COMBINATION EFFECTS OF CHEMICALS

Some initial perspectives from an environmental NGO

Dr David Santillo
Greenpeace Research Laboratories
Chemicals in mixtures - general observations

• Chemicals (additives or contaminants) in products, wastes, environmental compartments and foods occur, more often than not, as complex mixtures

• Exposure to complex mixtures should therefore be considered more a norm than an exception

• Toxicity of a mixture may be dominated by one chemical component, but equally may not

• Even assuming additivity models, assessments themselves can quickly become highly complex and uncertain
Chemicals in mixtures - general observations

Assessment of complex mixtures: the possibilities are endless...

- Mixture composition
- Component concentrations (relative and absolute)
- Receptors selected
- Duration of dose
- Timing of dose
- End points selected
- Predisposition to impacts
Chemical complexity in products
Loom band charms:
Hungary

14th June 2016
Hazardous Substances Advisory Committee 15th Meeting

Number of compounds isolated: 73

<table>
<thead>
<tr>
<th>CAS#</th>
<th>Name</th>
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<tbody>
<tr>
<td>000117-81-7</td>
<td>1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP) 1st</td>
</tr>
<tr>
<td>006422-86-2</td>
<td>1,4-Benzenedicarboxylic acid, 1,4-bis(2-ethylhexyl) ester (DEHT)</td>
</tr>
<tr>
<td>000872-05-9</td>
<td>1-Decene</td>
</tr>
<tr>
<td>036653-82-4</td>
<td>1-Hexadecanol 4th</td>
</tr>
<tr>
<td>000112-88-9</td>
<td>3-Octadecene</td>
</tr>
<tr>
<td>000629-78-7</td>
<td>Heptadecane</td>
</tr>
<tr>
<td>001731-92-6</td>
<td>Heptadecanoic acid, methyl ester</td>
</tr>
<tr>
<td>000544-76-3</td>
<td>Hexadecane</td>
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<td>000638-36-8</td>
<td>Hexadecane, 1,4-bis(2-ethylhexyl) ester (DEHT)</td>
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<td>Heptadecanoic acid, methyl ester</td>
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<tr>
<td>000112-39-0</td>
<td>Hexadecanoic acid, methyl ester 3rd</td>
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<tr>
<td>001750-51-2</td>
<td>Naphthalene, decahydro-1,6-dimethyl-</td>
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<tr>
<td>000629-92-5</td>
<td>Nonadecane</td>
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<tr>
<td>000593-45-3</td>
<td>Octadecane</td>
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<td>Octadecanoic acid, methyl ester</td>
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<tr>
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<td>Oxiraneoctanoic acid, 3-octyl, methyl ester 2nd</td>
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<td>000288-96-4</td>
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Compounds tentatively identified:

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<th>Name</th>
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<tr>
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<td>3-Methyl-1-(phenylthio)butan-2-one</td>
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<tr>
<td>002114-42-3</td>
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<td>017312-57-1</td>
<td>Dodecane, 3-methyl-</td>
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<tr>
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<td>001072-05-5</td>
<td>Heptane, 2,6-dimethyl-</td>
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<tr>
<td>017302-32-8</td>
<td>Nonane, 3,7-dimethyl-</td>
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<tr>
<td>026730-12-1</td>
<td>Tridecane, 4-methyl-</td>
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<tr>
<td>017301-23-4</td>
<td>Undecane, 2,6-dimethyl-</td>
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<table>
<thead>
<tr>
<th>Name</th>
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<tbody>
<tr>
<td>000117-81-7</td>
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<td>026730-12-1</td>
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<tr>
<td>017301-23-4</td>
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</table>
Loom band charms: Philippines

Number of compounds isolated: 54

<table>
<thead>
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<tbody>
<tr>
<td>000117-81-7</td>
<td>1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP) 1st</td>
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<tr>
<td>000084-69-5</td>
<td>1,2-Benzenedicarboxylic acid, diisobutyl ester</td>
</tr>
<tr>
<td>006422-86-2</td>
<td>1,4-Benzenedicarboxylic acid, 1,4-bis(2-ethylhexyl) ester (DEHT) 2nd</td>
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<tr>
<td>000112-88-9</td>
<td>1-Octadecene</td>
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<tr>
<td>007568-58-3</td>
<td>1-Propene-1,2,3-tricarboxylic acid, tributyl ester</td>
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<td>Benzenesulfonic acid, 4-methyl-, butyl ester</td>
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<tr>
<td>000077-94-1</td>
<td>Butyl citrate</td>
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<tr>
<td>00294-62-2</td>
<td>Cycloaddcane</td>
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<td>1-Hexadecanol</td>
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<tr>
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<td>Heptadecane</td>
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<td>000544-76-3</td>
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<td>Hexadecanoic acid, methyl ester</td>
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<td>000112-61-8</td>
<td>Methyl stearate</td>
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<tr>
<td>002566-91-8</td>
<td>Oxiraneoctanoic acid, 3-octyl-, methyl ester</td>
</tr>
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<td>000629-62-9</td>
<td>Pentadecane</td>
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<tr>
<td>000630-07-9</td>
<td>Pentatriacontane</td>
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<td>Phenol</td>
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<td>000077-90-7</td>
<td>Tributyl acetylcitrate 3rd</td>
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Compounds tentatively identified:

<table>
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<th>CAS#</th>
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<tbody>
<tr>
<td>056862-62-5</td>
<td>10-Methylnonadecane</td>
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<tr>
<td>006846-50-0</td>
<td>2-Methylpropanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl</td>
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<tr>
<td>017301-28-9</td>
<td>3,6-Dimethyldodecane</td>
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<tr>
<td>005444-75-7</td>
<td>Benzoic acid, 2-ethylhexyl ester</td>
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<tr>
<td>000530-11-8</td>
<td>Benzoic acid, tridecyl ester</td>
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<td>017851-53-5</td>
<td>Butyl isobutyl phthalate</td>
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<td>001795-15-9</td>
<td>Cyclohexanone, octyl-</td>
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<td>019879-11-9</td>
<td>Cyclohexanol, 1,2-dimethyl-, cis-</td>
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<td>061141-72-8</td>
<td>Dodecane, 4,6-dimethyl-</td>
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<td>Ethyl stearate</td>
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<tr>
<td>006418-41-3</td>
<td>Tridecane, 3-methyl-</td>
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Loom band charms: Germany

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<tbody>
<tr>
<td>006422-86-2</td>
<td>1,2-Cyclohexanedicarboxylic acid, diisononyl ester, 23 isomers 1st</td>
</tr>
<tr>
<td>006846-50-0</td>
<td>2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester 2nd</td>
</tr>
<tr>
<td>036653-82-4</td>
<td>1-Hexadecanol 3rd</td>
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<tr>
<td>000295-65-8</td>
<td>Cyclohexadecane</td>
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<tr>
<td>000112-34-5</td>
<td>Ethanol, 2-(2-butoxyethoxy)-</td>
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<tr>
<td>084852-15-3</td>
<td>Phenol, nonyl, 8 isomers</td>
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<tr>
<td>000108-95-2</td>
<td>Phenol</td>
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<td>000112-70-9</td>
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Number of compounds isolated: 50

Compounds identified to better than 90%:

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<tr>
<td>006422-86-2</td>
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<tr>
<td>006846-50-0</td>
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<td>1-Hexadecanol 3rd</td>
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<tr>
<td>000295-65-8</td>
<td>Cyclohexadecane</td>
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<tr>
<td>000112-34-5</td>
<td>Ethanol, 2-(2-butoxyethoxy)-</td>
</tr>
<tr>
<td>084852-15-3</td>
<td>Phenol, nonyl, 8 isomers</td>
</tr>
<tr>
<td>000108-95-2</td>
<td>Phenol</td>
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<tr>
<td>000112-70-9</td>
<td>1-Tridecanol</td>
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Compounds tentatively identified:

<table>
<thead>
<tr>
<th>CAS#</th>
<th>Name</th>
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<tbody>
<tr>
<td>000112-70-9</td>
<td>1-Tridecanol</td>
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</table>

14th June 2016
Chemical complexity in wastes
Electronics manufacturing facility #1

Number of compounds isolated: 31
Compounds identified to better than 90%: 4

<table>
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<tr>
<td>000084-66-2</td>
<td>Diethyl phthalate</td>
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<td>Benzenesulfonamide, N-butyl- $$ BM 4</td>
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<td>000084-74-2</td>
<td>Di-n-butyl phthalate</td>
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<td>00115-86-6</td>
<td>Triphenyl phosphate $$ TPP</td>
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Hazardous Substances Advisory Committee 15th Meeting
Number of compounds isolated: 30

Compounds identified to better than 90%: 9

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<td>000065-85-0</td>
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<td>2,4,7,9-Tetramethyl-5-decyne-4,7-diyl $$ Surfynol 104H</td>
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<td>002400-00-2</td>
<td>Benzene, (1-ethyldecyl)-</td>
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<td>1,2-Benzenedicarboxylic acid, diethyl ester $$ DEP</td>
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<td>Benzothiazole, 2-(methylthio)-</td>
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<tr>
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<td>2-Propanol, 1-chloro-, phosphate (3:1) $$ Amsgard TMCP</td>
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<tr>
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<td>Ethanol, 2-butoxy-, phosphate (3:1) $$ KP 140</td>
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<td>Bis(2-ethylhexyl)phthalate $$ DEHP</td>
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<tr>
<td>000115-86-6</td>
<td>Triphenyl phosphate $$ TPP</td>
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Electronics manufacturing facility #3 (combined sewer)
Sediment receiving combined sewer wastes

Number of compounds isolated: 253
Compounds identified to better than 90%: 55

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<td>000586-62-9</td>
<td>Cyclohexene, 1-methyl-4-[1-methylethylidene]-</td>
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<td>061141-72-8</td>
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<td>Benzoic acid, heptadecyl ester or Benzoic acid, tetradecyl ester</td>
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<td>...etc...</td>
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</table>
Human exposure through rudimentary electronics recycling
Assessment tools
IGHRC 2009

Figure 1. Flow chart outlining the risk assessment process for chemical mixtures

1. Define the mixture and the contact in which it is being used.
2. Are the key components known or can they be identified?
3. Are there sufficient data on the mixture itself or on a sufficiently similar mixture to use for the risk assessment?
4. Are the key components known or can they be identified?
5. Is the mixture simple or complex?
6. Most component-based approaches for complex mixtures have been developed for specific applications and the potential to use these approaches for new applications will need careful evaluation.
7. Determine the type of interaction and see if it is possible to quantify the effect on the overall toxicity of the mixture. If yes, conduct a risk assessment. If it is not possible to quantify the effect of the interaction, consider whether the assessment factors that have been used are appropriate to take account of the potential interaction and adjust or apply additional factors where necessary.

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Assessment tools
CEFIC 2015
“Pessimistic assumptions [...] are, therefore, likely to be no more reliable than optimistic assumptions or, indeed, capable of being differentiated from them.”

“[…] default uncertainty factors do not represent worst-case scenarios and were not intended to do so [...] the data available does not support an unwavering belief in the purported conservativeness of the overall default uncertainty factor of 100.”
Testing interactions in binary mixtures: metals and PFAAs
### Leaving Traces

**The hidden hazardous chemicals in outdoor gear**

**Greenpeace product test 2016**

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#### Chart: Norrona Lofoten Gore-tex pro jacket (Norway) vs Patagonia Men’s Super Alpine Jacket (Taiwan)

<table>
<thead>
<tr>
<th>PFC</th>
<th>Concentration in µg/m²</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBS</td>
<td>0.21</td>
<td>0.03</td>
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<tr>
<td>PFBA</td>
<td>1.72</td>
<td>0.2</td>
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<tr>
<td>PFPA</td>
<td>10.6</td>
<td>1.8</td>
</tr>
<tr>
<td>PFHpA</td>
<td>76.4</td>
<td>10</td>
</tr>
<tr>
<td>PFDoA</td>
<td>9.97</td>
<td>1.2</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.011</td>
<td>0.02</td>
</tr>
<tr>
<td>PFDA</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>6:2 FTOH</td>
<td>650</td>
<td>0.4%</td>
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</table>

**Sum PFC 730 µg/m²**

<table>
<thead>
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<th>Concentration in µg/m²</th>
<th>Percentage</th>
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<td>PFBS</td>
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<td>10</td>
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<tr>
<td>PFBA</td>
<td>19.2</td>
<td>6.5</td>
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<tr>
<td>PFPA</td>
<td>3.79</td>
<td>1.4</td>
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<tr>
<td>PFHpA</td>
<td>25.1</td>
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<tr>
<td>PFDoA</td>
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<tr>
<td>PFNA</td>
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<td>PFDA</td>
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<td>0.02</td>
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<td>6:2 FTOH</td>
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<td>10:2 FTOH</td>
<td>6.7</td>
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</table>

**Sum PFC 284 µg/m²**
### Table: Hazardous Substances

<table>
<thead>
<tr>
<th>Country</th>
<th>Sample Type</th>
<th>PFBA</th>
<th>PFPnA</th>
<th>PFPnH A</th>
<th>PFNA</th>
<th>PFDA</th>
<th>PFPnA</th>
<th>PFPnA</th>
<th>PFPnH A</th>
<th>PFNA</th>
<th>PFDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia</td>
<td>water</td>
<td>0.665</td>
<td>&lt;0.004</td>
<td>&lt;0.025</td>
<td>0.174</td>
<td>0.173</td>
<td>0.151</td>
<td>0.039</td>
<td>0.017</td>
<td>&lt;0.006</td>
<td>&lt;0.001</td>
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<tr>
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<td>field blank</td>
<td>0.495</td>
<td>&lt;0.065</td>
<td>&lt;0.065</td>
<td>0.026</td>
<td>0.029</td>
<td>0.026</td>
<td>0.029</td>
<td>0.026</td>
<td>&lt;0.026</td>
<td>&lt;0.026</td>
</tr>
<tr>
<td>China</td>
<td>water</td>
<td>0.253</td>
<td>&lt;0.005</td>
<td>&lt;0.025</td>
<td>0.012</td>
<td>0.054</td>
<td>0.058</td>
<td>0.012</td>
<td>0.016</td>
<td>&lt;0.009</td>
<td>&lt;0.009</td>
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<tr>
<td></td>
<td>field blank</td>
<td>0.526</td>
<td>0.732</td>
<td>0.962</td>
<td>0.273</td>
<td>0.328</td>
<td>0.087</td>
<td>0.030</td>
<td>0.007</td>
<td>&lt;0.011</td>
<td>&lt;0.011</td>
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<tr>
<td>Slovakia</td>
<td>water</td>
<td>0.521</td>
<td>0.216</td>
<td>0.063</td>
<td>0.137</td>
<td>0.191</td>
<td>0.117</td>
<td>0.047</td>
<td>0.021</td>
<td>&lt;0.036</td>
<td>&lt;0.036</td>
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<td>field blank</td>
<td>0.526</td>
<td>0.121</td>
<td>0.087</td>
<td>0.056</td>
<td>0.190</td>
<td>0.118</td>
<td>0.048</td>
<td>0.052</td>
<td>&lt;0.023</td>
<td>&lt;0.023</td>
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<tr>
<td>Switzerland</td>
<td>water</td>
<td>0.773</td>
<td>0.062</td>
<td>0.156</td>
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<td>0.581</td>
<td>0.253</td>
<td>0.051</td>
<td>0.033</td>
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<td>0.034</td>
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<td>&lt;0.025</td>
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<td>Chile</td>
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<td>0.038</td>
<td>0.038</td>
<td>0.025</td>
<td>0.065</td>
<td>0.048</td>
<td>0.015</td>
<td>0.025</td>
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<td>0.558</td>
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<td>0.058</td>
<td>0.572</td>
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<td>0.058</td>
<td>0.058</td>
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<td>&lt;0.017</td>
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<tr>
<td>Italy</td>
<td>water</td>
<td>0.468</td>
<td>0.061</td>
<td>0.064</td>
<td>0.084</td>
<td>0.098</td>
<td>0.035</td>
<td>0.098</td>
<td>0.098</td>
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<td>0.632</td>
<td>0.069</td>
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<td>0.068</td>
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<td>0.028</td>
<td>0.028</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
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<td>Turkey</td>
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<td>0.685</td>
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<td>0.050</td>
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<td>0.044</td>
<td>0.034</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
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</tbody>
</table>

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**Footprints in the Snow**

Hazardous POPs in remote locations around the globe.
Tendency towards higher complexity in environmental risk assessment of Plant Protection Products: to accept or to avoid?

Key messages from an NGO perspective

Mengjiao Wang, David Santillo & Paul Johnston
Greenpeace Research Laboratories
Innovation Centre, University of Exeter, UK
## Pesticides in European apples, 2015

<table>
<thead>
<tr>
<th>Country</th>
<th>No. of samples</th>
<th>Organic samples (without residues)</th>
<th>Number of residues found in conventionally grown apples</th>
<th>Mode of residues / mean number of residues found per conventional sample for each specified country</th>
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<tbody>
<tr>
<td>Austria</td>
<td>10</td>
<td>1</td>
<td>1 1 1 3 2 1 0 0 0</td>
<td>3 / 2.8</td>
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<tr>
<td>Belgium</td>
<td>4</td>
<td>1</td>
<td>0 0 1 0 2 0 0 0 0</td>
<td>4 / 3.3</td>
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<td>Bulgaria</td>
<td>5</td>
<td>2</td>
<td>0 0 2 0 0 0 0 0 1</td>
<td>2 / 4.0</td>
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<tr>
<td>Switzerland</td>
<td>8</td>
<td>2</td>
<td>1 3 0 1 0 1 0 0 0</td>
<td>1 / 1.8</td>
</tr>
<tr>
<td>Germany</td>
<td>39</td>
<td>6</td>
<td>4 12 7 5 3 1 0 1 0</td>
<td>1 / 2.0</td>
</tr>
<tr>
<td>France</td>
<td>13</td>
<td>1</td>
<td>6 3 0 0 3 0 0 0 0</td>
<td>0 / 1.3</td>
</tr>
<tr>
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<td>1</td>
<td>1 5 2 1 0 0 0 0 0</td>
<td>1 / 1.3</td>
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<td>0 3 2 2 1 2 0 0 0</td>
<td>1 / 2.7</td>
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<td>8</td>
<td>0</td>
<td>0 3 2 1 0 2 0 0 0</td>
<td>1 / 2.5</td>
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<td>Spain</td>
<td>14</td>
<td>3</td>
<td>0 1 0 3 3 1 1 2 0</td>
<td>3 / 4.3</td>
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</tbody>
</table>
Pesticides in European apple orchards, 2015

...numbers of residues

**Fig. 1** Frequency of pesticides detections in soil samples from apple orchards

**Fig. 2** Frequency of pesticides detections in water samples collected within 100m of apple orchards, adjacent to apple orchards
Pesticides in European apple orchards, 2015

...types of residues
Pesticides in pollen & beebread from European hives, 2013

<table>
<thead>
<tr>
<th>Country</th>
<th>Sampling period, 2013</th>
<th>Number of samples</th>
<th>Key pesticides (banned neonicotinoids and other frequently encountered pesticides*)</th>
</tr>
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<tbody>
<tr>
<td>Austria</td>
<td>May</td>
<td>3</td>
<td>Clothianidin (1) [4.7], Thiacloprid (1) [24], Tebuconazole (1) [30]</td>
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<td>Boscalid (2) [48-269], Folpet (1) [11], Tebuconazole (1) [159],</td>
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<td>Thopranate-methyl (1) [24]</td>
</tr>
<tr>
<td>France</td>
<td>Apr-Sep</td>
<td>12</td>
<td>Thiacloprid (8) [10-250], Amitraz (incl. metabolites) (1) [11],</td>
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<tr>
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<td>Azoxystrobin (2) [30-69], Boscalid (6) [12-144], Cypocrin (2) [454-590],</td>
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<td>Fenhexamid (1) [2550], Spiroxamine (1) [10],</td>
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<td>Thiphanate-methyl (1) [17], Trifloxystrobin (2) [20-1104]</td>
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<tr>
<td>Germany</td>
<td>May-Jun</td>
<td>15</td>
<td>Thiacloprid (8) [10-250], Amitraz (incl. metabolites) (1) [11],</td>
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<td>Azoxystrobin (2) [30-69], Boscalid (6) [12-144], Cypocrin (2) [454-590],</td>
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<td>Thiphanate-methyl (1) [17], Trifloxystrobin (2) [20-1104]</td>
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<tr>
<td>Greece</td>
<td>Jun-Jul</td>
<td>10</td>
<td>Amitraz (2) [20-33], Chlorpyrifos-ethyl (1) [536]</td>
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<td>Imidacioprid (2) [1-11], Chlorpyrifos-ethyl (3) [10-562],</td>
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<td>Thiphanate-methyl (1) [28], Trifloxystrobin (7) [22-220]</td>
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<tr>
<td>Luxembourg</td>
<td>May-Jun</td>
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<td>No pesticides detected</td>
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<tr>
<td>Poland</td>
<td>May-Jun</td>
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<td>Tebuconazole (1) [16], Thopranate-methyl (2) [10-68]</td>
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<td>Romania</td>
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<td>Thiphanate-methyl (2) [27-53]</td>
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<td>Spain</td>
<td>Jul-Aug</td>
<td>14</td>
<td>Imidacioprid (4) [7.6-148.5], Chlorpyrifos-ethyl (5) [11-705]</td>
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<tr>
<td>Sweden</td>
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<td>Clothianidin (1) [1.8], Boscalid (2) [147-1081]</td>
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<tr>
<td>Switzerland</td>
<td>Apr-Sep</td>
<td>10</td>
<td>Thiacloprid (1) [31], Cypocrin (2) [91-10169], Thiphanate-methyl (1) [21]</td>
</tr>
</tbody>
</table>

- 17 pesticides (14 fungicides & 3 insecticides/acaricides) in pollen near vineyards in Valle S Matteo, Italy (2013)
- 7 pesticides (6 insecticides/acaricides & 1 fungicide) in beebread from Gilena, Andalucia (stored from 2012)
Higher Tier Risk Assessment for PPP: Field relevance or spurious confidence?

- Although higher tier testing may appear to yield greater rigour and relevance, it also leads to less humility and precaution.
- Gaps in understanding and assessment may be less explicitly acknowledged.
- Potential for combination effects in mixtures will remain particularly hard to account for, especially in higher tier testing.
  - e.g. taking the 17 pesticides in one single pollen sample, if tested only in pairs, would already require 136 different combinations...in groups of 3, this rises to 680 combinations.
Higher complexity in PPP risk assessment: to accept or avoid?

**DO ASSUME:**
- that the use of pesticides in the field will lead to exposure (to non-target species and, possibly, humans)
- that wildlife and humans will experience exposure to pesticides as mixtures of active substances (and of other ingredients)

**DON’T ASSUME:**
- that under higher tier testing and assessment, all bases will be covered
- that there will be no surprises
Combination effects of chemicals: some ways forward?

• Conceptual frameworks and decision trees may help guide assessment of combination effects in relatively simple mixtures of chemicals, but may rapidly reach limits

• EuroMIX initiative may yield greater insight for ‘key’ mixtures, but not clear yet how those will be selected, nor how far this will lead to robust tools for general application (nor extent of animal testing)

• Reliable assessment of combination effects of chemicals in complex mixtures (which are what are routinely encountered in the real world) will remain extremely difficult, if not impossible
Combination effects of chemicals: some ways forward?

• Need far more focus upstream on reducing exposures to such mixtures of chemicals through actions at source:
  • Avoid use of known hazardous substances wherever possible (including through substitution with safer alternatives)
  • Simplify the formulation of products as far as possible (and control & monitor composition)
  • Minimize the generation of wastes and their complexity (including by auditing and control of inputs to waste streams)
• For existing/legacy pollution, take whatever practical steps are available to minimise exposure, to contain contaminated materials and/or remediate contaminated sites