Generator (Military)-D-750-Exhaust	PM1112
86089212103870	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Hydraulic unit-D-120-Exhaust	PM1112
86089212104260	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Lift (Military)-D-120-Exhaust	PM1112
86089212104270	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Light-D-50-Exhaust	PM1112
86089212105900	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-50-Exhaust	PM1112

EIC	EIC Name	PM Profile
86089212105910	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-120-Exhaust	PM1112
86089212105920	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-175-Exhaust	PM1112
86089212105930	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-250-Exhaust	PM1112
86089212105940	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-500-Exhaust	PM1112
86089212105950	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Other tactical support equipment-D-750-Exhaust	PM1112
86089212106480	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Pressure Washers-D-175-Exhaust	PM1112
86089212106920	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Pump (Military)-D-50-Exhaust	PM1112
86089212106930	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Pump (Military)-D-120-Exhaust	PM1112
86089212108550	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Start Cart-D-120-Exhaust	PM1112
86089212108560	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Start Cart-D-500-Exhaust	PM1112
86089212109030	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Test Stand-D-120-Exhaust	PM1112
86089212109040	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Test Stand-D-175-Exhaust	PM1112
86089212109050	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Test Stand-D-250-Exhaust	PM1112
86089212109060	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Test Stand-D-500-Exhaust	PM1112
86089212109700	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Welder-D-50-Exhaust	PM1112
86089212109710	Off-Road Equipment – Military Tactical Support Equipment – Diesel – Welder-D-120-Exhaust	PM1112