Effects of Energetic Particle Precipitation on the Mesosphere and Stratosphere

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Outline

Ionisation of the atmosphere by EPP
- Energy spectrum
- Penetration depth
- Production of NO$_x$, HO$_x$, ions
- Ion models vs. parameterizations

Direct effects – SPEs
- Observations: MIPAS, ACE, GOMOS, HALOE, POAM, ODIN-SMR, SCIAMACHY, MLS
- NOx and ozone
- Ion (cluster) reactions: HO$_x$, Cl$_x$, HNO$_3$
- N$_2$O
- Model results: Jackman, Verronen, Winkler, Semeniuk

Indirect effects: EEPs
- Downward transport through dark mesosphere
- Dynamics vs. source strength
- Effects on stratospheric chemistry

Modeling of effects on ozone
- Short and medium term – days to winters
- Long terms – solar cycle
Sun-Earth connection

Solar particles (e, p)

 Ionization, Dissociation

 NO\textsubscript{x}, HO\textsubscript{x}

 Catalytic ozone destruction

 mid-/long-term

 short-term

 N\textsubscript{2}, O\textsubscript{2}, O

 EEP (electrons)

 Energies: 10-300 keV

 Deposition: 75 – 110 km

 Mesosphere, Termosphere

 SPE (protons)

 Energies: 10-100 MeV

 Deposition: 40 – 75 km

 Stratosphere, Mesosphere

 Vertical transport

 Ozone layer

 Turunen et al. 2009
Energy deposition, penetration depth

- EPPs deposit their energy at different layers of the atmosphere depending on their penetration depth.
- Energy required to create one ion pair is assumed to be 35 eV (Porter et al., 1976) or 36 ev (Rees et al., 1989).
- Ionization rates estimated from energy deposition, various approaches.
Formation of NO$_x$ and HO$_x$ from ion-electron pairs

NO$_x$: Dissociation of N$_2$ and O$_2$ to N$_2^+$, O$_2^+$, N$^+$, O$^+$, and NO$^+$; formation of exited-state N(2D) and ground-state N(4S); 2N(2D) + O$_2$ → 2NO

HO$_x$: end of complex ion chemistry including protonated water cluster ions (up to 20 water molecules per proton)

Ion chemistry models calculate produced NO$_x$ and HO$_x$ ab initio (for example SIC, Verronen et al., Turunen et al.)

Parameterizations are also used: 2 HO$_x$ molecules per ion pair in the USM, <2 HO$_x$ molecules per ion pair in the middle and upper mesosphere; 1.25 N atoms per ion pair, separated into 0.55 N(4S) and 0.7 N(2D) per ion pair (Jackman et al., 2008)

NO$_x$ and HO$_x$ formation (plus further ion cluster formation) are the basis for all subsequent observed chemical changes in the stratosphere and mesosphere.
Source: P. Verronen, PhD thesis; after Turunen
Ozone depletion – catalytic cycles

$\text{HO}_x$ and $\text{NO}_x$ react as catalytic substances in stratospheric ozone depletion cycles:

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
\text{Net: } \text{O}_3 + \text{O} & \rightarrow 2 \text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
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\text{Net: } 2 \text{O}_3 & \rightarrow 3 \text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{ZO} + \text{HO}_2 & \rightarrow \text{HOZ} + \text{O}_2 \quad (\text{Z: } \text{Cl}, \text{Br}) \\
\text{HOZ} + \text{hν} & \rightarrow \text{OH} + \text{Z} \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{Z} + \text{O}_3 & \rightarrow \text{ZO} + \text{O}_2 \\
\text{Net: } 2\text{O}_3 & \rightarrow 3\text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{Net: } \text{O}_3 + \text{O} & \rightarrow 2 \text{O}_2
\end{align*}
\]

Etc. etc.
Ozone depletion – catalytic cycles

\[
\begin{align*}
\text{HO}_x \text{ and NO}_x \text{ react as catalytic substances in stratospheric ozone depletion cycles:} \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \\
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\end{align*}
\]

Turunen et al., 2009
Direct effects – SPEs – NO$_x$ and O$_3$

Why direct effect? Because effect is generated locally due to penetrating EPPs, without intermediate transport.

Solar proton event Oct/Nov 2003: one of the largest events observed, many observations from a suite of satellite instruments available: MIPAS, SCIAMACHY, GOMOS, ODIN-SMR.

Aftermath of the event in Arctic winter 2003/04: additional observations by ACE-FTS, HALOE, POAM.

Solar proton event Jan 2005: observed by MIPAS, MLS, ACE-FTS, ODIN-SMR, …

López-Puertas et al., 2005
Other observations - SPE 2003 / 2005  
– NO$_x$ and O$_3$

**Seppälä et al., 2005**

**Figure 4.** (top) GOMOS daily (January 1 – 24, 2005) zonal mean night-time ozone mixing ratio [ppmv] at latitudes 65°N – 75°N. Note the destruction of the tertiary ozone maximum at 72 km altitude following the SPE on January 17, 2005. Contour lines as in Figure 3. (bottom) Ozone % change (January 15 – 24) from the average of January 10 – 14. The contour lines are (−80, −70, −60, −50, −40, −30, −20, −10%). X-axis is the same as for the model results in Figure 2. Note the different x-axis in the two panels.
Model results – SPE 2003 – \( \text{NO}_x \) and \( \text{O}_3 \)

**NO\(_2\) change (ppbv) 70\(^\circ\)N–90\(^\circ\)N (night)**

- **MIPAS**
- **WACCM**
- **WACCM – no SPEs**

**O\(_3\) change (%) (day+night)**

- **MIPAS 90\(^\circ\)S–70\(^\circ\)S**
- **MIPAS 70\(^\circ\)N–90\(^\circ\)N**
- **WACCM 90\(^\circ\)S–70\(^\circ\)S**
- **WACCM 70\(^\circ\)N–90\(^\circ\)N**

2\(\sigma\) significance

Seasonal change

Jackman et al., 2008
Model results – SPE 2003 – NO$_x$ and O$_3$

**NO$_2$ change (ppbv) 70°N–90°N (night)**
- MIPAS

**O$_3$ change (%) (day+night)**
- MIPAS 90°S–70°S
- MIPAS 70°N–90°N

**WACCM – no SPEs**

**Detailed discussion: 2nd HEPPA Model/Measurement workshop on Wednesday**

- 2σ significance
- Seasonal change

Jackman et al., 2008
Direct effects – SPEs – nitrogen, chlorine and hydrogen compounds

MIPAS observations during SPE Oct/Nov 2003
Further parameters from MIPAS available: Temperature, HNO$_4$, CH$_4$, H$_2$O, CO, BrONO$_2$
(⇒ poster Höpfner et al.), H$_2$O$_2$ (⇒ poster Versick et al.).

MLS observations during SPE Jan 2005: OH and HO$_2$ (⇒ talk and poster Verronen et al.; poster Versick et al.)

HALOE observations during SPE July 2000: HCl (⇒ poster Winkler et al.)
Model results – SPE 2000/ 2003 – nitrogen and chlorine compounds

**MIPAS**

**N$_2$O**

**CMAM model**

$\text{N}_2\text{O}$ enhancements can be explained by $\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O}$.  

Funke et al., 2008

**HNO$_3$ (46 km)**

**Production rates**

$\text{HNO}_3$ enhancements can be reproduced by inclusion of **ion-ion recombination** between $\text{NO}_3^-$ and $\text{H}^+$ cluster ions.  

Verronen et al., 2008

**HOCI change**

$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$

$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$

$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCI} + \text{O}_2$.

**HALOE Jul 2000**

**Reactions with negative chlorine ions**

Winkler et al., 2009

**Jackman et al., 2008**

$\text{HNO}_3$ (46 km)

Production rates

**HALOE Jul 2000**

Reactions with negative chlorine ions

Winkler et al., 2009
Model results – SPE 2000/2003 – nitrogen and chlorine compounds

MIPAS N₂O CMAM model

HOCI change

\[ \text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl} \]

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCI} + \text{O}_2 \]

Verronen et al., 2008

Production rates

HNO₃ (46 km)

HNO₃ enhancements can be reproduced by inclusion of ion-ion recombination between NO₃⁻ and H⁺ cluster ions. Verronen et al., 2008

Detailed discussion: 2nd HEPPA Model/Measurement workshop on Wednesday

HALOE Jul 2000

Reactions with negative chlorine ions

Winkler et al., 2009

N₂O enhancements by \( \text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} \)

HNO₃ (46 km)
Model results – SPE 2003 / 2005 – hydrogen compounds

OH during SPE Jan 2005

Case I: January 18, 12:10 LT

Case II: January 20, 12:05 LT

O$_3$ during SPE Jan 2005

MLS observations, SIC (full ion chemistry)

1-D modelling

Verronen et al., 2006

H$_2$O$_2$ during SPE Jan 2005

MIPAS observations, KASIMA 3D-CTM modelling

Versick et al., Poster session
Summary direct (SPE) impact of EPP:

- High energetic protons penetrate deeply into the mesosphere and stratosphere and deposit their energy there
- ~ 35 eV produce one ion-electron pair
- Ions generate - via more or less complicated ion (cluster) chemistry – NO\textsubscript{x} (mainly in the stratosphere) and HO\textsubscript{x} (mainly in the mesosphere)
- NO\textsubscript{x} and HO\textsubscript{x} are involved in catalytic ozone destruction cycles ⇒ immediate ozone depletion observed and modeled
- Further perturbation of stratospheric/mesospheric chemistry is observed: HNO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, BrONO\textsubscript{2}, HNO\textsubscript{4}, N\textsubscript{2}O, CO, CIONO\textsubscript{2}, HCl, ClO, CIONO\textsubscript{2}, OH, HO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, …
- Some of the chemical reactions can be modeled (by direct gas-phase or ion (cluster) chemistry), some are not yet understood.

Further topics to be discussed:

- Impact of (secondary) electrons vs. protons
- Effects on temperature and dynamics (e.g. via ozone depletion)
- …
Indirect EPP effects

What are indirect EPP effects?
NO$_x$, HO$_x$ or other species (ions) are affected at higher altitudes by EPP. Changed atmospheric composition is transported downwards into the mesosphere/upper stratosphere and affects chemical composition there.

Auroral to high energetic electrons produce NO$_x$ and HO$_x$ in the upper mesosphere/lower thermosphere region (80 – 120 km). The polar winter vortex acts as a “bathtub sink” where air is sucked down during polar winter. But: The lifetime of HO$_x$ is much too short to survive downward transport. Only relevant species is NO$_x$. NO is produced in the MLT and can survive transport through the mesosphere in darkness only. Why?

talk by Esa Turunen (?)
Mixing

Polar night

Illuminated

Planetary waves

110
90
70
40
30

Altitude (km)

For this reason the NO$_x$ downward transport is confined to the dark polar vortex and not, as one could think, to the auroral oval!

Mesospheric Losses

Photolysis & Chem. Reac.:

NO + hv → N + O
NO + N → N$_2$ + O
require illumination!

Productions

Energetic electron precipitation (EEP)
continuous + variable
N$_2$ + e$^-$ → N + N + e$^-$ → NO + O

Transport

Polar winter

Ozone layer

Isolation from other latitudes

Isolation from other latitudes
NO$_x$ in Antarctic polar winter 2003: confinement to the dark vortex

MIPAS data

Funke et al., 2005
NO$_x$ in Antarctic polar winter 2003: confinement to the dark vortex

Funke et al., 2005

MIPAS data
Energetic particle precipitation effects on the Southern Hemisphere stratosphere in 1992–2005


Figures 7 and 10. Maximum (black, solid) and average (dotted) excess NO$_x$ densities in 2-week time periods from 15 May through 15 September, calculated as described in the text and Figure 6. Gray solid lines denote the number of molecules derived from the maximum excess densities (right axis, gigamoles). For clarity, the number of molecules in year 1994 has been allowed to run off-scale; numbers peak at 0.2 GM.

Figure 7. Maximum (black, solid) and average (dotted) excess NO$_x$ densities in 2-week time periods from 15 May through 15 September, calculated as described in the text and Figure 6. Gray solid lines denote the number of molecules derived from the maximum excess densities (right axis, gigamoles). For clarity, the number of molecules in year 1994 has been allowed to run off-scale; numbers peak at 0.2 GM.

SH: Deposited NO$_x$ in stratosphere reveals high interannual variability and correlates well with auroral activity and NO produced in the thermosphere.

Figure 10. EPP-NO$_x$, calculated from the maximum NO$_x$ residuals as in Figure 9 (dots, solid line, left axis) compared to auroral hemispheric power (top), medium energy electron hemispheric power (middle), and SNOE column NO from 97 to 150 km averaged over the sunlit region poleward of 60°S (bottom). Energetic particle and SNOE data (gray) are averaged over the months of May–July and are referenced to the right vertical axes. Correlation coefficients are given in each panel.
High variability observed
High NO\textsubscript{x} although geomagnetic activity was low: 2006, 2009
Unusually strong descent in 2004, 2006, 2009
NH stratospheric excess NO\textsubscript{x} amounts seem to be ruled more by dynamics than by production

See also talks by Randall and Funke
Vivid discussion: Arctic winter 2003 - 2004

Dynamic origin or in situ production?

- Correlation with dynamic tracers confirm downward transport of NO\textsubscript{x} produced in the thermosphere (e.g. Funke et al., 2007; Hauchecorne et al., 2007)

- Semeniuk et al. (2005) found that SPE-generated thermospheric NO\textsubscript{x} is not sufficient to explain amounts
  \(\Rightarrow\) additional production by auroral electrons

- Seppälä et al. (2007) found indication for contributions from aurorally generated NO\textsubscript{x}
Impact of EEP-generated NO$_x$ on stratospheric chemical budget: NO$_y$

1. Formation of upper stratospheric HNO$_3$

   - MIPAS observations (Stiller et al., 2005)
   - Every-year occurrence of upper strat. HNO$_3$ maximum confirmed by ODIN-SMR observations (Orsolini et al., 2009)
   - Mechanism proposed by de Zafra and Smyshlyaev (2001):
     \[ \text{N}_2\text{O}_5 + \text{H}^+(\text{H}_2\text{O})_n \rightarrow \text{H}^+(\text{H}_2\text{O})_{n-1} + 2\text{HNO}_3 \] (only for $z > 40\text{km}$)
     - $\text{N}_2\text{O}_5$ is formed immediately from NO$_x$ under dark conditions
     - Note: this is a different ion cluster reaction than during/after SPE!
     - Mechanism confirmed by KASIMA model calculations (see Poster Reddmann et al.)

2. NO$_x$ has impact on further NO$_y$ species (e.g. BrONO$_2$, ⇒ poster Höpfner et al.)
Impact of EPP-generated NO$_x$ on stratospheric chemical budget: O$_3$

- Both SPE-generated NO$_x$ (and HO$_x$) and EEP-generated and descended NO$_x$ lead to additional ozone depletion.
- Short-term (days to winters) and long-term (solar cycle) effects.

Vogel et al., 2008
Impact of EPP-generated NO\textsubscript{x} on stratospheric chemical budget: Long-term O\textsubscript{3}

WACCM3 without SPEs
WACCM3 with SPEs
Both mean value minus average 1979-1980
* Observed ozone minus the observed average 1979-1980
NO\textsubscript{y} production by SPEs
\(\Rightarrow\) Effect is very small

Long-term (decadal and longer) impact of EEP produced and descended NO\textsubscript{x}? Should be larger and more regular than by SPE-produced NO\textsubscript{x}!
\(\Rightarrow\) Callis et al., 1998 covered 1979-1988
Summary: Indirect impact of EPP:

- NO$_x$ and HO$_x$ produced by auroral and high energetic electrons in the upper mesosphere and lower thermosphere
- Only NO$_x$ is long-lived enough to be transported into the stratosphere by polar winter descent
- Transport through mesosphere possible only in darkness due to NO photolysis $\Rightarrow$ confinement to dark polar winter vortex
- Import of NO$_x$ during Antarctic winter highly variable and well correlated with geomagnetic activity $\Rightarrow$ ruled by source strength
- Typical import amounts: 1 to 3 GMoles N per winter, this is about 5 to 15 % of the N$_2$O source.
- Arctic winters: extremely variable with exceptional winters 2004, 2006, 2009. High amounts also for years with low geomagnetic activity $\Rightarrow$ dynamical variability more important
- Winter 2003/2004: Discussion about descent vs. local production, contribution of SPE vs. EEP-generated NO$_x$
- Excess NO$_x$ has impact on NO$_y$ partitioning (upper stratospheric HNO$_3$ maximum produced by N$_2$O$_5$ conversion on protonated water ion clusters), BrONO$_2$, ClONO$_2$, …
- Excess NO$_x$ (and HO$_x$ in the mesosphere) leads to short-term and medium-term (few months) ozone depletion
- Long-term ozone depletion by SPEs not significant
- Long-term ozone depletion by EEPs?
Certainly I have mentioned by far not all work regarding EPP impacts.

My apologies if any relevant observations, analyses, and modeling work are missing.

Thank you for your attention!