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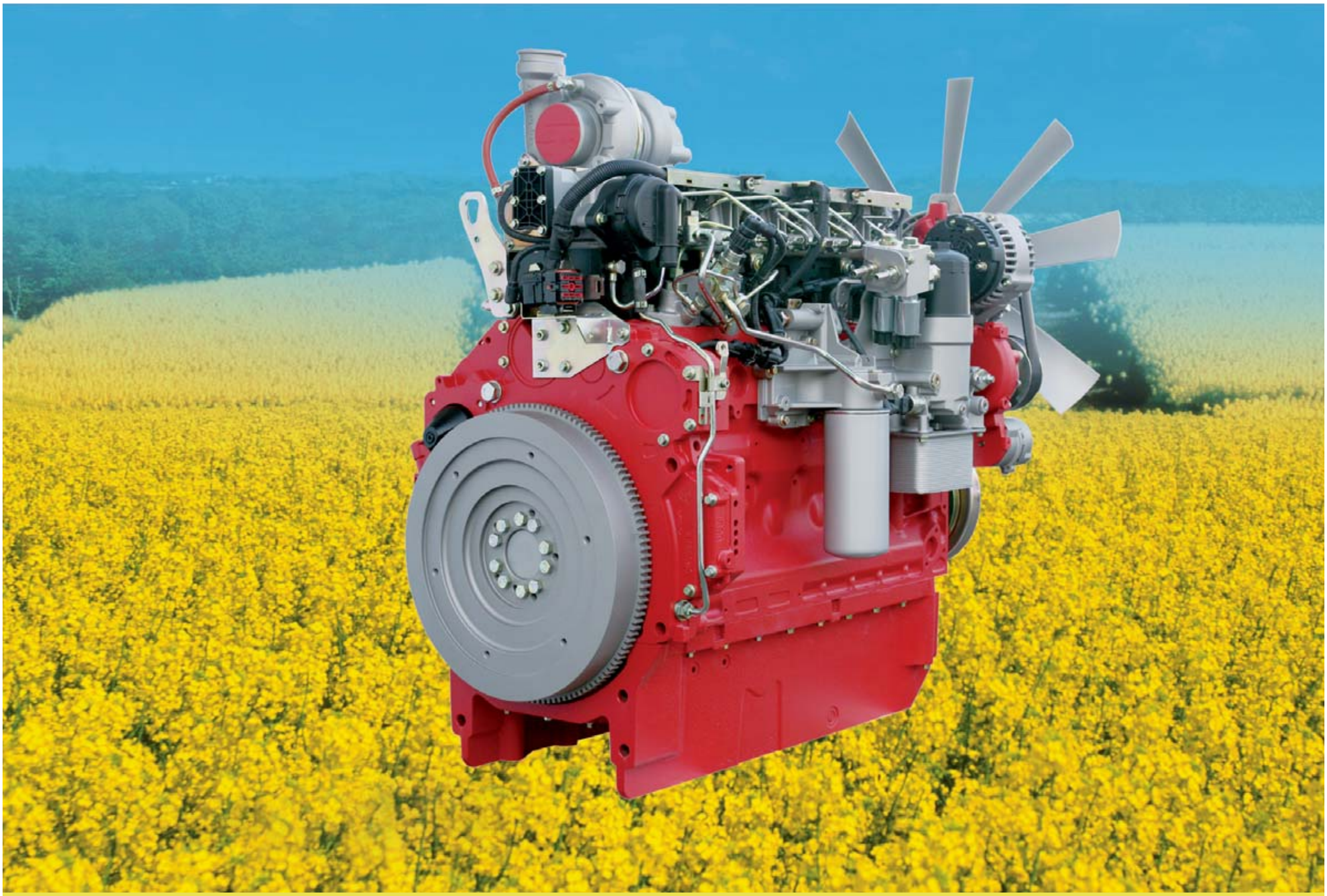
MTZ WORLDWIDE

06 June 2012 | Volume 73

Sonderdruck/Offprint
aus/from MTZ 6|2012
Springer Vieweg
Springer Fachmedien Wiesbaden GmbH

ELEMENTBELASTUNGEN VON ABGASNACHBEHANDLUNGSSYSTEMEN DURCH BIODIESEL

ELEMENT POLLUTION OF EXHAUST AFTERTREATMENT SYSTEMS BY USING BIODIESEL



ELEMENT POLLUTION OF EXHAUST AFTERTREATMENT SYSTEMS BY USING BIODIESEL

Biodiesel is a particularly attractive fuel for agricultural machinery. However, the introduction of new emission standards has made the use of exhaust gas treatment systems in agricultural vehicles essential. The combination of biodiesel and exhaust gas treatment causes problems, because the biodiesel contains traces of inorganic elements. These turn into ash during the combustion process in the engine, which can result in permanent damage to the components of the exhaust gas treatment system. Deutz and ASG have investigated the impact of current grades of biodiesel on the systems in real-life operation.

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MOTIVATION

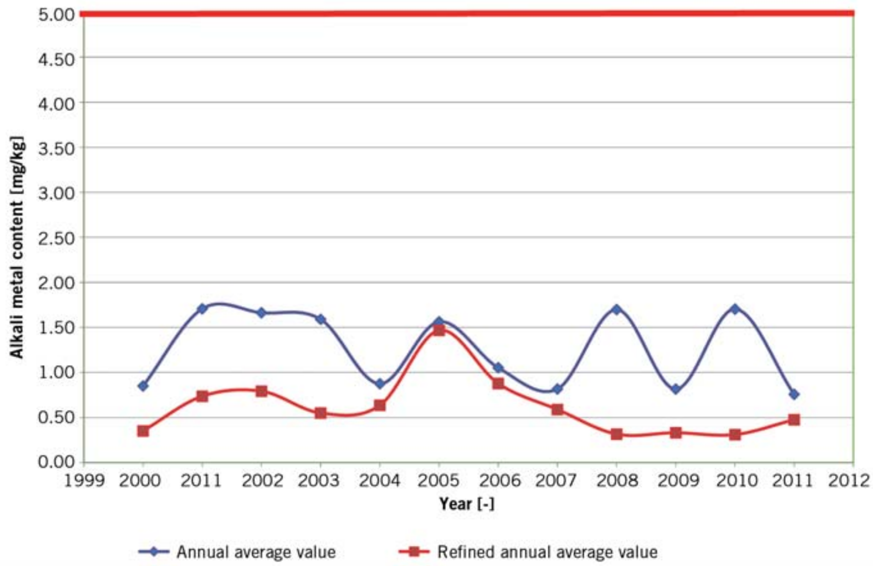
The substitution of fuels based on mineral oils with biofuels is a method to achieve political goals, considerably reduce CO_2 emissions and save fossil fuels. The EU Commission is pursuing a specific goal in the transport sector, namely that at least 10 % of the conventional fuels used in Europe should be replaced by fuels from renewable sources by the year 2020. This plan is entitled Renewable Energy Action Plan. It is supported by the European Community Law through the Fuel Quality Directive (2003/30/EC) and the Renewable Energy Directive (2009/28/EC). These directives are part of the European climate and energy package that the European Council decided upon in December 2008. The EU member states have recognised that this goal can primarily only be reached with biofuels; as such, they have submitted their national action plans to the Commission accordingly [1].

From the point of view of the engine manufacturer Deutz, biodiesel possesses certain fuel characteristics that are associated with negative effects in both the engine's injection system and lubricant system. If certain precautionary measures are observed, engines can still be reliably operated with pure biodiesel. For example, Deutz has approved various engine series for use with biodiesel [2]. Especially in the area of agricultural engineering, biodiesel approvals could be attractive due to the tax advantages associated with the fuel.

The ever-tightening exhaust gas limits for heavy duty diesel engines can only comply with these requirements if exhaust aftertreatment measures are used (e.g. diesel particle filters and/or selective catalytic reduction (SCR)). Using biodiesel in combination with these aftertreatment technologies is afflicted by additional problems, as biodiesel contains traces of inorganic elements such as sodium, potassium, calcium and magnesium. When combusted in the engine, inorganic elements generate ashes (e.g. oxides) which are partially transferred into the aftertreatment components, thereby inhibiting their efficiency on a long-term basis.

The limits for inorganic elements specified in the European Norm for Biodiesel DIN EN 14214 [3] are as follows: maximal 5 mg/kg of Na+K, maximal 5 mg/kg of Ca+Mg. If these limits really do reflect the actual biodiesel quality that can be seen in the field today, they are at a level that would cause irreversible damage to the aftertreatment components at their current level of technological development.

As part of a study supported by the Union zur Förderung der Oel- und Proteinpflanzen e.V. (UFOP) [4], analysis results of market-relevant biodiesel specimens from the years 2000 to 2011 were evaluated. This was done to provide developers of engines and exhaust aftertreatment systems with realistic data with which they could estimate the potential carriers of ash-forming substances and catalyst contaminants. This data was based on the databases of the Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V. (AGQM) and Analytik-Service GmbH (ASG).



❶ Annual average values and refined annual average values for the total concentration of alkali metals in biodiesel

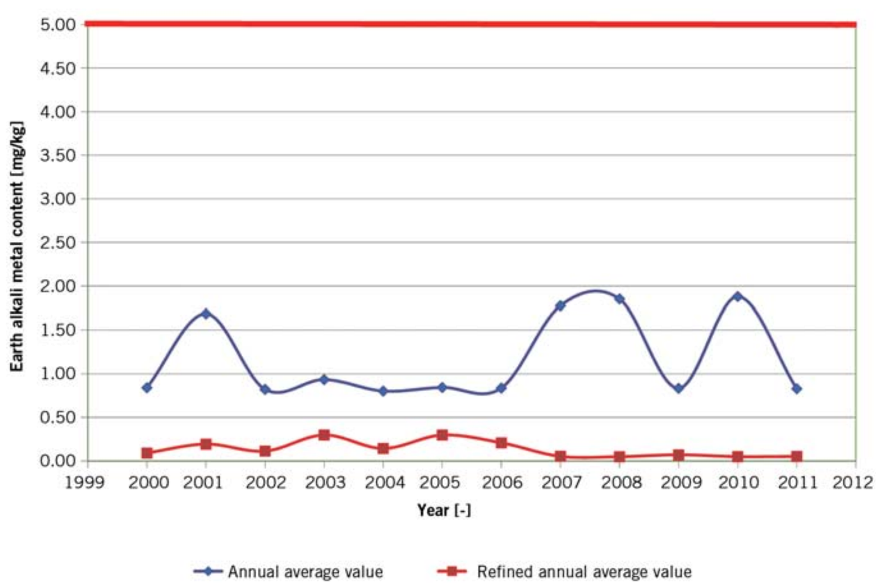
STATUS OF CURRENT ENGINE AND AFTERTREATMENT TECHNOLOGY

The exhaust legislation has been drastically tightened up in Europe throughout the last 20 years. This has caused the limits for nitrous oxide (NO_x) to be reduced by 97 % and the limit for particle mass has been reduced by approximately 98.5 %. The introduction of the exhaust class Euro IV has led to SCR technology coming out on top as the leading exhaust aftertreatment technology for heavy commercial vehicles. A limit for the number of particles is to be introduced from Euro VI onwards; adhering to this will only be possible by means of a combination of the SCR system and the particle filter.

Emission stage IIIA has been in force since January 2006 and working mobile machines have been able to comply with it solely by measures that affect the inside of the engine. These include charge air cooling, exhaust gas return and increasing the injection pressure. However, since 2011, the introduction of exhaust class IIIB has made the use of exhaust aftertreatment inevitable. To this end, Deutz has decided on the following technological courses:

: particle filter in combination with exhaust gas return for construction equipment and other industrial purposes
: SCR (vanadium-tungsten titanium dioxide VWT) without exhaust gas return for agricultural purposes.

SCR technology was selected for agricultural purposes as a particularly low level of fuel consumption is required for this market. As nitrous oxide can be effectively reduced through aftertreatment using SCR technology, the engine can be set up for optimal consumption by selecting an earlier fuel injection point.



❷ Annual average values and refined annual average values for the total concentration of alkaline earth metals in biodiesel

BIODIESEL FIELD TEST 2008/2009 (UFOP PROJECT 540/80)				
ENGINE	**PERFORMANCE / TORQUE**	**DISPLACEMENT**	**EXHAUST CLASS**	**OIL QUALITY**
TDC2013 L04 4V	158 kW bei 2300 rpm / MDmax: 800 Nm	4.8 l	Euro IV/V with VWT-SCR	ACEA E7 DQC III-10 Element contents for contamination calculation: Ca: 3.350 mg/kg Mg: 10 mg/kg P: 1.300 mg/kg Zn: 1.400 mg/kg
TDC2013 L06 4V	235 kW bei 2300 rpm / MDmax: 1200 Nm	7.2 l		
BIODIESEL FIELD TEST 2010/2011 (UFOP PROJECT 540/103)				
ENGINE	**PERFORMANCE / TORQUE**	**DISPLACEMENT**	**EXHAUST CLASS**	
TDC 7.8 L6	238 kW at 2200 rpm / MDmax: 1500 Nm, CR: 2000 bar	7.8 l	Class COM IIIB with VWT-SCR	
TDC 6.1 L6	203 kW at 2100 rpm / MDmax: 1200 Nm, CR: 2000 bar	6.1 l		
TDC 6.1 L6	174 kW at 2100 rpm / MDmax: 1070 Nm, CR: 1600 bar	6.1 l		

❸ Engines, exhaust aftertreatment systems and lubricating oils from both the biodiesel field tests as the basis for the calculations

BIODIESEL SURVEY

In the last 11 years, AGQM has gathered more than 8000 analytical data containing phosphorous and metallic content from unannounced inspections of biodiesel manufacturers. The method of choice for determining element contents is the ICP OES method (inductively coupled plasma optical emission spectrometry). Alkali and alkaline earth metals are measured with the testing method DIN EN 14538 [5] and the phosphorous content is measured with the DIN EN 14107 [6] method.

In the first stage, the annual average value was calculated; this meant that all the test results that were under the lower limit of determination (e.g. <0.5 mg/kg) were not considered. This data was also integrated in the second stage. This took place on the basis of the re-evaluations of the raw data and made the annual average value more precise. ❶ and ❷ show the results that were calculated for the total concentration of alkalis and alkaline earth metals for the years 2000 to 2011. At the upper end of the scale, the highest permissible value (in accordance with DIN EN 14214) is shown as 5 mg/kg; this is the total concentration of alkali or alkaline earth metals.

Alkaline metals like sodium and potassium are brought into the fuel via the transesterification catalysts during the process of biodiesel manufacturing. In contrast, the alkaline earth metals Calcium and Magnesium mostly enter the fuel via the vegetable oil that is used during manufacturing or they can be brought in via the washing water that is used when the biodiesel is washed. Basically, the annual average values calculated are considerably lower than the associated limit values. There tends to be more alkali and alkaline earth metals in biodiesel. The refined average values always undercut the associated annual average values.

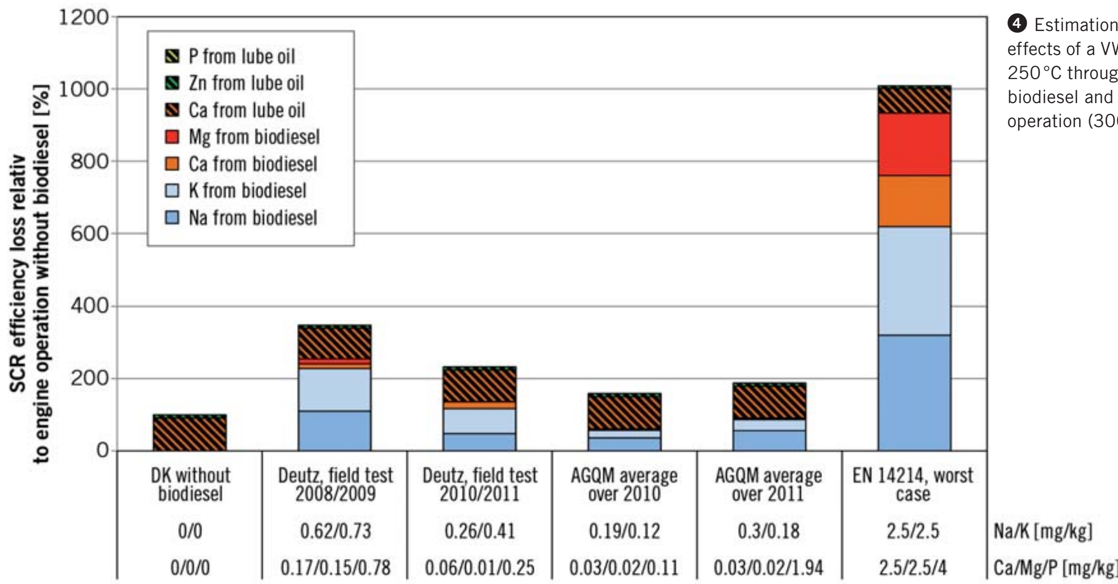
EFFECT OF ASH ACCUMULATION ON AFTERTREATMENT SYSTEMS

Contamination of SCR catalysts by metals has been comprehensively described in the literature and basic elements such as potassium and sodium show an especially high contaminative effect [7-10]. The contamination is based on the fact that the acid reaction centres of the SCR catalyst are neutralised and as such, are no longer available to take up the ammonia, which is also alkaline in nature. The result is a drop in effectiveness right up to complete deactivation. According to the investigation results of a FVV project [7], as much as 0.1 % mass of potassium in the washcoat of a vanadium-SCR catalyst led to a drop in effectiveness of approximately 20 %. Sodium is a similarly strong contaminant, the alkaline earth metals calcium and magnesium usually have a lower, but still considerable contaminant effect.

On the basis of the contaminant data available in the literature, a calculative method has been developed to estimate the contamination of a VWT-SCR catalyst as it would be expected to occur when biodiesel with defined element contents is burned. Contamination through elements that result from the lubricant due to the oil consumption are also considered. Oil consumption makes up just 0.05 % of fuel consumption, but the risk of contamination through lubricant components should not be neglected, as higher element concentrations are present in them. This is a short description of the manner in which SCR contamination is calculated:

: calculation of the element emissions from fuel consumption and oil consumption as well as the element content in biodiesel and lubricant (data from ❸, assumption that 30 % of the oil consumption will occur due to evaporation – i.e. without elements being emitted)
: calculation of element concentrations in the washcoat as a function of the lifespan. Assumption of a defined deposition rate (2.5 %, determined on the basis of washcoat analyses from the field test project)
: calculation of the contamination caused by the use of element-specific contamination rates through the FVV project [7] and summation of all the elements.

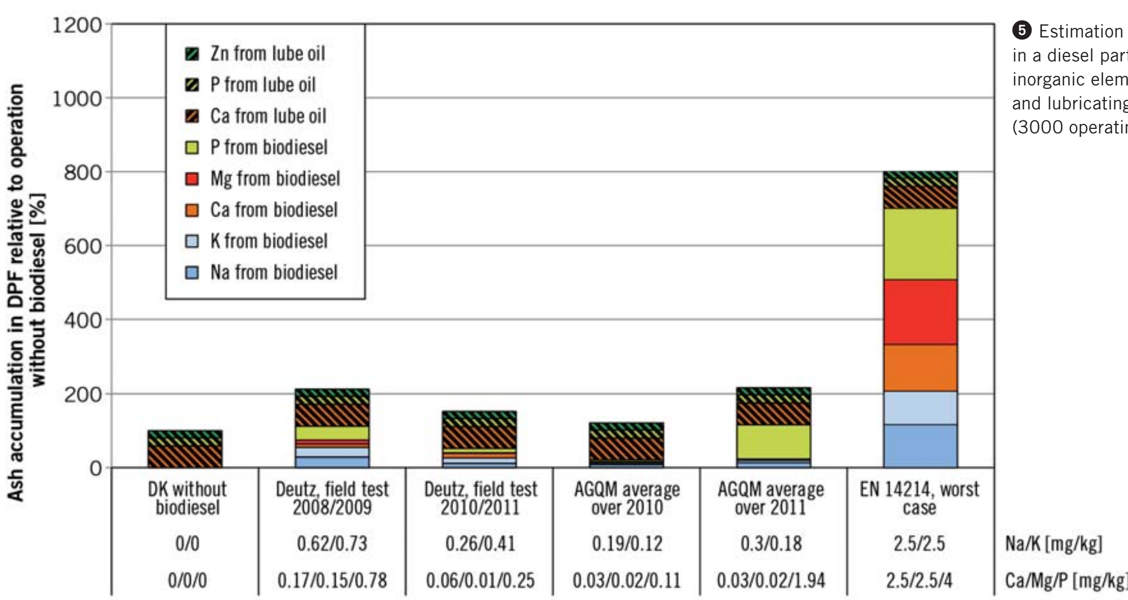
❹ shows the calculated VWT-SCR reductions in efficiency for various biodiesel qualities in terms of element contaminations (100 % relates to diesel without biodiesel). If the biodiesel producers were to actually manufacture a marginal biodiesel in accordance with DIN EN 14214, a nine-fold contamination effect would occur; this level of contamination would be far too high. This would make using biodiesel in engines with SCR exhaust aftertreatment technology impossible. In contrast, on the basis of the 2010 AGQM data as well as the Deutz field test data as part of UFOP project 540/103 of 2010/11, contamination through biodiesel is possible where this biodiesel is itself



❹ Estimation of the contaminant effects of a VWT-SCR coated catalyst at 250 °C through inorganic elements from biodiesel and lubricating oil at tractor operation (3000 operating hours)

only just above contamination through lubricant. When the effectiveness of the SCR catalysts were measured again in both field tests, a lower reduction of effectiveness was found in comparison with the calculations [11, 12]. Due to the results that are at hand, Deutz has decided to approve class IIIB engines with SCR exhaust aftertreatment systems for operation with B100. This approval is given under the proviso that the SCR catalyst always be replaced after 3000 h of biodiesel operation.

A similar calculation procedure was used for the accumulation of ashes in particle filters. A retention rate of 100 % is assumed here. ❺ shows the results of this calculation for the same application as above. Here, too, 100 % relates to diesel without biodiesel. The relation of the damaging effects of the various fuel qualities is very similar for both the ash contaminant and the SCR contamination. A (hypothetical) marginal biodiesel in accordance with DIN EN 14214 would have a eleven-fold greater level of ash accumulation than a biodiesel-free diesel fuel and would clog the filter in less than 500 h. This will become relevant from the introduction of the EU class VI in 2014, as both particle filters and SCR catalysts will be used. This will also be the case for agricultural machinery. In terms of the ash accumulation, it must be stated that the real biodiesel qualities deliver a considerably better image than a worst case quality that exhausts the specification limits.



❺ Estimation of ash contaminant in a diesel particle filter caused by inorganic elements from biodiesel and lubricating oil at tractor operation (3000 operating hours)

SUMMARY AND OUTLOOK

The evaluation of the AQGM and field test data shows that the quality of biodiesel is considerably better in the field than the associated limit values permit. Two studies from the USA delivered similar results [13, 14]. In this context, it is appreciated that AGQM now publishes the results of their unannounced quality inspection on an annual basis. The low concentrations of elements are an important factor for the approval of EU class IIIB Deutz agricultural engines.

A fundamental re-evaluation of biodiesel approvals is necessary for future EU class IV engine concepts and the use of exhaust aftertreatment technologies that is associated with them (Fe-Zeolith-SCR-Substrate, DOC). Due to the contamination problems, the engine manufacturer is of the opinion that urgent action must be taken to considerably reduce the limit values of EN 14214 and develop the analytical methods that are associated with it. Measures to reduce the element content in lubricating oil have already been implemented. The measures implemented by the engine manufacturers to reduce lubricating oil consumption have also been largely exhausted.

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