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Diesel engine exhaust – Is a more complete view necessary?

Dirk Dahmann, Bochum

Focus, Dahmann, MDEC 2010
05.07.2011

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Overview

- Introduction and general remarks
- Exhaust particles
- Classification
- Analytical methods
- Nitrogen Oxides
- Basics
- Exposure situation in salt/potash and hard coal mining
- European developments
- Conclusions

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Introduction

- This presentation will try to look at some possible developments (some of which are already present)
- Sope: Focus on the European/German Perspective
- However: Diesel Exhaust in Miners Study (DEMS) by NCI/NIOSH 2010 (exposure determination) is publicly available since 27.9.2010
- ❖ http://annhyg.oxfordjournals.org/content/early/recent downloadable
- I shall occasionally refer to these papers

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Diesel Exhaust in Miners Study (DEMS) by NCI/NIOSH

- Current state of publications:
  - The Diesel Exhaust in Miners Study: I. Overview of the Exposure Assessment Process
  - The Diesel Exhaust in Miners Study: II. Exposure Monitoring Surveys and Development of Exposure Groups
  - The Diesel Exhaust in Miners Study: III. Interrelations between respirable elemental carbon and gaseous and particulate components of diesel exhaust derived from area sampling in non-metal mining facilities
  - The Diesel Exhaust in Miners Study: IV. Estimating historical exposures to diesel exhaust in underground nonmetal mining facilities
- Epidemiological part not yet published!

Diesel exhaust…

- is a very complex mixture of gaseous and particulate components and phases and
- leaves the engine in a condition far off the environmental equilibrium and will reach the workers‘ breathing zones in a markedly different state.
- If you are exposed long enough and in high enough doses/concentrations it will possibly make you sick.
- All of this is not new and manufacturers have developed many tools and concepts to make sure that the engines produce less exhaust and to clean the exhaust after it has been produced.
- … so what might be new?

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Diesel exhaust – the particles

Classification

- „probably carcinogenic in humans" IARC 1989
- "likely to pose a lung cancer hazard in humans" US EPA 2002
- „ potential human carcinogen" NIOSH 1988

- The recent DEMS study is intended to clarify this situation but the epidemiological part is not yet published
- Another recent study did find a significant increase in a specific subgroup

Follow-up of German Potash Miner's Study

- 1st Study (Säverin et al., „Diesel exhaust and lung cancer mortality in potash mining", 1999)
- Follow-up (Neumeyer-Gromen et al. „ Diesel motor emissions and lung cancer mortality—Results of the second follow-up of a cohort study in potash miners", 2009)
  - "*All sensitivity analyses of this study show moderate to 2-fold risk elevations, some of which are statistically significant*. "

This (and possibly other results) may lead to a re-evaluation of Diesel particulates e.g. by IARC.

Carcinogenic to humans – possibly, probably, definitely?

- In Europe/Germany the consequences of this differentiation do have very small consequences.
- Probable or definite carcinogens are treated almost identically with respect to risk analysis or technical preventive measures.
- But this may be different in other legal systems.

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Diesel particulates in Germany

- Since 2005 we don‘t have a threshold limit any more!
- The German ministry of labour has skipped all technically founded TLVs for carcinogens because there was no „risk-base“ associated to the old ones („TRK-Werte“)
- „*Everybody was content to comply with a technical TLV whose health relevance was completely unknown!*“
- This leaves companies in quite some uncertainty, as they no longer have a clear tool to prove that they did what was needed.
- So what is done instead?

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TRGS 554 „Diesel exhaust“ (an „official guideline“)

- http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/pdf/TRGS-554.pdf?__blob=publicationFile
- All exhaust components need to be taken into account (and risk minimized)
- Special mention of „secondary components“ e.g. from exhaust treatment.
- Priority to particle prevention (carcinogenicity)
- „Exhaust treatment systems“ (no longer particle filters) number one measure.
- STOP concept (substitution before technical before organisational, before personal measures)
- And a complete sub chapter on mining!

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TRGS 554 „Diesel exhaust“ – Technical measures

- A catalogue of technical measures is given to select from.
- If all engines in the workplace are equipped with suitable exhaust treatment devices no further measures are required.
- No measurements required.
- Companies do still perform occasional exposure quantifications to get an idea about the success of their measures (*and to get a better standing in legal matters*).
- However, the number of systematic exposure measurements has decreased!

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•What about analytical methods?

- Elemental carbon seems to be the analyte of choice at least in exposure groups of high to moderate exposure (like in mines).
- The DEMS study uses REC (respirable elemental carbon), determined with the themo-optical method (NIOSH 5040).
- Intercomparisons with the EC-method used in Europe have shown very good agreement in mining environments!
- However, ever lower REC-concentrations in the exhaust of cleaner and cleaner engines as well as changing particle compositions from non-fossile fuels begin to show the limitations of the coulometric and thermo optical methods.
- **Finally, are we right to weigh the particles instead of counting them?**

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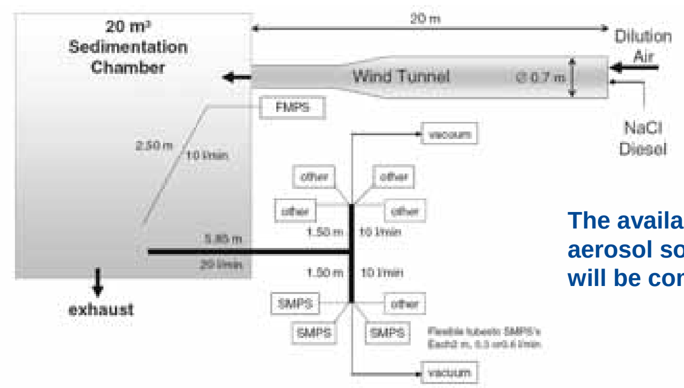
What about analytical methods?

- The aerosol produced by the diesel engine contains „ultrafine“ particles.
- As long as the particle size distribution from the diesel engine remains closely similar, mass based as well as number based analytical methods will give similar (directly comparable!) results.
- In the future, number based threshold limits coming from the field of „nanoparticle“ exposure evaluation might influence the evaluation of „urban aerosol“ directly of indirectly.
- For example IGF uses Diesel aerosol in our „Nano Test Facility“ as test aerosol besides others for calibration and testing of nanoparticle monitors and samplers.

General Lay-Out of IGF Nano-Test Facility:



The available aerosol sources will be completed

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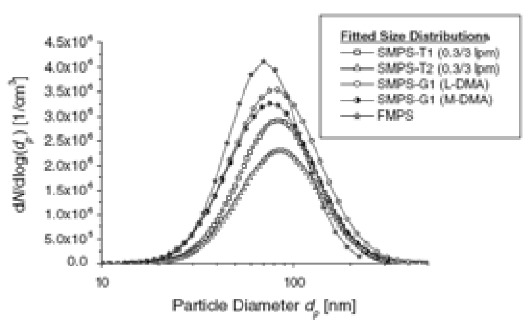
Example of a round robin test at IGF:



Example for diesel soot. Instrument parameters „harmonized“.

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Nanoaerososols and Diesel exhaust

- Currently a general threshold limit for nanoparticles (i.e. man-made ultrafine particles created with special properties for specific purposes) is discussed worldwide.
- Some suggestions are in the region of a few 1000 to 20000 particles per cm^3.
- In urban aerosol the background concentration is at about 10000 Particles/cm^3 - and 90 % of this come from „combustion aerosols".
- *So at some point in the future this will have the consequence to lead to an increased demand for number based exhaust particle quantification in workplaces.*

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NITROGEN OXIDES?

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Nitrogen oxides – what‘s there?

Oxidation state of Nitrogen	Chemical Formula	Name
+1	N_2O	Dinitrogenmonoxide („laughing gas“)
+2	NO	Nitrogenmonoxide
+3	N_2O_3	Dinitrogentrioxide
+4	NO_2	Nitrogendioxide
+4	N_2O_4	Dinitrogentetroxide
+5	N_2O_5	Dinitrogenpentoxide

Exkursion: „Laughing gas“

- Application
  - As anaesthetic (mainly in dentistry),
  - As aerosol propellant mainly for whipped cream (acidic carbon dioxide would be unfriendly to the cream),
  - As oxygen carrier in combustion processes
- *Unintentional generation*
  - During selective catalytical reduction (SCR) of NO or NO_2 for example using urea
- Legal issues
  - Very different views in various countries
- TLVs (8-hours)
  - Between 25 ppm (NIOSH) and 100 ppm (majority of others)
- N_2O is a potent „greenhouse gas“.

NO and NO_2 – Intentional use

- NO
  - As a medical gas (2001 EU) for example for treatment of newly born childs with lung problems
- NO_2
  - For the preparation of nitric acid
  - As rocket fuel (here the dimere, N_2O_4)
  - In exhaust gas treatment (Cleaning of particle filters)

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NO und NO_2 – unintentional generation

- NO as well as NO_2 are always generated in combustion processes or just by application of high temperatures in the presence of air depending on the actual process.
  - Welding
  - Combustion engines
  - Blasting
- In catalytical exhaust treatment (sometimes)
  - For example in connection with the use of platinum metals

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NO and NO_2 – a little bit of physical chemistry

1. Dimerisation of NO_2 into N_2O_4 takes place at low temperatures. (Below 0°C the equilibrium rests with the reddish brown N_2O_4 at almost 100%!)
2. Chemical equilibrium between NO and NO_2 in air! NO converts into NO_2 under ambient conditions. This equilibrium is, however, a lot more complex than the one before. („Third order kinetics“)

Example: Original exhaust from a diesel engine consist of about 95% NO and 5% NO_2. In „some time“ the concentration of NO_2 will rise at the expense of the NO-concentration.

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NO und NO_2 – Hazard („dangerous properties“)

NO (Synopsis from the German database GESTIS)

- Nitrogenmonoxide is created within and by the human body.
- It has an acute negative effect on the blood and the central nervous system in high concentrations.
- Chronic effects have hardly been described
- Acute toxicity was described as markedly lower than the one from NO_2 (3 – 20%) (1995)
- BUT: Where NO is present, there is also always NO_2

NO und NO_2 – Hazard („dangerous properties“)

NO_2 (Synopsis from the German database GESTIS)

- Acute irritative effects on mucuous membranes – breathing airways
- Mainly concentration-depending less dose-depending
- The chronic effects, which have been reported, do refer to lung function deficiencies.

NO and NO_2 – Compiled TLV-situation

Component	Existing TLVs	Where
NO_2	2-3 ml/m³ (ppm) 5 ml/m³ (ppm)	EU Former German
NO	25 ml/m³ (ppm)	Almost everywhere

...to be continued!

Exposure in underground mines!

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Workplace examples – Potash and salt mining

Published under…

http://www.igf-bbg.de/adobe/Veroeff22.pdf

Exposure Assessment in German Potash Mining

Dirk Dahmann, Christian Monz, Heinrich Sönksen

International Archives of Occupational and Environmental Health (2007) 81:95–107

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Short description of the 2 potash mines in the study

- Room and pillar
- Threes shift system
  - Drilling
  - Blasting (only between shifts)
  - Loading and hauling
- Intensive use of large diesel engines
- State of the art of exposure control
  - Electrical engines where technically feasible
  - No particle filter traps at the time of measurement (NO_2-conversion!)

Short description of the data set

- Over 500 shift measurements of respirable dust, inhalable dust, respirable elementary carbon, NO, NO_2, CO and CO_2
- Two potash mines were visited - each two times for a longitudinal epidemiological study on lung function parameters (Federal institute of occupational safety and health, Berlin; published elsewhere; Lotz et al., 2006)
- 11 jobtitles were covered in detail

Short description of the sources

- Respirable elementary carbon is only resulting from the diesel engines
- Main source of NO is the diesel exhaust
- Main source of NO_2 ist the blasting procedure
  - However, there is interconversion between the two in ambient air
  - However, if you use the „wrong“ particle filters there is considerable contribution by the filters

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NO- Shift exposure

NO (ppm)	
Number of measurements	409
Average	2.57
Standard Deviation	1.93
95-percentile	5.73

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NO- Shift exposure

NO (ppm)		NIOSH DEMS (2010)
Number of measurements	409	666
Average	2.57	0.2-1.49
Standard Deviation	1.93	-
95-percentile	5.73	-

NO_2- Shift exposure

NO_2 (ppm)	
Number of measurements	417
Average	0.74
Standard Deviation	0.56
95-percentile	1.78

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NO_2- Shift exposure

NO_2 (ppm)		NIOSH DEMS (2010)
Number of measurements	417	689
Average	0.74	0.1-0.6
Standard Deviation	0.56	-
95-percentile	1.78	-

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REC- Shift exposure

REC (µg/m³)	
Number of measurements	546
Average	100
Standard Deviation	0.070
95-percentile	240

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REC- Shift exposure

REC (µg/m³)		NIOSH DEMS (2010)
Number of measurements	546	779
Average	100	40-384
Standard Deviation	0.070	-
95-percentile	240	-

Highest short time exposure during shift

NO (ppm) – 15 min	
Number of measurements	347
Average	4.15
Standard deviation	4.28
95-percentile	12.45

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Highest short time exposure during shift

NO_2 (ppm) – 15 min	
Number of measurements	344
Average	1.66
Standard deviation	1.01
95-percentile	3.60

2. Campagne: Hardcoal mining

Published under…

"Exposure assessment for nitrogen oxides and carbon monoxide in German hard coal mining"

Dirk Dahmann · Peter Morfeld · Christian Monz · Birgit Noll · Frank Gast

Int Arch Occup Environ Health

Published online 8.4.2009

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Methods- Direct reading instruments (1min averaging)

Measurement ranges

- NO, Electrochemical cell, 0-125 ppm
- NO_2, Electrochemical cell, 0-20 ppm
- CO, Electrochemical cell, 0-500 ppm

Problems

- Cross sensitivities (NO – CO)
- Influence of varying moisture content of ambient air
- Calibration
- Wide measurement ranges
- So we attributed „validity" categories to the data
- No coal-mine-specific explosion protection available (just regular one) therefore access highly restricted

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Short description of the mining process

- Long wall caving technique employing shearer loaders or coal planes
- Roadway building either by head-cutting machines or blasting during shifts
- Diesel engines in trains (material and manpower transport) and one-rail suspended trains (material transport near the seam)
- …and no, there is currently no measurement technique available for REC in this mining sector (exposure controll always by balancing ventilation against specific engine „demand").

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Measured jobs

•Dieseltrain drivers
•One-rail-suspended rail trains („cats")
•Blasting specialists

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Number of personal measurements

- Cat drivers : 12
- Train drivers: 8
- Blasting specialists: 5
- (Only 15-Minute.averages at the site of „highest risk“ in the latter cases)

- The data was was used in an epidemiological study by Morfeld et al. 2009

Results

Average shift exposures of engine drivers in coal mining

Component	Average shift exposures of cat-drivers (ppm)	Average shift exposures of train-drivers (ppm)	Average shift exposures of diesel engine drivers (ppm) (=sum of both categories)
NO	**1.36**	**1.35**	**1.35**
NO_2	**0.023**	**0.52**	**0.21**
CO	2.55	2.68	2.6

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Exposure of blasting specialists

Identity of the measurement	CO, 15 min concentration (ppm) (Worst-case situation)	NO, 15 min concentration (ppm) (Worst-case situation)
1	27	4.8
2	7.7	1.4
3	87	14.5
4	2.52	0.44
5	10	2.3

In all cases: NO_2 very low! (LDL)
Note that the measurements were performed directly after blasting!
Equilibrium not reached!

Highly variable, but occasionally quite considerable!

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For comparison (other hard coal studies):

	This study	Kihl (1998)	Wagner and Simon (1997)	Robertson et al. (1984)
NO_2 (ppm)				
Train drivers	0.52	0.08–0.29	–	0.05–0.84
EHB-drivers	0.023	0.05–1.89	–	
Blasting specialists	0.014	0–0.13	*0–0.06*	
NO (ppm)				
Train drivers	1.35	1.33–1.54	–	0.48–3.74
EHB-drivers	1.36	0.28–2.50	–	
Blasting specialists	0.84	0–1.7	*0.1–0.67*	

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NO and NO_2 – New threshold limit values in Germany?

Component	Proposal 2009	Old MAK-TLV	Origin
NO	**0,5 ppm**	5 ml/m³ (ppm)	Germany
NO_2	**0,5 ppm**	25 ml/m³ (ppm)	EU

Rationale: Not just lung function impairment
Lung function measurements „not sensitive enough“.

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What is going on now?

- German authorities „discuss“ the new proposal

- EU also has published ideas in this matter:
- NO: Latest proposal was 1 ppm (2004)
- NO2: Latest proposal of scientific advisory group 0.2 ppm (2008)

- As shown, in potash mining and in coal mining these levels can not be complied to.

Summary: Now, IS an extended view necessary?

- With respect to a classification by e.g. IARC as human carcinogen?
- **Maybe!** Rumours about a re-classification based on novel studies are existing.
- With respect to the analytical techniques applied for the particle phase?
- **No!** REC is still the analyte of choice. It can be determined by TOM and the European methods („coulometry") with very good comparability in mining environments.
- **Yes!** Particle counting methods (SMPS, FMPS, CPC etc.) will become more important in the future.
- With respect to „new" components in the exhaust?
- **Yes!** Nitrogen oxides will draw attention. In Europe discussion about a proposed very low TLV level has started and is there to stay.

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- ISSA Mining Section as a forum for international exchange

- **And of course to the colleagues in IGF who actually performed the work!**

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Glückauf!

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