Diesel engine exhaust –
Is a more complete view necessary?

Dirk Dahmann, Bochum

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
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](http://annhyg.oxfordjournals.org/content/early/recent)
downloadable
  □ I shall occasionally refer to these papers

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?

**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.

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

- **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!

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!
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 thermo-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?**

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 or 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.

Example of a round robin test at IGF:

Example for diesel soot. Instrument parameters „harmonized“.
Nanoaerosols 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 cm³.
- In urban aerosol the background concentration is at about 100000 Particles/cm³ - 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.
Nitrogen oxides – what's there?

<table>
<thead>
<tr>
<th>Oxidation state of Nitrogen</th>
<th>Chemical Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>N₂O</td>
<td>Dinitrogenmonoxide (&quot;laughing gas&quot;)</td>
</tr>
<tr>
<td>+2</td>
<td>NO</td>
<td>Nitrogenmonoxide</td>
</tr>
<tr>
<td>+3</td>
<td>N₂O₃</td>
<td>Dinitrogentrioxide</td>
</tr>
<tr>
<td>+4</td>
<td>NO₂</td>
<td>Nitrogendioxide</td>
</tr>
<tr>
<td>+4</td>
<td>N₂O₄</td>
<td>Dinitrogentetroxide</td>
</tr>
<tr>
<td>+5</td>
<td>N₂O₅</td>
<td>Dinitrogenpentoxide</td>
</tr>
</tbody>
</table>

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 NO₂ 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)
  - N₂O is a potent "greenhouse gas".
NO and NO₂ – Intentional use

- **NO**
  - As a medical gas (2001 EU) for example for treatment of newly born childs with lung problems

- **NO₂**
  - For the preparation of nitric acid
  - As rocket fuel (here the dimere, N₂O₄)
  - In exhaust gas treatment (Cleaning of particle filters)

NO und NO₂ – unintentional generation

- NO as well as NO₂ 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
**NO and NO₂ – a little bit of physical chemistry**

1. **Dimerisation** of NO₂ into N₂O₄ takes place at low temperatures. (Below 0°C the equilibrium rests with the reddish brown N₂O₄ at almost 100%!)  

2. **Chemical equilibrium between NO and NO₂ in air! NO converts into NO₂ 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% NO₂. In „some time“ the concentration of NO₂ will rise at the expense of the NO-concentration.

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**NO und NO₂ – 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 NO₂ (3 – 20%) (1995)
- BUT: Where NO is present, there is also always NO₂
NO und NO₂ – Hazard („dangerous properties“)

NO₂ (Synopsis from the German database GESTIS)

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

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NO and NO₂ – Compiled TLV-situation

<table>
<thead>
<tr>
<th>Component</th>
<th>Existing TLVs</th>
<th>Where</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>2-3 ml/m³ (ppm) 5 ml/m³ (ppm)</td>
<td>EU Former German</td>
</tr>
<tr>
<td>NO</td>
<td>25 ml/m³ (ppm)</td>
<td>Almost everywhere</td>
</tr>
</tbody>
</table>

...to be continued!
Exposure in underground mines!

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

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 (NO₂-conversion!)
Short description of the data set

- Over 500 shift measurements of respirable dust, inhalable dust, respirable elementary carbon, NO, NO₂, CO and CO₂
- 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 NO₂ 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
**NO- Shift exposure**

<table>
<thead>
<tr>
<th>NO (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>409</td>
</tr>
<tr>
<td>Average</td>
<td>2.57</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.93</td>
</tr>
<tr>
<td>95-percentile</td>
<td>5.73</td>
</tr>
</tbody>
</table>

NIOSH DEMS (2010)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>666</td>
</tr>
<tr>
<td>0.2-1.49</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### NO₂- Shift exposure

<table>
<thead>
<tr>
<th>NO₂ (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>417</td>
</tr>
<tr>
<td>Average</td>
<td>0.74</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.56</td>
</tr>
<tr>
<td>95-percentile</td>
<td>1.78</td>
</tr>
</tbody>
</table>

### NO₂- Shift exposure

<table>
<thead>
<tr>
<th>NO₂ (ppm)</th>
<th>NIOSH DEMS (2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>689</td>
</tr>
<tr>
<td>Average</td>
<td>0.1-0.6</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>-</td>
</tr>
<tr>
<td>95-percentile</td>
<td>-</td>
</tr>
</tbody>
</table>
### REC- Shift exposure

<table>
<thead>
<tr>
<th>REC (µg/m³)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>546</td>
</tr>
<tr>
<td>Average</td>
<td>100</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.070</td>
</tr>
<tr>
<td>95-percentile</td>
<td>240</td>
</tr>
</tbody>
</table>

### NIOSH DEMS (2010)

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>779</td>
<td>40-384</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Highest short time exposure during shift

#### NO (ppm) – 15 min

<p>| | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>347</td>
</tr>
<tr>
<td>Average</td>
<td>4.15</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>4.28</td>
</tr>
<tr>
<td>95-percentile</td>
<td>12.45</td>
</tr>
</tbody>
</table>

#### NO₂ (ppm) – 15 min

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Number of measurements</td>
<td>344</td>
</tr>
<tr>
<td>Average</td>
<td>1.66</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.01</td>
</tr>
<tr>
<td>95-percentile</td>
<td>3.60</td>
</tr>
</tbody>
</table>
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

Methods- Direct reading instruments (1min averaging)

Measurement ranges
• NO, Electrochemical cell, 0-125 ppm
• NO₂, 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
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 control always by balancing ventilation against specific engine „demand“).

Measured jobs

- Diesel train drivers
- One-rail-suspended rail trains („cats“)
- Blasting specialists
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 used in an epidemiological study by Morfeld et al. 2009

Results

Average shift exposures of engine drivers in coal mining

<table>
<thead>
<tr>
<th>Component</th>
<th>Average shift exposures of cat-drivers (ppm)</th>
<th>Average shift exposures of train-drivers (ppm)</th>
<th>Average shift exposures of diesel engine drivers (ppm) (=sum of both categories)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>1.38</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.023</td>
<td>0.52</td>
<td>0.21</td>
</tr>
<tr>
<td>CO</td>
<td>2.55</td>
<td>2.68</td>
<td>2.6</td>
</tr>
</tbody>
</table>
### Exposure of blasting specialists

<table>
<thead>
<tr>
<th>Identity of the measurement</th>
<th>CO, 15 min concentration (ppm) (Worst-case situation)</th>
<th>NO, 15 min concentration (ppm) (Worst-case situation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>87</td>
<td>14.5</td>
</tr>
<tr>
<td>4</td>
<td>2.52</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>2.3</td>
</tr>
</tbody>
</table>

In all cases: **NO₂ 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):

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>NO₂ (ppm)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Train drivers</td>
<td>0.52</td>
<td>0.08–0.29</td>
<td>–</td>
<td>0.05–0.84</td>
</tr>
<tr>
<td>EHB-drivers</td>
<td>0.023</td>
<td>0.05–1.89</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Blasting specialists</td>
<td>0.014</td>
<td>0–0.13</td>
<td>0–0.09</td>
<td></td>
</tr>
<tr>
<td><strong>NO (ppm)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Train drivers</td>
<td>1.35</td>
<td>1.33–1.54</td>
<td>–</td>
<td>0.48–3.74</td>
</tr>
<tr>
<td>EHB-drivers</td>
<td>1.36</td>
<td>0.28–2.50</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Blasting specialists</td>
<td>0.84</td>
<td>0–1.7</td>
<td>0.1–0.67</td>
<td></td>
</tr>
</tbody>
</table>
NO and NO₂ – New threshold limit values in Germany?

<table>
<thead>
<tr>
<th>Component</th>
<th>Proposal 2009</th>
<th>Old MAK-TLV</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.5 ppm</td>
<td>5 ml/m³ (ppm)</td>
<td>Germany</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.5 ppm</td>
<td>25 ml/m³ (ppm)</td>
<td>EU</td>
</tr>
</tbody>
</table>

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

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.

A happy thank you for intense discussion to:

- K+S Aktiengesellschaft in particular Dr. Heinrich Sönksen
- RAG in particular Frank Gast
- Dr. Peter Morfeld of Institute for Occupational Epidemiology and Risk Assessment of Evonik Industries
- BAuA (Federal agency for occupational safety and health) (also for financial support) in particular Dr. Gabriele Lotz
- ISSA Mining Section as a forum for international exchange

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