“Old”, “New” and “Novel” Flame Retardants in the Environment - Analytical Methods and Levels

Sicco Brandsma, Jacob de Boer, Pim Leonards
Outlines

• “Old” Brominated flame retardants
  • PBDEs, BDE209, TBBP-A and HBCD

• “New” Brominated flame retardants
  • BDBPE, DBDPE, TBB, TBPH and PBT

• “Alternative” Flame retardants
  • PFRs

• “Novel” Flame retardants
  • European research project ENFIRO
“New” brominated flame retardants

DBDPE (decabromodiphenylethane)

BTBPE (1,2 bis(2,4,6-tribromophenoxy)ethane)

TBPH (bis-2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate)

TBB (2-ethylhexyl-2,3,4,5-tertabromobenzoate)
Analytical methods for “New” BFRs

- Analytical methods described in literature for different matrices

  - Dust  ➔ Stapleton et al. (2008), Ali et al. (2011)
  - Air  ➔ Sjordin et al. (2001), Takigami et al. (2009)
  - Sediment  ➔ Hoh et al. (2005), Lopez et al. (2011)
  - S. sludge  ➔ Kierkegaard et al. (2004), Ricklund et al. (2008)
  - Wastewater  ➔ Klosterhause et al. (2008), Zhou et al. (2010)
  - Biota  ➔ Law et al. (2006), Luo et al. (2009)
  - Blood  ➔ Karlsson et al. (2007)
Extraction of “New” BFRs

• Different extraction methods
  • Soxhlet
  • ASE
  • Ultrasonic extraction
  • SPE

• Wide range of solvent mixtures
  • Petroleum ether
  • Toluene
  • Dichloromethane
  • Hexane
  • Acetone
Cleanup methods for “new” BFRs

• Cleanup methods for abiotic and biotic samples
  • Sulphuric washing
  • Deactivated or sulphuric acid impregnated silica column
  • Florisil column
  • SPE cartridges
  • Alumina column
  • Sulphur removal (activated copper, AgNO3 on silica, TBA reagents and GPC)
Critical parameters for “new” BFRs

- Sulphuric acid treatment can only be used for DBDPE
- Non-destructive cleanup methods needed for BDBPE, TBB and TBPH
- TBA reagents may caused debromination of DBDPE
- DBDPE, TBB and TBPH undergo photodegradation
- Difficulties encountered in the analysis of DecaBDE are also expected for DBDPE
  - Poorly soluble in organic solvent
  - Higher boiling point than DecaBDE
  - Thermally degrades to mainly bromotoluenes
  - Blank problems
Instrumental analysis for DBDPE, BDBPE

- LR-ECNI-MS monitoring m/z 79/81 for DBDPE and 79/81 and 250.8/252.8 for BDBPE

- HR-EI-MS m/z 969/971 for DBDPE m/z 685/687 for BDBPE

- LR-ECNI-MS more sensitive than HR-EI-MS less specific

- Labeled DBDPE could not be used as IS for LR-ECNI-MS

- 13C BDE 209 used as alternative for LR-ECNI-MS

- DBDPE degrades on the GC column use column <15 meter
GC-ECNI-MS chromatogram of DBDPE, BDBPE

Sediment sample of the Western Scheldt
TBB was quantified using ion fragment (m/z) 357 (Quant) and 471 (Qual)

TBPH was quantified using ion fragments (m/z) 463 (Quant) and 515 (Qual)
GC-ECNI-MS chromatograms revealing the relative retention times of the primary BDE congeners, TBB and TBPH on a 15 m DB5-MS column.
**LC-MS/MS**

- LC-APPI-MS/MS in negative mode developed by Abdallah et al. (2009) for analyzing 14 PBDEs in house dust
- LC-MS/MS (APPI/APCI) in negative mode was also used by Zhou et al. (2010) to measure the “new” BFRs in combination with the PBDEs HBCD and TBBP-A

### Advantages

- no thermal degradation
- use of 13C labeled standards
- Measuring all compounds in one run
  - no column changes

### Disadvantages

- Less sensitive then GC-ECNI-MS

<table>
<thead>
<tr>
<th></th>
<th>GC/LR-ECNI-MS</th>
<th>LC-MS/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD</td>
<td>30 fg - 1.7 pg*</td>
<td>12 - 30 pg*</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>+ +</td>
<td>- -</td>
</tr>
<tr>
<td>Selectivity</td>
<td>No</td>
<td>yes</td>
</tr>
<tr>
<td>Labeled standards</td>
<td>No (only for BDE209)</td>
<td>yes</td>
</tr>
<tr>
<td>Thermal degradation</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Expensive</td>
<td>+ -</td>
<td>+</td>
</tr>
<tr>
<td>Expert training</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Library search</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

*Eljarrat et al. (2002)
*Abdallah et al. (2009)
J Mass Spectrom 37: 76-84
Anal. Chem., 81, 7460–7467
### Levels in the environment (I)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>DBDPE concentrations</th>
<th>Range DBDPE</th>
<th>BTBPE concentrations</th>
<th>Range BTBPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1916 pg/m³ (Shi et al., 2009), 1–22 pg/m³ (Venier and Hites, 2008) up to 120 pg/m³ (Hoh and Hites, 2005)</td>
<td>1–1916 pg/m³</td>
<td>0.1–10 pg/m³ (Hoh and Hites, 2005)</td>
<td>0.1–30.7 pg/m³</td>
</tr>
<tr>
<td>Air (e-waste)</td>
<td>0.6–77 ng/m³ (Kierkegaard et al., 2004) 7 ng/m³ (Karlsson et al., 2006a,b)</td>
<td>0.7–77 ng/m³</td>
<td>&lt;0.6–39 ng/m³ (Pettersson-Juulander et al., 2004) 5.6–67 ng/m³ (Sjödin et al., 2001)</td>
<td>5.6–67 ng/m³</td>
</tr>
<tr>
<td>Dust</td>
<td>Average 47 µg/kg in Swedish house dust (Karlsson et al., 2007) Average 270, 170, and 400 µg/kg in UK homes, offices, and cars respectively (Harrad et al., 2008) &lt;10 to 11070 µg/kg dw, median 201 µg/kg dw (Stapleton et al., 2008). 353 µg/kg dw (Sawal et al., 2008)</td>
<td>&lt;10 to 11070 µg/kg dw</td>
<td>Average 4.8 µg/kg in Swedish house dust (Karlsson et al., 2007) Average 120, 7.2, and 7.7 µg/kg in UK homes, offices, and cars respectively (Harrad et al., 2008) 1060 µg/kg dw (Sawal et al., 2008) 1.6–789 µg/kg dw (Stapleton et al., 2008)</td>
<td>4.8–1060 µg/kg dw</td>
</tr>
<tr>
<td>Dust e-waste</td>
<td>&lt;1.2–50 µg/kg dw (Shi et al., 2009)</td>
<td>&lt;2.50 to 139 µg/kg dw</td>
<td>14.6 to 232 µg/kg (median 107 µg/kg)</td>
<td>14.6–232 µg/kg dw (Shi et al., 2009).</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>100 µg/kg dw (Kierkegaard et al., 2004) 266 to 1995 (median 1183) µg/kg dw (Shi et al., 2009). DBDPE range 57–220 µg/kg dw (mean 81 µg/kg dw Europe, 31 µg/kg dw North America); ratio DBDPE/BDE-209 = 0.008–0.83 (Ricklund et al., 2008a,b) DBDPE digested sludge 66–95 µg/kg dw (mean 81 µg/kg dw), BDE-209 digested sludge 650–1100 µg/kg dw (mean 800 µg/kg dw) (Ricklund et al. 2008)</td>
<td>266 to 1995 µg/kg dw</td>
<td>0.31 to 1.66 µg/kg dw (Shi et al., 2009).</td>
<td>0.31–1.66 µg/kg dw</td>
</tr>
<tr>
<td>Sediment</td>
<td>24 µg/kg dw (Kierkegaard et al., 2004) 38.8 to 364 µg/kg (mean 247) µg/kg dw (Shi et al., 2009).</td>
<td>24–364 µg/kg dw</td>
<td>0.05 to 2.07 µg/kg dw (Shi et al., 2009)</td>
<td>0.05–6.7 µg/kg dw</td>
</tr>
<tr>
<td>Soil</td>
<td>28.1 µg/kg dry wt (Shi et al., 2009).</td>
<td>28.1 µg/kg dw</td>
<td>0.05 µg/kg dw (Shi et al., 2009).</td>
<td>0.05 µg/kg dw</td>
</tr>
<tr>
<td>Birds</td>
<td>Muscle: 9.6–16.3 µg/kg dw (mean 12.7), Liver: 13.7–54.6 µg/kg dw (mean 34.4), Kidney: 24.5–124 µg/kg dw (mean 64.5) (Shi et al., 2009) ND to 1.7 µg/kg lw (Gao et al., 2009). Range 4–800 µg/kg lw in various tissues (Luo et al., 2009)</td>
<td>ND–800 µg/kg lw</td>
<td>Muscle: 0.07–0.39 µg/kg dw (median 0.19), Liver: 0.27–2.41 µg/kg dw (median 1.23), Kidney: 0.12–0.89 µg/kg dw (median 0.45) (Shi et al., 2009)</td>
<td>0.05–2.41 µg/kg dw</td>
</tr>
<tr>
<td>Fish</td>
<td>&lt;0.03–3.7 µg/kg lw (K. Law et al., 2006)</td>
<td>&lt;0.03 to 3.7 µg/kg lw</td>
<td>0.01 µg/kg (Karls et al., 2006a,b)</td>
<td>0.01–0.96 µg/kg</td>
</tr>
<tr>
<td>Bird egg</td>
<td>1.3 to 288 µg/kg ww (Gauthier et al., 2007)</td>
<td>1.3 to 288 µg/kg ww</td>
<td>0.11 µg/kg (Karls et al., 2006a,b)</td>
<td>0.11–0.96 µg/kg</td>
</tr>
<tr>
<td>Tree bark</td>
<td>ND to 0.73 µg/kg dw (Qiu and Hites, 2008; Zhu and Hites, 2006)</td>
<td>ND to 0.73 µg/kg dw</td>
<td>0.96 µg/kg lw in egg yolk (Verreaux et al., 2007)</td>
<td>0.96 µg/kg</td>
</tr>
<tr>
<td>Panda tissue</td>
<td>ND to 863 µg/kg lw (Hu et al., 2008).</td>
<td>ND to 863 µg/kg lw</td>
<td>ND to 863 µg/kg lw</td>
<td>101 µg/kg</td>
</tr>
<tr>
<td>Children's toys</td>
<td>5540 µg/kg (Chen et al., 2009)</td>
<td>5540 µg/kg</td>
<td>101 µg/kg (Chen et al., 2009)</td>
<td>101 µg/kg</td>
</tr>
</tbody>
</table>

*Covaci et al., (2011) Environ. Internat. 37, 532–556*
Levels in the environment (II)

- PBB and TBPH
- TBPH and TBB sewage sludge of WWTP San Francisco, US (Klosterhaus et al. 2008)
  - TBB: 40 to 1412 ng/g dw
  - TBPH: 57 to 515 ng/g dw
  - In the same ranges or higher than HBCD and decaBDE

- In finless porpoises from Hong Kong and China (Lam et al. 2009)
  - TBB: <0.4 -70 ng/g lw
  - TBPH: <0.04-3859 ng/g lw

- In house dust from Boston, US (Stapleton et al. 2008)
  - TBB: <6.6 to 15,030 ng/g (median 133 ng/g)
  - TBPH:1.5 to 10,630 ng/g (median 142 ng/g)
Conclusions

- GC-ECNI-MS sensitive method to measure BDBPE, DBDPE, TBB and TBPH
- The ‘new’ BFRs can be analyzed in the same run as PBDEs
- GC column < 15 meter (degradation of DBDPE)
- Use of non-destructive cleanup methods is needed (no acids)
- Combine cleanup with PBDEs
- LC-MS/MS in APPI/APCI mode good alternative
- Detected in the environment (limited data)
More “new” BFRs

- Determination of new brominated flame retardants and PBDEs in sediment and SPM from the Western Scheldt (Lopez et al. 2011)

<table>
<thead>
<tr>
<th>Molecular structure</th>
<th>Compound</th>
<th>Molecular structure</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Molecular structure" /></td>
<td>Pentabromochlorocyclohexane (PBCH) (isomers A, B, C and D) CAS [87-84-3]</td>
<td><img src="image2" alt="Molecular structure" /></td>
<td>2,3,4,5,6-Tetra-iodo-p-xylene (pTIX) CAS [24388-38-2]</td>
</tr>
<tr>
<td>Br Cl</td>
<td>MW = 513.09</td>
<td>Br</td>
<td>MW = 421.75</td>
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<tr>
<td>Br Br</td>
<td>$S_{\text{water}} = 0.055 \text{ mg/L}$</td>
<td>Br Br</td>
<td>$S_{\text{water}} = 0.000935 \text{ mg/L}$</td>
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<tr>
<td>Br Br</td>
<td>$\log P_{\text{octanol-water}} = 4.72$</td>
<td>Br Br</td>
<td>$\log P_{\text{octanol-water}} = 6.99$</td>
</tr>
<tr>
<td>Br Cl</td>
<td><img src="image3" alt="Molecular structure" /></td>
<td>Tetra-iodo-4-chlorotoluene (TIX) CAS [39569-21-6] MW = 422.19</td>
<td>2,3,4,5,6-Pentabromotoluene (PBT) CAS [87-83-2] MW = 486.62</td>
</tr>
<tr>
<td>Br</td>
<td>$S_{\text{water}} = 0.016 \text{ mg/L}$</td>
<td>Br</td>
<td>$S_{\text{water}} = 0.0000935 \text{ mg/L}$</td>
</tr>
<tr>
<td>Br Cl</td>
<td>$\log P_{\text{octanol-water}} = 5.63$</td>
<td>Br</td>
<td>$\log P_{\text{octanol-water}} = 6.99$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><img src="image4" alt="Molecular structure" /></td>
<td>Tetra-iodo-tetrahydrophthalic anhydride (TBPhA) CAS [632-79-1] MW = 463.7</td>
<td><img src="image5" alt="Molecular structure" /></td>
<td>Tris(2,3-dibromopropyl) phosphate (TBP) CAS [126-72-7]</td>
</tr>
<tr>
<td>Br Cl O</td>
<td>$S_{\text{water}} = 0.016 \text{ mg/L}$</td>
<td>Br Br</td>
<td>MW = 697.64</td>
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<tr>
<td>Br Br</td>
<td>$\log P_{\text{octanol-water}} = 5.63$</td>
<td>Br</td>
<td>$S_{\text{water}} = 0.0000935 \text{ mg/L}$</td>
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<tr>
<td>Br Cl O</td>
<td></td>
<td>Br</td>
<td>$\log P_{\text{octanol-water}} = 6.99$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image6" alt="Molecular structure" /></td>
<td>1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) CAS [37853-59-1] MW = 687.64</td>
<td><img src="image7" alt="Molecular structure" /></td>
<td>Decabromodiphenyl ethane (DBDPE) CAS [84852-53-9] MW = 971.1</td>
</tr>
<tr>
<td>Br Br</td>
<td>$S_{\text{water}} = 0.2 \text{ mg/L}$</td>
<td>Br Br</td>
<td>$S_{\text{water}} = 0.00072 \text{ mg/L}$</td>
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<tr>
<td>Br Br</td>
<td>$\log P_{\text{octanol-water}} = 9.15$</td>
<td>Br Br</td>
<td>$\log P_{\text{octanol-water}} = 11$</td>
</tr>
</tbody>
</table>
Cleanup method

- Quantification was conducted by IS. $^{13}$C BDE209 was used for octa-, nona-, and decaBDE and DBDPE. BDE58 and $^{13}$C BDBPE was used for the other BFRs.

- PBCCH, TBoCT, pTBX, PBT, TBPhA, TBDPP and BTBPE were analysed together with the PBDEs on a 50 m column.

- DBDPE was analysed in the same run as octa-, nona-BDEs and BDE209 on a short column to avoid on-column degradation.
Spatial distribution sediment
Concentrations in sediment (ng/g dw)

Upstream Scheldt estuary

- Wielingen
- Terneuzen
- Hansweert
- Oude doel

Chemicals:
- BDE209
- DBDPE
- BDE47
- PBCCH D
- BDBPE
- PBT
- TBoCT
- PBCCH A
- pTBX
Results and Conclusions

• Analytical procedure to determine PBCCH, TBoCT, pTBX, TBPhA, PBT, BDBPE, and DBDPE together with PBDEs in sediments and in suspended particulate matter

• First identification of PBCCH, pTBX and TBoCT in sediment and SPM

• The concentrations of these new flame retardants ranged from 0.05 to 0.30 µg/kg dry weight
Organophosphorus Flame Retardants (PFRs)
Introduction

• Phase-out production and use of PBDEs
• Increased use of alternative FRs (e.g. PFRs)
• Worldwide production volume of FRs
  • 14% PFRs compared to 21% for BFRs*
• Detected in various matrices e.g. water, air sediment
• Limited information on PFRs in biota

*(www.cefic/efra.com)
Objectives

• Determination of PFRs in the pelagic and benthic food web of the Western Scheldt
PFRs

- TiBP
- TBP
- TCEP
- TCPP
- TDCPP
- TBEP
- TPP
- TEHP
- TCP
- DBPhP
- DPhBP
Cleanup

Fat retaining
Matrix: 250 mg of fish oil

Fat retaining

0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%

AI Ox  GPC  Silica  SPE HLB  SPE PPT  SPE NH2

Fat retaining

18-125%  86-115%  75-120%  48-238%  10-164%  68-128%

Recovery
PFRs

No cyclic  Too much matrix  Too much matrix  Poor recovery  No cyclic  Best solution

Summary
### PFRs in Belgian home dust (n=33) µg/g

<table>
<thead>
<tr>
<th>FRs</th>
<th>DF (%)</th>
<th>Mean</th>
<th>Median</th>
<th>P95</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OPFRs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEP</td>
<td>0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiBP</td>
<td>100</td>
<td>4.20</td>
<td>2.99</td>
<td>8.81</td>
<td>0.70–15.6</td>
</tr>
<tr>
<td>TnBP</td>
<td>100</td>
<td>0.25</td>
<td>0.13</td>
<td>0.63</td>
<td>0.03–2.70</td>
</tr>
<tr>
<td>TCEP</td>
<td>86</td>
<td>0.49</td>
<td>0.23</td>
<td>1.72</td>
<td>&lt;0.08–2.65</td>
</tr>
<tr>
<td>TCPP</td>
<td>100</td>
<td>4.82</td>
<td>1.38</td>
<td>14.5</td>
<td>0.19–73.7</td>
</tr>
<tr>
<td>TBEP</td>
<td>100</td>
<td>6.58</td>
<td>2.03</td>
<td>23.1</td>
<td>0.36–67.6</td>
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<tr>
<td>TPP</td>
<td>100</td>
<td>2.02</td>
<td>0.50</td>
<td>7.28</td>
<td>0.04–29.8</td>
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<tr>
<td>TDCPP</td>
<td>97</td>
<td>0.57</td>
<td>0.36</td>
<td>0.99</td>
<td>&lt;0.08–6.64</td>
</tr>
<tr>
<td>TCP</td>
<td>97</td>
<td>0.44</td>
<td>0.24</td>
<td>1.10</td>
<td>&lt;0.04–5.07</td>
</tr>
<tr>
<td>ΣOPFRs</td>
<td>19.4</td>
<td>13.1</td>
<td>70.3</td>
<td></td>
<td>1.92–94.7</td>
</tr>
</tbody>
</table>

| **BFRs** |        |      |        |     |           |
| BDE-209 | 98     | 0.59 | 0.31   | 0.92| <0.001–5.30|
| ΣPBDEs  | 0.70   | 0.36 | 1.14   |     | 0.003–6.33 |
| ΣHBCDs  | 1.74   | 0.13 | 2.46   |     | 0.010–42.70|
| TBBPA   | 85     | 0.04 | 0.01   | 0.09| 0.002–0.42 |

Life Cycle and Risk Assessment of Environmental Compatible Flame Retardants
Prototypical case study

ENFIRO

EU research project FP7: 226563
Objectives ENFIRO

• To study the substitution options for some BFRs

• ENFIRO delivers:
  • Comprehensive dataset on the viability of production, application
  • Risk assessment
  • Life cycle assessment (LCA)
Work plan

Prioritization and Selection

Hazard Characterisation

Exposure, fate, model.

FR Capability studies

Application studies

Risk assessment
- Environmental
- Public Health
- Occupational Health

Impact assessment studies

Dissemination
ENFIRO: HFFRs for screening study

Inorganic FRs (n=7)

$$\text{Zn}^{2+} \quad \begin{array}{c}
\text{Sn} \\
\text{O} \\
\text{O} \\
\end{array} \quad \text{OH} \quad \text{OH}$$

Organophosphorus & salt FRs (n=5)

$$\begin{array}{c}
\text{P} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}$$

Nitrogen based organic FR (n=1)

$$\begin{array}{c}
\text{NH}_2 \\
\text{H}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{NH}_2 \\
\end{array} \quad \left[ \begin{array}{c}
\text{O} \\
\text{P} \quad \text{O} \\
\text{OH} \quad \text{OH} \\
\end{array} \right]_n$$

Intumescent systems (n=2)

Nanoclay (n=1)
Three level assessments

FR
Risk assessment
- Environment
- Human health

Material
Technological assessment
- Application
- Fire performance
- Leaching behaviour

Product
Impact assessment studies
- Life cycle assessment
- Life cycle costing
- Social life cycle assessment
Assessment of FR/polymer material

- Leaching FR to air (off-gassing)
- Leaching FR to water (concentrations and toxicity)
- Toxic gasses after fire tests
- Weathering
AlPi leaching from PBT pellets and moulded plates

DIN 383414
Al and P leaching from PBT pellets (PG3)

DIN 38414
Al and P leaching from PBT pellets (PG4)

TCLP
Al and P leaching from PBT pellets (PG3)

TCLP
Al and P leaching from PBT pellets (PG4)
Final conclusion

- New BFRs can be analysed by LC versus GC \( \rightarrow \) Both
- Alternative flame retardant \( \rightarrow \) only brominated or include PFRs
- What if we only use metal based FRs like ATH \( \rightarrow \) problem solved?

Source: SRI Consulting 2005 and 2008
Acknowledgement

ENFIRO funded by the EU (226563)