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Secondary Emissions when using fuel additives for regeneration?

Secondary Emissions from Fuel-borne DPF Regeneration Additives.

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Whilst the use of the DPF can bring very significant particulates reductions, it is prone to block and all known methods to regenerate have their own associated drawbacks. Regeneration performance is used as the justification for launching Octel's second generation additive. The performance of the additive against its possible drawbacks – secondary emissions – are described using data from IFP and Matter Engineering and conclusions drawn.

Use of a DPF has drawbacks; aside from fuel economy penalties, the possibilities of adversely affecting legislated or non-legislated emissions and the accumulation of ash are common to all, though the latter is particularly acute where a fuel-borne regenerant is used. The potential non-legislated emissions effects are, thanks largely to the VERT program, now identified as; polychlorinated-dibenzodioxins or –dibenzofurans (PCDD/F), polycyclic aromatic hydrocarbons (PAH) and nitro-PAH, nanoparticulate numbers, active surface of emitted particulates and metals. Only two additive metals have so far passed the VERT appraisal process and, given the cost involved and that Octel owned one such (iron as Satacen® or Plutocen®) it may seem strange to try to approve a third additive.

Octel in-house testing at 5 steady state conditions, at constant metal treat rate, used an XUD-9A engine on a test bench and varied additive composition across the range 100% Fe, 0% Sr to 0% Fe, 100% Sr. More frequent, more complete regenerations were shown to occur at around 80% Fe, 20% Sr. This synergy could be exploited to provide lower average backpressure (better fuel economy) or lower additive treat rate (longer filter change interval).

The engine technology was noted to have a very significant, but imperfectly understood, impact on whether the use of the additive affected legislated emissions. Favourable effects are frequently found. PAH emissions reductions are, as expected, found on using the DPF with additive. Some analysis of nitro-PAH, metals and particle-size emissions had previously been obtained. Data from a new VSET (VERT Secondary Emissions) test is being acquired to support this and to examine the PCDD/F performance.

Particle Induced X-ray Emission (PIXE) spectroscopic analysis of filter papers from MVEG testing has shown that iron emissions from the DPF/additive combination are comparable to those from base fuel. Sr emissions were found to be lower, speculatively this has been linked to the presence of Sr with Ca in lube oil formulations. Additionally, use of the DPF produced lower emissions of Cu, Pb and Zn. Nitro-PAH emissions were determined by extraction of the particulate mass. Converted to emissions units, the additive/DPF combination is shown to produce very significant reductions even of 1-nitropyrene.

SMPS measurements from a Liebherr D914T engine operating at the steady-state points on the ISO8178/4 cycle showed the use of the additive, in the absence of the DPF, to be associated with a dramatic increase in the number of nucleation mode (< 40 nm) particles. Use of a thermodenuder ensures that these have solid cores. The Ibiden DPF is confirmed as having excellent efficiency for these and all other particles examined. The use of the NanoMet equipment gave a surprising result. Despite the large numbers of ultrafine particles associated with the use of the additive in the absence of the DPF, the active surface area decreased. Further, the change in the PAS/DC ratio indicated that a different type of particle had resulted from additive use, one with less surface-bound hydrocarbon. Tentatively, it would seem that the best explanation for these observations is that where the additive is present, the morphology of the accumulation mode agglomerate changes from chain-like to a more spherical arrangement. Such would, at least intuitively, offset against increased surface area due to nucleation mode particles and reduce the opportunity for SOF materials to condense on the surface.

In conclusion, a metal should still only be used in order to ensure efficient regeneration of the DPF. Where this is done, the metals of the combination additive are efficiently retained, and unlooked for benefits obtained. The metals appear to affect accumulation mode particle morphology, but in the positive sense of a reduction (were the DPF ever to fail). Increased emissions of nitro-PAH do not seem to be a concern, on the basis of the limited evidence to hand.

Thanks are due to Andreas Mayer of TTM for his assembly and management of the testing program and for Mr Mosimann of the NanoMet team for the early provision of results. Previous testing of the Octel additive has been carried out under the supervision of Jean-Baptiste Dementhon at IFP.

Secondary Emissions from Fuel-borne DPF Regeneration Additives

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- **A downside to the DPF and regeneration additives**
- **Octel’s 2nd Generation additive, why?**
- **Measuring the Octel additive against the downsides**
  - IFP data
  - Matter Engineering data
- **Conclusions to date**
- **Thanks**

DPF Regeneration

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- **All known approaches have their own set of advantages and drawbacks**
- **The drawbacks associated with the use of metallic fuel additives are:**
  - Ash Accumulation
  - Potential for adverse effects on legislated emissions
  - Potential for adverse effects on non-legislated emissions

Non-Legislated Emissions Effects

- **The potential for effects on non-legislated emissions includes:**
  - PCDD/F
  - PAH and nitro-PAH
  - Numbers of ultra-fine particles
  - Surface area of ultra-fine particles
  - Metals emissions

Octel's Second Generation Additive

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At the time of writing, the following apply:

- **There is only one positive 'approval' process for DPF and regeneration method (VERT)**
- **Only two metallic fuel additives have passed**
- **Octel, through acquisition of ODL owned iron (Plutocene, Satacen)**

So why bother to try for a second?

Bench Testing of Octimax™ (1)

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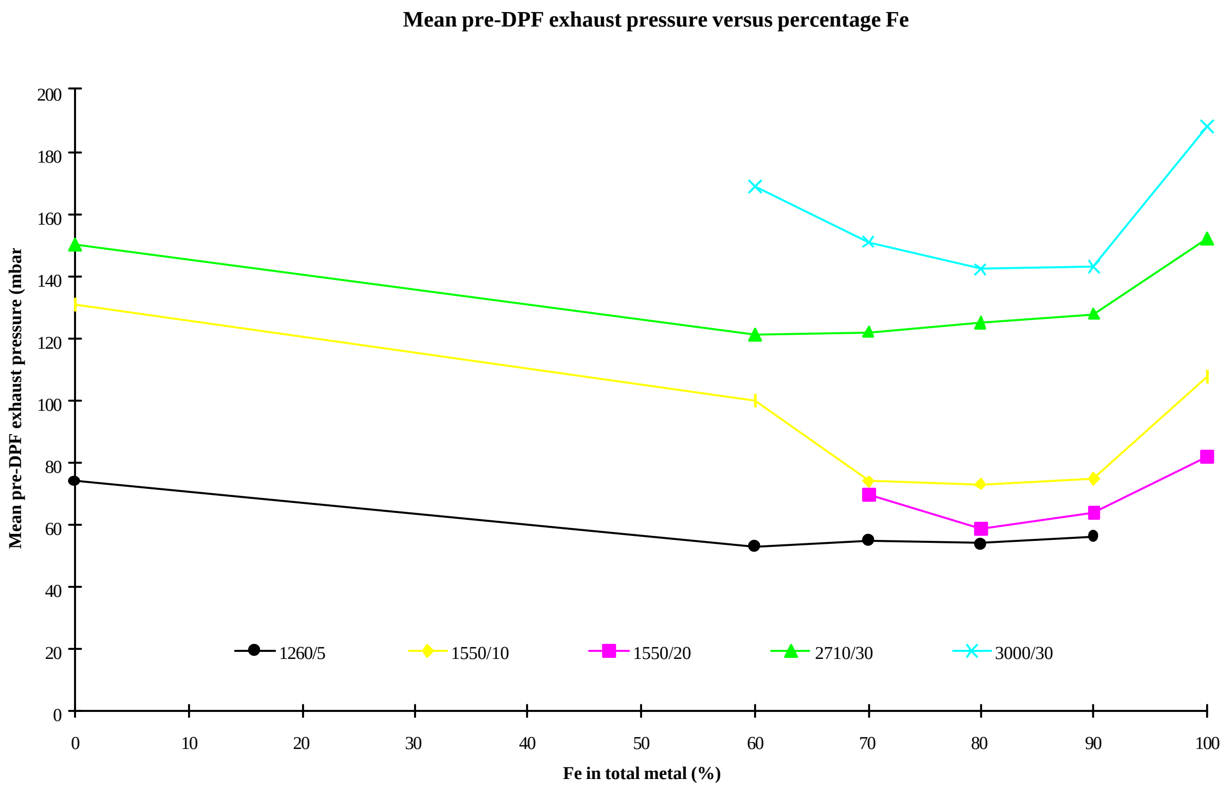

Bench testing of Octimax™ (2)

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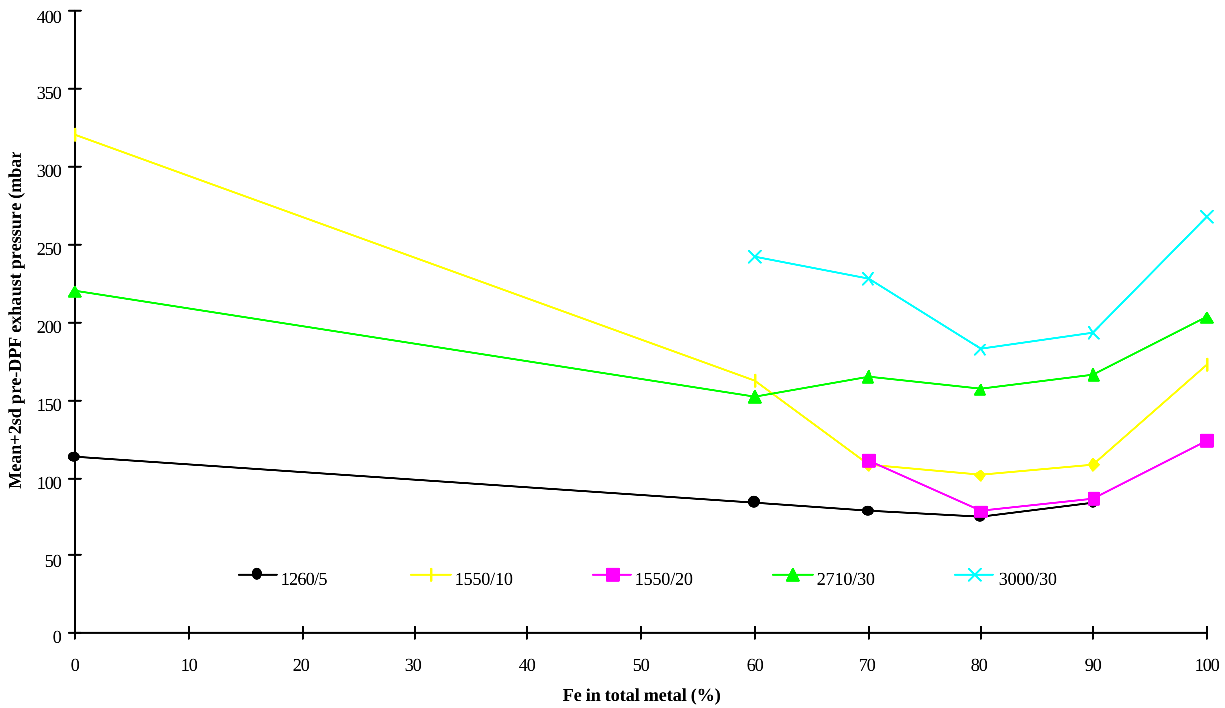
Mean + 2sd pre-DPF exhaust pressure versus percentage of Fe in added metal



Bench testing of Octimax™ (3)

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Mean pre-DPF exhaust pressure

Speed/load	Fe/Sr ratio 20/0	18/2	16/4	14/6	12/8	0/20	Benefit of 80% Fe vs. 100%
1260/5		56	54	55	53	74	
1550/10	108	75	73	74	100	131	32%
1550/20	82	64	59	70			28%
2710/30	152	128	125	122	121	150	18%
3000/30	188	143	142	151	169		24%

Mean+2sd pre-DPF exhaust pressure

Speed/load	Fe/Sr ratio 20/0	18/2	16/4	14/6	12/8	0/20	
1260/5		84	75	78	84	113	
1550/10	173	109	102	109	162	321	41%
1550/20	124	86	78	111			37%
2710/30	203	167	157	165	152	220	23%
3000/30	268	193	183	228	242		32%

Advantages of Octimax™ vs. Fe

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The decrease in DPF back-pressure corresponds to:

- **Broader operating range in retrofit application**
- **Lower fuel consumption penalty, or**
- **Lower additive treat cost and prolonged service interval for the DPF**

Eliminating the negatives

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- Legislated emissions testing can show benefit, (typically) no-harm or (once) a need to trade-off
- Independent SMPS testing showed no problems
- Independent testing of PAH showed expected DPF advantage
- Metals emissions testing performed
- Nitro-PAH emissions testing performed

Emissions measurements by IFP

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	S	Cl	Ca	Cr	**Fe**	Ni	Cu	Zn	**Sr**	Pb
No additive No DPF	620	335	46	<2	26	<1	185	40	16	19
No additive, DPF	<30	308	19	4	24	<1	24	4	<6	<4
Additive No DPF	780	349	50	7	600	3	110	38	119	15
Additive, DPF	80	370	15	5	32	3	4	2	<2	<3

- **MVEG cycles for VW Golf 1.9 ltr TDI, Corning Ex80™ trap**
- **Analysis of filter papers by PIXE analysis at CERN**
- **Absolute emissions levels could not be determined, but relative values are valid**
- **All figures are ± 20%**
- **Indication is that for Octimax™ plus DPF Sr emissions are lower than for base fuel *(Sr in Ca additive in lube oil?)***

Nitro-PAH Emissions (ì g/g particulate)

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	W/o additive W/o trap	With additive W/o trap	W/o additive With trap	With additive With trap
Particulate sample weight (mg)	5.01	4.39	0.67	0.32
1-nitro-naphtalene	0.36	0.24	0.46	0.68
2-nitro-naphtalene	0.91	0.78	0.53	0.73
1-nitro-3-methyl-naphtalene isomer	0.07	0.15	0.05	0.04
3-nitrofluoranthene	<0.01	<0.01	<0.05	<0.05
1-nitropyrene	23	8	1.3	0.84
6-nitro-chysene	<0.01	<0.01	<0.05	0.2
6-nitro-benzo(a)pyrene	0.11	0.11	<0.05	<0.05

- **Above determined by IFP using GC-NICI-MS in single ion monitoring after extraction (CH_2Cl_2) and clean-up of extract**
- **Absolute benefit on volatile components is small**
- **Knowing particulate emissions in g/km enables an estimate in emissions units**

Nitro-PAH emissions (ng/km)

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	W/o additive W/o trap	With additive W/o trap	W/o additive With trap	With additive With trap
1-nitro-naphthalene	34.2	25.2	2.8	4.1
2-nitro-naphthalene	86.5	81.9	3.2	4.4
1-nitro-3-methyl-naphthalene isomer	6.7	15.8	0.3	0.2
3-nitrofluoranthene	<1	<1.1	<0.3	<0.3
1-nitropyrene	2,185	840	7.8	5.0
6-nitro-chrysene	<1	<1.1	<0.3	1.2
6-nitro-benzo(a)pyrene	10.5	11.6	<0.3	<0.3

Further questions to be answered

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- ***With what size of particle is the Sr associated?***
- **What is the speciation of Sr emitted?**
- ***Does the presence of Sr affect the active surface area?***
- **Does the presence of Sr affect PCDD/F emissions?**

- **The answer - a measurement program using EMPA, AHTA, ETH and SUVA managed by Andreas Mayer**
- ***Today, propose to describe two aspects only***

SMPS, base fuel, thermodenuder

Matter Engineering AG

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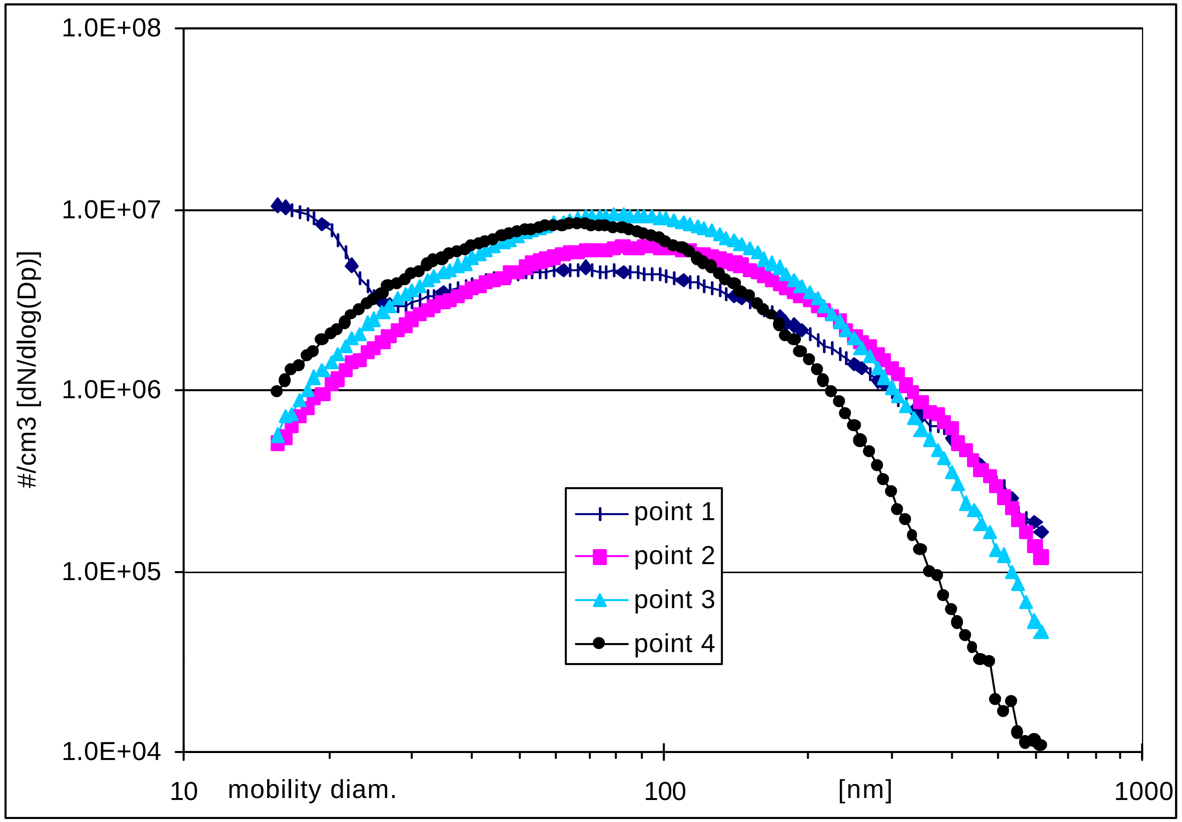

SMPS, base fuel plus Octimax™, thermodenuder (Matter Engineering AG)

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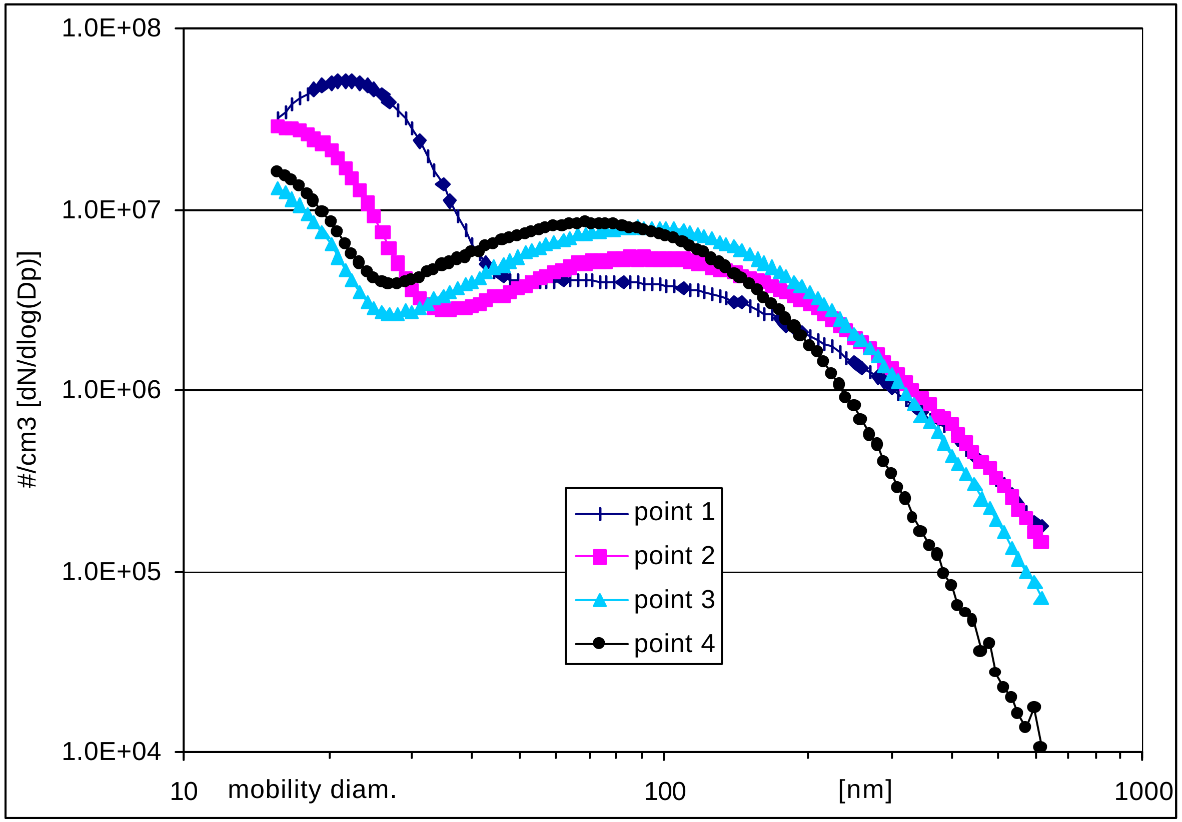

SMPS, additised fuel, Ibiden DPF, thermodenuder (Matter Engineering AG)

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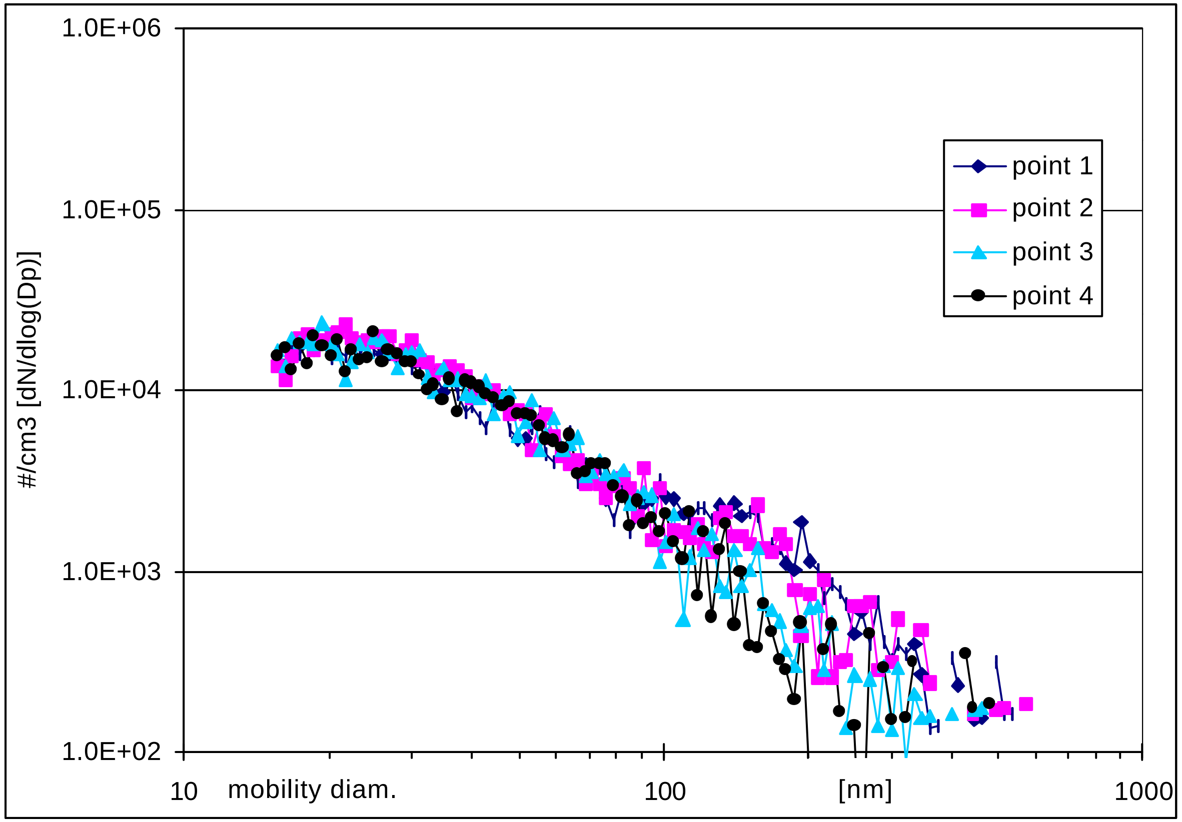

SMPS Data: Inferences

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ISO 8178/4 Test point	Base Fuel				Additised Fuel			
	Run 1		Run 2		Run 1		Run 2	
	Peak size (nm)	Peak Ht. (x 10^6)	Peak size (nm)	Peak Ht. (x 10^6)	Peak size (nm)	Peak Ht (x 10^6)	Peak size (nm)	Peak Ht. (x 10^6)
1	88.2	4.76	68.5	4.71	94.7	4.15	N/A	N/A
2	94.7	6.63	94.7	6.09	94.7	5.50	91.4	5.33
3	82.0	9.28	82.0	9.30	88.2	8.53	88.2	7.92
4	63.7	7.85	68.5	8.22	68.5	8.47	68.5	8.39
5	98.2	5.93	98.2	6.28	101.8	4.81	109.4	5.72
6	85.1	4.17	105.5	4.30	101.8	3.31	113.4	3.08
7	82.0	3.32	82.0	3.44	88.2	2.06	88.2	1.90
8	N/A	N/A	61.5	6.82	63.8	N/A	66.1	0.67

- **The metals are, or are associated with, particles smaller than about 40 nm (can be confirmed - simultaneous ELPI samples taken)**
- **Simplistic analysis suggests that accumulation mode particles are made fewer and larger (and less mass on ELPI stages 3-12)**
- **The DPF is very effectively removing these smaller particles generated in the presence of the additive**

NanoMet Measurement
(Matter Engineering AG)

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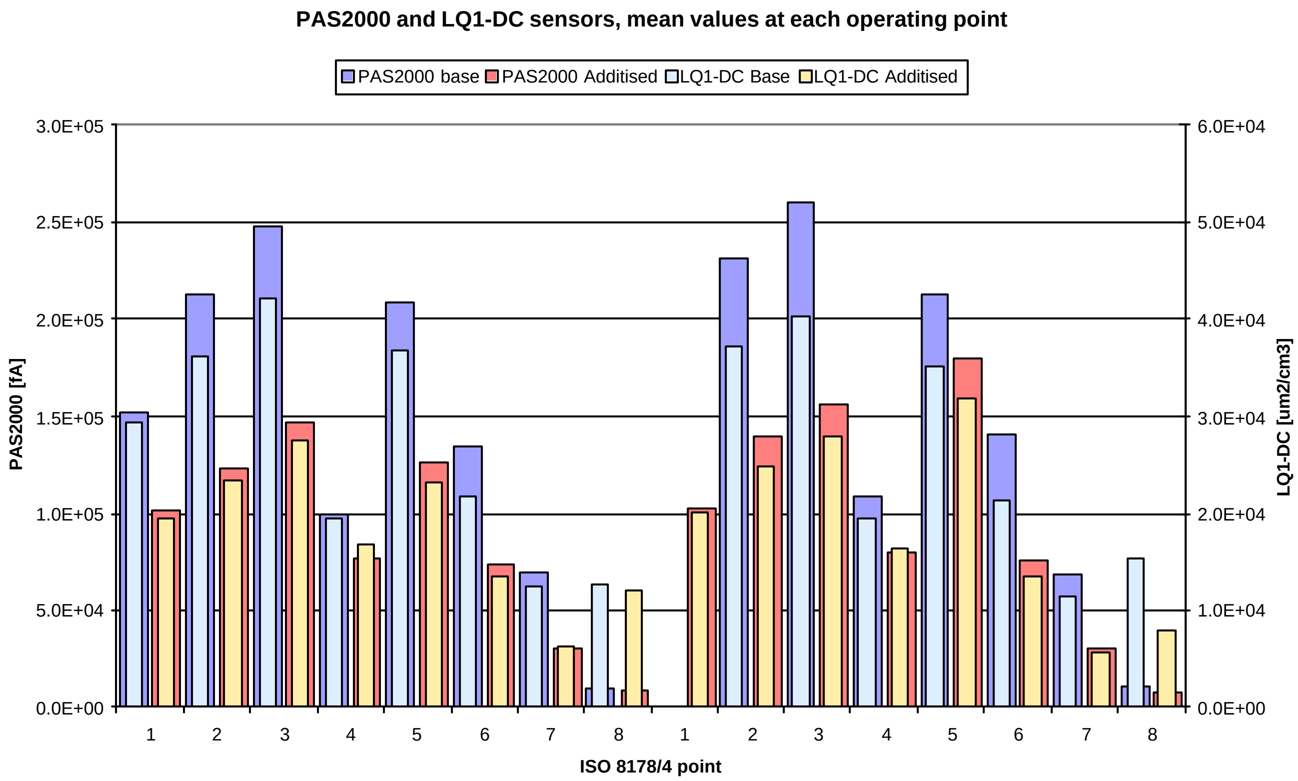

NanoMet PAH/Surface ratio
(Matter Engineering AG)

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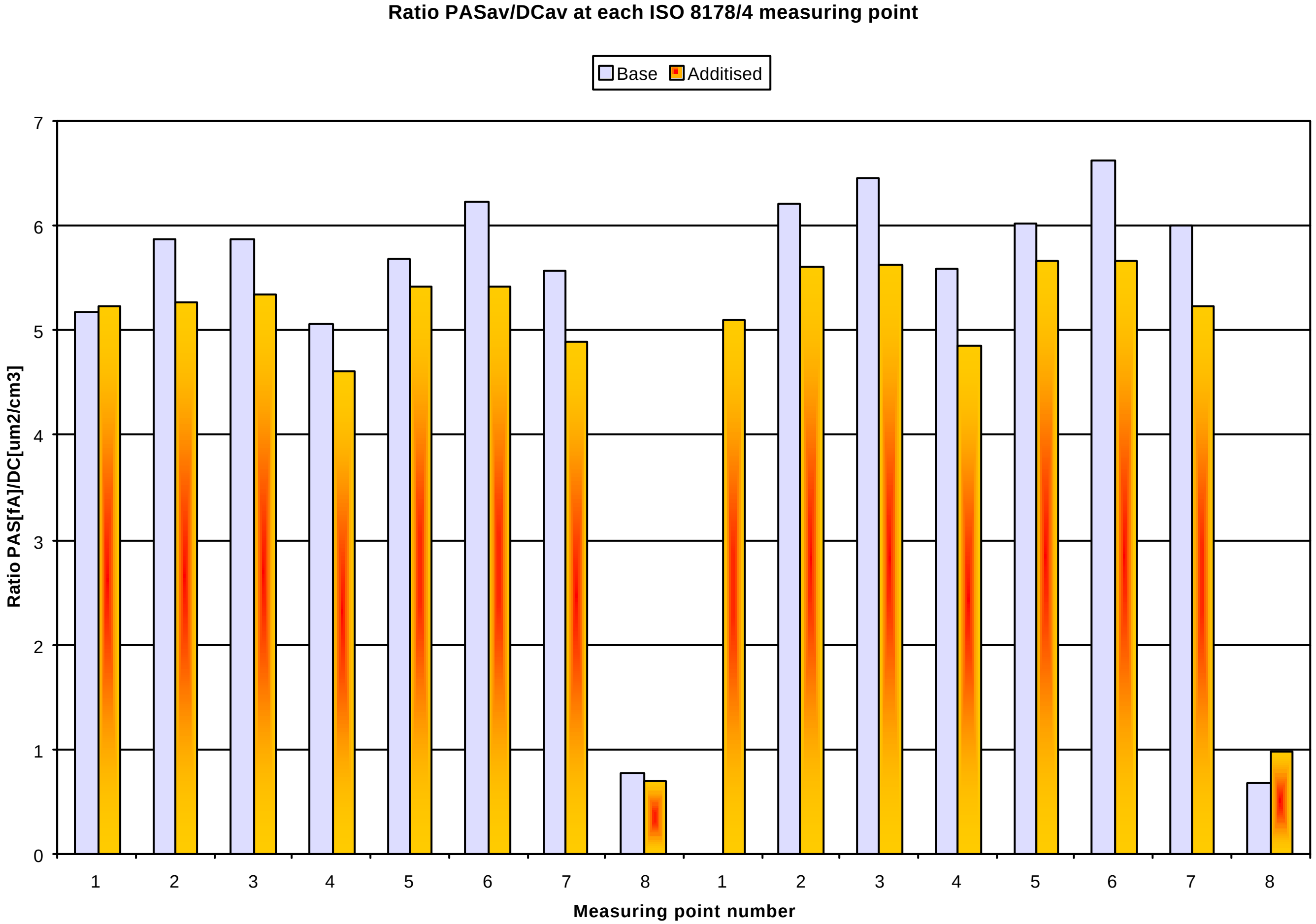

NanoMet Results: Effects Noted

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- **Effects of using Octimax™ additive at 25 ppm m/m in low sulphur diesel are:**
  - The specific surface area of the particulate decreases
  - The PAS signal decreases, presumably indicating lower surface-resident PAH
  - The ratio of PAS/DC if anything, decreases

Nanomet Results: Interpretation

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The alternatives include:

- **DC fails to 'see' Fe/Sr particles**
- **Some of the C-particles are burning out or agglomerating**
- **The 'cloud' of ultrafine Fe/Sr particles are smooth spheres and the aerodynamically 'larger' C-based ones are highly irregular**
- **The metals affect all particle morphology (smoother and rounder)**

The extra metal, how are we doing?

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- **As expected:**
  - The metals produce large amounts of ultrafine particles
  - These particles are efficiently trapped by the filter
- **More surprisingly:**
  - The metals give a particulate of overall lower active surface area, with relatively less PAH
  - Nitro-PAH does not appear to be an issue
- **Overall, thus far, none of the possible negatives relating to the use of Sr have manifested**

Thanks are due to the following

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- **Andreas Mayer** **TTM**
- **Mr Mosimann** **Matter Engineering**
- **Jean-Baptiste Dementhon** **IFP**