Executive summary:

Some brominated flame retardants (BFRs) have unintended negative effects on the environment and human health. Less toxic alternatives appear to be available already but comprehensive information on their possible toxicological effects are lacking. The European Commission-funded project ENFIRO investigated the substitution options for some BFRs and compared the hazard, exposure, fire, and application performances. Based on these results risk and impact assessments were carried out. In total 14 halogen-free flame retardants (HFFRs) as alternatives for decaBDE, TBBP-A, and brominated polystyrenes were selected. These flame retardants were studied in five applications - printed circuit boards (PCBs), electronic components, injection moulded products, textile coatings and intumescent paint.

ENFIRO showed that all of the selected alternative flame retardants do fulfil the regulatory fire test. A method was developed using intrinsic flammability properties as well as a simple method for characterizing the fire performance and fire toxicity of polymers using three parameters (fire spread, smoke/carbon monoxide, inefficiency of combustion). With this model a comparative fire performance assessment of HFFRs vs BFRs could be made. An important finding was that halogen free systems have clear benefits as demonstrated, e.g. less visible smoke, in some cases lower peak heat release rate with halogen free products, and less toxic components in smoke. Both polymers with brominated and halogen-free FR showed similar loss in mechanical properties compared to the polymer alone. All formulations (HFFR and BFR) showed equal or better performance regarding processability for injection moulding. For all polymer systems investigated a HFFR option was found. An important part of the project was the input received from the Stakeholder forum on formulations. The results for the PCBs showed that the HFFRs were as good as or better compared to the reference PCBs produced using BFRs. A novel intumescent coating system was developed for pure HIPS, showing good fire performance results and excellent results were obtained for the industry fire standards relevant to the electronics industry as well.

From the initial selection of 14 alternative flame retardants seven were found to be less toxic and also accumulated less in the food chain than some of the BFRs. Environmental fate models predicted that the organic HFFRs would be found primarily in soils, sediments and dust and to a lesser extent in water and air. Controlled air emission experiments showed that all organic HFFRs emitted from polymers at elevated temperature but not at lower temperatures. Leaching experiments showed that both HFFRs and BFRs can leach to water. For some polymers no differences in leaching behaviour were found between BFRs and HFFRs, but some HFFR systems had higher leaching properties than polymeric based BFRs. The type of polymer is the main parameter determining the leaching behaviour. Analysis of organic HFFRs in dust from microenvironments and environmental samples showed highest concentrations on and around electronic equipment, in sediment and sewage sludge.

The environmental and human risk assessments showed that the predicted environmental and human exposure concentrations were below the toxicity thresholds for the selected HFFRs. However, the lower risk of HFFRs compared to BFRs is mainly due to the lower hazards of the HFFRs, and not due to a lower exposure. Reducing the leaching of HFFRs from polymer materials is a next challenge for the development of new FRs. The comparative life cycle assessment (LCA) of BFR vs HFFRs, using a laptop as case study showed that the waste phase was the most relevant. Especially, the formation of brominated dioxins out of BFRs during improper electronics waste treatment had a strong negative impact on the LCA-scores. Overall the LCA performance of the HFFR scenario was better than for the BFR scenario. The same life cycles were also evaluated on social criteria using a Social Life Cycle Assessment. Several hotspots are found in the raw material mining phase. In conclusion, ENFIRO showed that viable alternative flame retardants are available. Some HFFRs showed less risk for the environment and human health, and show similar fire performance and technical application capabilities as BFRs.

Project Context and Objectives:

ENFIRO follows a prototypical case study approach, in which the alternative FRs are evaluated regarding their flame retardant properties, their influence on the function of products once incorporated, and their environmental and toxicological properties. The main objectives are:
- To deliver a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment of the alternative FRs.
- To recommend certain flame retardant/product combinations for future study based on risk and impact assessment studies.

ENFIRO evaluated viable substitution options for a number of BFRs (decaBDE, TBBP-A and brominated polystyrene). There are several non-brominated FRs existing on the market. However, there is limited information available about their environmental and toxicological impact. Furthermore, the alternatives should not be applied before tests have shown that they do not adversely affect the quality of consumer products.

ENFIRO approach

ENFIRO follows a practical approach in which HFFRs are evaluated and compared to BFRs regarding their flame retardant properties, their influence on the function of products once incorporated, and their environmental and toxicological properties. This is achieved by performing screening and case studies, which will gather a comprehensive set of information on environmental behaviour and toxicological impact, as well as an assessment of the performance of the FR in a specific application. The case studies will give recommendations for industrial and governmental stakeholders for the replacement of BFRs and viable alternative FRs.

The ENFIRO approach developed follows a chemical substitution cycle anchored in four major elements. In the first element the alternative HFFRs are prioritized and the most viable alternatives are selected. These flame retardants were studied in five applications - printed circuit boards (PCBs), electronic components, injection moulded products, textile coatings and intumescent paint. The second major element focussed on the technical performance (fire and application), hazard and exposure assessment of the selected HFFRs. Finally, the collected information was analysed in a comparative hazard and risk assessments (third element), and in combination with information on costing and socio-economics of the HFFR/products the outcome was digested in impact assessment studies using life-cycle assessments (LCA) (fourth element). This finally resulted in a recommendation of certain HFFR/product combinations. ENFIRO used a unique approach to assess the data at three different levels: the chemical (flame retardant), material and the product.

The project followed a tiered approach, starting in the first tier with a prioritization and selection of alternative FRs taking into account the viability of production, application, flammability, hazard, and exposure of the FRs. This generated a list of viable alternatives and identified knowledge gaps. To fill some of the data gaps screening studies of the selected FRs were performed. The screening studies focused on relative rapid hazard characterization tests, exposure assessment modeling and fire performance tests.

Based on the evaluation of the screening results and literature information a further selection of viable FRs was narrowed down to be able to carry out in-depth studies on a selection (Tier 2). These studies covered chronic toxicity tests, neurotoxicity, battery of in vitro tests, persistency, and monitoring of the alternative FRs in the outdoor and indoor environments. In parallel, elaborated fire performance (realistic fire smoldering and flaming incidents) tests and technical assessments of the FRs in various applications were compared with traditional BFR systems.

The hazard and exposure results were integrated in a risk assessment to investigate the possible risk of alternative FRs for humans and the environment. The outcome of that assessment, together with socio-economic information, was used in life cycle assessments to quantify the analysis of the environmental, economical and social impacts and compare the impacts of the different substitution options with each other. Finally, a list of viable FR/product combinations was provided.

In conclusion, ENFIRO used the full cycle of the chemical alternative chain and developed a novel three level assessment approach based on the

flame retardant, material, and product, by the comparison of the alternative FRs with the BFRs:
i) Flame retardant: hazard characterization, exposure and risk assessment
ii) Material: fire performance and application studies
iii) Product: impact assessment (life cycle assessment (LCA), market study, social life cycle assessment

ENFIRO had the following objectives:
1. Collect information on the availability of alternative FRs, their characteristics in relation to fire safety regulations, environmental behaviour, possible toxic effects, economic aspects, compatibility with polymer production, and impact on the function and reliability of end products.
2. Select substitution options for specific BFRs based on this pre-study and prioritize FRs for further study in a small number of case studies.
3. Technical assessment studies on application requirements regarding production properties and application functions.
4. Technical assessment on five alternative FR/product combinations; printed circuit boards, electronic components, injection moulded products, textile coatings and intumesent paints.
5. Determine the toxicological effects and environmental behaviour of the selected FRs.
6. Determine the technical qualities of the FRs and their behaviour and possible effects when incorporated in products
7. Perform a risk assessment based on all environmental and human hazard information from the toxicological and environmental, exposure, fate and modelling studies of the alternative FRs.
8. Determine and predict the social and economic effects of replacing the specific BFRs by the selected alternative FRs.
9. Perform life-cycle assessment (LCA) analysis to advice on the safe production and use of one or more of the alternative FRs studied.
10. Recommend certain FR/product combinations for future study based on LCA, LCC and risk assessment studies.
11. Disseminate the knowledge to stakeholders (producers, formulators, users), environmental organisations and policy representatives.

These objectives are the backbone of the project, and ENFIRO is organised in 9 work packages. The scientific WPs focus on the prioritization and selection of alternative FRs (WP2), the hazard characterization (WP3), exposure, fate and modeling (WP4), flame retardant capability studies (WP5), application studies (WP6), risk assessment (WP7), and impact assessment (WP8). WP 1 is dedicated to management and WP9 to dissemination.

A stakeholder forum (ESF) was established consisting of 17 members, including FR producers, formulators, NGOs, and a waste recycler (WP9). These stakeholders were regularly informed on project progress, and they provided valuable input from the field for all work packages.

Being the most important area of use of BFRs, electrical and electronic equipment (E&E) was one of the areas that are studied. The focus was on printed circuit boards and electronic components since they dominate the use of BFRs. In addition, injection moulded products, textile coating, and intumescent paints are addressed. The work started with a search of scientific literature as well as industrial reports on non-halogenated FRs (WP2). Information was collected on the availability of the FRs, their characteristics in relation to fire safety regulations, and in relation to their environmental behaviour and possible toxic effects. In addition, economic aspects related to alternative FRs were collected as well as information on compatibility with polymer production and impact on the function and reliability of end products. A prioritisation and selection of HFFRs was carried out after which the most viable FR/product combinations were further studied in screening studies (WPs 3-6). The screening studies were performed to fill some of the data gaps and to further select the most viable FRs to study in more detail (case studies). In the screening phase WPs 3 and 4 focused on the hazard characterisation, exposure and fate. WP5 focused on the FRs themselves, their emissions and fire retardancy, whereas WP6 provided information on the technical suitability of the FRs when used as such or as mixtures in specific applications (PCBs, moulded products, coatings, etc.). The information of the WPs 3-6 was assessed in WP7 – Risk assessment. All information was digested in a full life-cycle assessment in WP8, including an analysis of costs and socio-economic aspects. This finally resulted in a recommendation of certain FR/product combinations.

Project Results:

Prioritization and selection (WP2)
As the first phase of ENFIRO a prioritization and selection of alternative flame retardants was carried out. The main objective was to select and prioritize a range of non-brominated FRs that are viable alternatives to specific commercial BFRs on the market through literature and other reliable scientific sources based on how they affect the material's characteristics of the polymers that are flame retarded. Such characteristics included compatibility, electrical properties, and various ageing properties and was based on already available data on toxicity, exposure risks and environmental fate. This results in the assessment of viability criteria for specific FR applications that consist of flame retarded marketable polymers.

At the start of the project an overview of existing data on alternative FRs was made. One of the most important findings was that large data gaps and contradicting information still exists for alternative FRs, which also showed the need for ENFIRO. The combination of polymers with HFFR that were selected and considered to be commercially viable alternatives to specific commercial BFRs (TBBP-A, decaBDE, brominated polystyrene (BPS)). Selection criteria were that the FRs should be halogen-free, commercially available, and some information on the compatibility behaviour in polymer materials should be available. The list of HFFRs was further updated after consultation of the ENFIRO Stakeholder Forum (ESF) consisting of FR producers, formulators, end-users, environmental organisations, and others, and after initial screening tests. The list contains phosphorus FRs, inorganic tin-based FRs, nanoclays and combination of nanoclays with phosphinates. Based on the selected HFFRs a literature survey of fire behaviour including general characteristics of flame retardant chemicals, thermal degradation properties of the selected flame retardants, and a literature survey on the flammability and toxicity of the selected prototype base polymers and FRs was made. Literature data on the flame retardancy of selected systems using HFFRs with comparison to BFRs were also presented.

One of the objectives of ENFIRO was to perform an ecotoxicological and health hazard characterisation of the selected HFFRs. Literature data on acute toxicity and ecotoxicity tests of the selected HFFRs was collected. The ecotoxicity data showed that a lack of data or contradictory data exists for HFFRs making it difficult to assess the hazard of the alternative flame retardants and points to the need for reliable experimental data. This was further confirmed for data on specific molecular and cellular end points with emphasis on geno-, endocrine-, and neuro-toxicity. Some of these toxicity end points were studied in ENFIRO to fill the data gaps on Ah-receptor, mutagenicity, thyroid hormone binding, endocrine disruption, and neurotoxicity.

Available data for physical-chemical properties for the selected non-halogenated flame retardants was reviewed. The physical-chemical data was used to assess environmental fate and behaviour. It was found that estimation tools for organic substances exist but no reliable estimation tools are available for inorganic substances, to our knowledge, which means that the assessment of environmental occurrence of inorganic FRs was a major challenge. A review of the physical-chemical properties and the persistence, bioaccumulation and (eco)toxicity data for the alternative flame retardants was published (Waaijers et al 2013).

Information on the economic aspects of the prioritized HFFRs was collected as well. The focus was to give an overview about the FR market and about the related industry which is highly influenced by recent trends. Pinpointed were those economic data that were collected through the ENFIRO project with the help of the project partners and the ESF members, in order to complete the Life Cycle Costing.

A schematic presentation of the most viable flame retardants was made per technical area, application, polymer, BFR and alternative FR, but a ranking was not possible as too many data gaps existed.

Fire performance (WP 5)
The objective of the fire performance studies was to quantify the severity of the toxicity, smoke and heat flux of alternative HFFRs against BFRs in fire (smoldering and flaming) incidents.

The measurements selected to assess the flammability and toxicity of BFR substitutes are: tendency to dripping, solid degradation in mg scale, gaseous products in mg scale, cone calorimeter in standard atmosphere, special calorimeter in controlled atmosphere, species production in modified ISO TS19700 tube furnace. These properties have led to the assessment of alternative FRs and comparison with BFRs by quantitatively assessing the following parameters: tendency to dripping, (low) heat release rate, late ignition, strength of char, (low) smoke yield and production rate, (low) toxicity and corrosion. Based on these properties the global effects of these materials in fire have been addressed by quantifying their behaviour in standard tests (UL94, LOI), their behaviour in large fires, impact on life and property safety and damage.

A large number of FR/polymer materials were compounded based on the selected HFFRs. The selection of BFRs is done according to their dominance in the market for each of the base polymers selected i.e. PBT/GF, PC/ABS, epoxy resin, PA66/GF, EVA and PPE/HIPS. Alternative FRs included phosphorus FRs (e.g. metal phosphinates), inorganic tin-based FRs, nanoclays and combination of nanoclays with phosphinates. Details of formulations were compiled and used to select the prototype base polymers and FR for compounding. Polymer compounding and UL94 characterisation has been done utilising twin-screw extrusion and injection moulding (for ABS formulations) and high-shear mixers / curing in RTV silicone moulds (for epoxies). The FRs involved in this study includes BFRs (benchmark), phosphorus FRs (phosphinates), inorganic tin-based FRs, nanoclays and combination of nanoclays with phosphinates. A large number of FR/polymer combinations have been compounded (PA6.6, PBT, PPE/HIPS, PC/ABS, epoxy resin encapsulates, EVA), for the FR/polymer combinations. Polymer formulations have been optimized using UL94 test as regulated for industrial applications. A thickness of 3.2mm for UL94 tests was first chosen but then replaced by 0.8mm to address more demanding industrial applications. Large batches of compounded materials (pellets and moulded plates) were prepared for the fire performance, application, leaching, and air emission studies.

Intumescent coatings have also been investigated for flammability and toxicity by applying it onto one of the compounded polymers, HIPS. The coatings were either waterborne (better when possible) or solvent-borne coatings, white (or anyway opaque layers) or transparent thin films. In parallel, significant issues of weathering (e.g. according to ISO EN ISO 4892-3) and adhesion were addressed.

Before fire performance tests were performed on the compounded materials an overview on previous data on the flammability and toxicity of BFRs and alternative FRs was made. Information on the experimental apparatus was described and major previous results for PA66, PPE/HIPS, PC/ABS and PBT were presented and summarized.

Assessment of flammability and toxicity
The flammability and toxicity of thermoplastic retardant polymers and thermoset materials were assessed. In addition, the intumescent coating prepared by one of the partners were tested for flammability and application (weathering, adhesion) properties. All formulations were investigated in TGA/FTIR/DSC/ATR and cone calorimeter.

Based on these results and analysis, a method was developed to characterize both the UL94 and the fire behaviour of materials using parameters related to fire growth and smoke production deduced from data obtained from cone calorimeter experiments. This method is outlined for PBT +GF and similar figures for all materials were made.

The use of nanoclay (nano-MMT) combined with Alpi (PG3B) reduces the characteristic fire growth by 60% in comparison to the formulation containing only Alpi (PG4A). The nano-MMT formulation also provides a characteristic fire spread growth in the same order of magnitude as the halogenated formulation (brominated polystyrene, PG2), but also yields around 15% lower smoke. It is noted that all formulations have smoke yield higher than the desirable 0.05g/g. The efficiency of combustion provides useful information to assess the production of toxic species. Thus, it is considered that the formulation with the BFR (PG2), with an efficiency of combustion about 0.45, produced much more unburned species than the HFFR formulations (PG3B and PG4A) having an efficiency of 0.85. In conclusion, although the Alpi formulation (PG4A) could be a possible alternative to the brominated formulation (PG2), the formulation of Alpi with nanoclay (PG3B) is the best alternative (even superior to brominated formulation PG2) regarding the characteristic fire spread growth and smoke yield.

Severity of the toxicity, smoke and heat flux of BFRs against alternative FRs in realistic fire (smoldering and flaming) incidents
Major results are outlined in the following summary with the focus on PBT with glass fibre (GF) as an example of the results. In addition, a discussion of the tube furnace results is also included in this summary.

To illustrate the severity of toxicity and smoke of BFRs against alternative FRs an example for PBT with glass fibre will be given. A simple method was developed for characterising the fire performance and toxicity of polymers using three parameters. One parameter is related to fire spread and growth (simulating UL-94 and the FIGRA of SBI), the second parameter is the smoke yield (simulating the SMOGRA of SBI) and the third parameter is the inefficiency of combustion (related to unburned hydrocarbon compounds and possibly, their toxicity). The developed methodology was used to compare brominated and halogen free fire retardants in PBT with glass fibres (GF) and confirmed that studied environmentally friendly alternatives to brominated fire retardants offer comparable fire performance with lower toxicity. Note that even though the parameters are extracted for over - ventilated conditions, they are expected to have the same relative significance for under -ventilated conditions based on under ventilated experiments in the controlled atmosphere flammability apparatus, the Tube Furnace and in corridors. The developed methodology and proposed parameters are applicable for charring, non charring and intumescent materials and has been applied to all the fire retarded polymers used in the ENFIRO program. Another possibly important parameter is how much of the initial material is left behind as residue. This is not significant for fire spread and fire growth but it can provide the amount of total fuel load in a fully developed fire, not relevant for the present applications. Finally, we also propose and show that the heat release rate for thermally thin materials can be characterized by using the measurements in TGA where the maximum mass loss rate in nitrogen (appropriately normalized by the initial mass and heating rate) is multiplied by the heat of combustion measured in the cone calorimeter.

The measurements were carried out in cone calorimeter in accordance with ISO 5660. In order to minimise the conduction heat loss to insulation and to facilitate the prediction of these tests using a numerical model, a sample holder was constructed as reported. Additional measurements were performed in Mettler Toledo TGA under nitrogen to determine properties for thermally thin conditions.

In conclusion, we have developed both a detailed numerical method using intrinsic flammability properties as well as a simple method for characterizing the fire performance and fire toxicity of polymers using three parameters based on measurements in the cone calorimeter at four different heat fluxes supported by thermal and gas analysis in FTIR from TGA and Tube Furnace.

Intumescent coating

Pure HIPS are difficult to flame retard to V(0) without halogen. A novel intumescent coating has been developed by one of the partners and was investigated for flammability and toxicity by applying it to HIPS. The materials was either waterborne (better when possible) or solvent-borne coatings, white (or anyway opaque layers) or transparent thin films. In parallel, significant issues of weathering (e.g according to ISO EN ISO 4892-3) and adhesion were addressed. The developed intumescent coating system have proven efficient and makes HIPS fulfill V(0) and fulfill the glow wire test. This could have significant commercial potential.

General conclusions for toxicity based on results from the tube furnace

A simple method was developed for characterising the toxicity of polymers using the effective heat of combustion. This parameter assessed the inefficiency of combustion by comparing unburned hydrocarbon compounds and possibly, their toxicity. Namely, we compared the actual heat of combustion (obtained from cone calorimeter) divided by the theoretical heat of combustion and the results was subtracted from one. The developed methodology was used to compare results from Cone calorimeter with the results from the tube furnace. Due to the complexity of the analysis, only PG (PBT + GF) formulations were studied in tube furnace in great detail. All major permanent gases evolved by means of FTIR coupled to the tube furnace were identified. We have shown the existence of highly toxic hydrogen bromine evolved from formulations containing BFRs. The toxicity parameter was compared with concentrations of carbon monoxide and methane between various formulations. It was shown that (especially for methane) the findings based on the inefficiency of combustion in Cone calorimeter were valid for overventilated conditions but were not so obvious during underventilated conditions and pyrolysis under nitrogen. This will require further studies.

Moreover, the comparison of carbon monoxide production from different formulations during overventilated conditions showed that the addition of fire retardants (BFR or HFFR) increases the production of CO (total and yield). For the other two conditions (i.e., under-ventilated and paralysis in N2), although it seems that the FRs increases the transient CO concentration, there is only small difference between formulations with different flame retardants in terms of total CO production and yield.

Summary fire performance

There is no single drop in replacement for BFRs by HFFRs available for the polymer systems. We have investigated primarily thermoplastics, but also thermosets (epoxy) and elastomers (EVA). Important input was received from the Stakeholder forum on the formulations. The used formulations were optimized only for UL94 performance and not for other properties.

A simple method was developed for characterizing the fire performance and fire toxicity of polymers and confirmed that environmentally friendly alternatives to brominated fire retardants offer comparable fire performance with lower impact on environment. We have been able to match the performance of BFRs as regards regulatory tests, e.g. UL94 for electronics, and LOI for e.g. cable materials. HFFR systems in addition have clear benefits as demonstrated in cone calorimeter tests, e.g. less visible smoke, in some cases lower peak heat release rates with halogen free products, and less toxic components in smoke. In some cases high filler loadings have to be used for HFFRs to fulfil V(0) which affects mechanical properties, but these were not optimized in ENFIRO. In other cases HFFRs are equally or more efficient (e.g. PA66 glass fibre) than BFRs. A novel intumescent coating for HIPS was developed that fulfilled the UL94 and industrial fire performance tests.

Applications studies (WP6)

The overall objective was to perform technical assessments of the use of alternative FRs in various applications by comparison with traditional FR systems. The applications were printed circuit boards, electronic components, injection moulded products, textile coatings, and intumescent paint.

Printed Circuit Boards (PCBs)

The objectives were to identify and assess the reliability risks with selected HFFRs for use in printed circuit boards using a physic-of-failure approach. That is, possible failure mechanisms caused by the HFFRs were identified based on how the products were manufactured and used for some typical applications.

The requirements put on laminates used for production of printed circuit boards (PCBs) are in many aspects much more severe than requirements put on other plastic materials. Important properties that may be affected by the flame retardant used include electrical properties, thermal stability, chemical stability, mechanical properties and adsorption of humidity. Consequently, substitution of BFRs by HFFRs in PCBs may affect the reliability of the end-products in a number of ways. How the reliability is affected is a combination of intrinsic material properties and the impact of manufacturing processes on the properties of the end product. Therefore, merely testing the material properties of a laminate with a HFFR will not be enough to prove that it can be used without jeopardizing the reliability of electronic products. Adequate verification that the reliability is not jeopardized requires that PCBs are produced using ordinary production processes and that they pass through soldering processes before reliability testing is performed. Therefore, adequate reliability assessments can only be done using commercially available laminates for production of PCBs. Furthermore, it is crucial to understand which failure mechanisms that may cause failures and the physics-of-failure for these mechanisms.

The main failure mechanisms in PCBs identified that may be affected by the flame retardant used are:
- Cracking of metal platings in plated through holes (PTH barrels) and internal interconnect failures between PTH barrels and conductors in inner layers
- Fracturing of the resin and adhesion failures between the resin and other materials
- Current leakage due to formation of conductive anodic filaments
- Current leakage due to decreased surface insulation resistance and electrochemical migration

One of the objectives with ENFIRO was to evaluate the viability of some specific HFFRs in various products. To fulfil this objective, it was necessary to get information from the laminate manufactures of the HFFRs used in their laminates. However, the type of HFFR used in commercially available laminates is in most cases considered proprietary information and it was only possible to get information of the HFFR used from one laminate producer. This laminate contained a mixture of DOPO, ATH, boehmite and phosphazene. In addition to the laminates from this laminate producer, laminates with HFFRs from three other laminate manufacturers were also evaluated. A laminate with TBBPA was used as reference. Four test methods were chosen for the technical assessment of the laminates with HFFRs. These were:
- Interconnect stress test (IST) for testing the impact on the reliability of PTH barrels and interconnects between PTH barrels and inner layers.
- DELAM test for testing the impact on fracturing in the resin and adhesion failures between the resin and other materials
- CAF test for testing the impact on formation of Conductive Anodic Filament (CAF)
- ECM test for testing the impact on Surface Insulation Resistance (SIR) and Electrochemical Migration (ECM)

The results from the reliability assessments of the laminates containing HFFRs were generally as good as for the reference laminate containing TBBPA or better. The laminates with HFFRs showed especially good resistance against formation of CAF, the failure mechanism that is perhaps most likely to be affected by the flame retardant used.

Electronic Components
The objectives were to identify and assess the reliability risks with selected HFFRs for use in encapsulated electronic components using a physic-of-failure approach. A complicating factor that affected the work on electronic components was that the aim of ENFIRO was to study commercially available HFFR alternatives to brominated polymer systems for IC encapsulation. It turned out after the initial search that the brominated systems had been replaced with highly cross linked epoxy systems without flame retardants. Due to reliability concerns with halogen-free flame retardants, especially phosphorus-based, component manufacturers are very reluctant to use these in encapsulation materials.

Thus, there was really no substitution case to study. The contents of this deliverable therefore were changed from the original plan and additionally more effort was directed to tasks on printed circuit boards.

Injection Moulded Products

Within the ENFIRO project alternatives to traditional brominated flame retarding systems for thermoplastics were developed and evaluated. Some of these alternate systems call for quite substantial amounts of additives to the polymer matrix to be effective. Such large contents, up to 30 percent per weight, will affect the properties of the products as well as the processability of the material. A total of 13 UL-94 optimised (V0 pass) products of alternative flame retarding systems have been compared to their unaltered base plastics concerning their mechanical properties. The tensile and impact behaviour as well as processability of the injected moulded materials has been tested.

The tensile and impact properties are roughly similar for brominated and halogen-free flame retardant formulations. When flame retardants are added to a glass fibre reinforced plastic the tensile modulus decreases. When flame retardants are added to an unfilled plastic the tensile modulus increases. The loss in tensile strength is typically 25-50% when flame retardants are added to the formulations. Exceptions from this are PC/ABS (TBBPA Sb_2O_3 PTFE) and PBT GF (Alpi Nano-MMT), which both show approximately 65% decrease in tensile strength.

For PPE/HIPS (decaBDE:ATO) and PA66 (melamine cyanurate) the tensile strength is unaffected by the flame retardants. Strain at break is affected the most for PC/ABS, which show a decrease of 92-98% while the reduction for glass fibre reinforced PA is 5-15% only. Impact resistance is affected the most for PC/ABS where it is reduced by more than 95%, glass fibre reinforced PA is least affected, down 20-40%.

All formulations have similar or better flowability (similar or lower viscosity) compared to the reference materials. Some flame retardants seem to act as lubricants/plasticizers resulting in higher flowability, i.e. lower viscosity, for example RDP and to some extent BPS.

Textile Coatings

The objective was to evaluate the HFFRs for textile coating applications where currently BFR are used. The efficiency of flame retardants is dependent on the textile polymer systems. Therefore, two different fibre types were investigated with two different coating polymers frequently used on the market. Polyamide (PA) weave and polyethylene terephtalate (PET) weave (also referred to as polyester) are used as filament plain weaves. The coating polymers were water based emulsion systems without cross linkers. The polymers in the two emulsions are acrylic respectively polyurethane. A reference was also made for comparing the studied systems with best practise. This best practise was composed with decaBDE/antimony trioxide (ATO) system. Dispersions with alternative FRs (APP, MPP, PER), coating of substrates, and fire testing of the coatings were performed. Test vehicles were tested for fire retardant behaviour, peel adhesion strength between weave and coating, tensile properties of pure coating and friction. Representative textiles were used in this study and test vehicles were fire tested according to appropriate fire standards, required for the specific use. Dispersions of acrylic and polyurethanes were used for coatings on PET and PA weave.

Results showed that for suitable flame retardancy for PUR on PET weave 30% of MPP is needed. The combination with APP and PER is not more effective. A formulation of three HFFRs (MPP+APP+PER) gives improved extinguishing compared to decaBDE/ATO. This HFFR combination is suitable for PUR on PA weave. The minimum amount of HFFR needed is 20% in solid coating, and the effectiveness is similar to decaBDE.ATO. Acrylics on PET weave can be flame proofed with 30% APP, but the combination with MPP and PER is not more effective. In this case also the combination of MPP+APP+PER gives similar extinguishing compared to decaBDE/ATO systems. For acrylics on PA weave none of the tested HFFRs seem to be effective. Tensile tests were performed on the coating according to modified SS-EN ISO 13934-1:1999. Bromine containing formulations show high tensile strength and maintained or improved elongation at break for both PUR and acrylic. The HFFR formulations are good for acrylic but poor elongation at break for PUR. The test also showed that the bromine formulations make a more flexible coating which is an advantage in many cases. The peel tests showed that optimised HFFR formulations (MPP+APP+PER) with PUR on PET weave had a 57% drop compared to decaBDE/ATO systems. The PUR on PA weave system performed better with the HFFRs and showed only a 17% drop of peeling compared to the decaBDE/ATO. Interestingly, the acrylic coating on PET and PA weave gave no adhesion with the decaBDE/ATO system but the MPP, APP, PER system gave adhesion.

Summary application performance

For textiles, the developed HFFR formulations have slightly lower coefficient of friction than the bromine containing formulations both for polyurethanes and for acrylics. In many applications reduced friction is a positive factor at use. The combination with MPP+APP+PER is good for PUR on PA weave, minimum is 20% in solid coating. Tensile test mainly shows a drop in elongation at break compared to decaBDE/ATO. For all flame retardant plastic formulations (both HFFR and BFR) equal or better performance on processability for injected moulding products was found. The tensile and impact properties are roughly similar for brominated and halogen-free flame retardant formulations. The results of HFFRs in the printed circuit boards showed as good or better results compared to the BFRs.

Hazard characterisation (WP3)

The objective of the hazard characterisation was to perform ecotoxicological studies of selected HFFRs using water and sediment toxicity tests and to perform a health hazard characterisation of the HFFRs on a molecular and cellular level, with emphasis on geno-, endocrine-, and neuro-toxicity using in vitro studies and a limited number of ex vivo validation studies.

It was found that a great number of the selected HFFRs have a very poor solubility in water and in organic solvents. As a result considerable efforts have been made to test different methods to dissolve the FRs in water or organic solvents. For these FRs so called water-accommodated fractions were prepared resulting in maximum water soluble concentration that was used for the toxicity tests.

Acute toxicity to Daphnia magna

Several compounds were not acutely toxic, five of them (MPP, Mg(OH)2, RDP, ZHS and ZS) showing no effect at their water solubility (Sw) (EC50 greater than Sw) and two of them (ATH and BDP) showing 25-26% effect at Sw. For the FRs that were toxic below their water solubility, clear dose-

response relationships were observed. Alpi, APP and DOPO showed a low acute toxicity. ATO was classified as moderate toxic. TPP and TBBP-A exerted a high toxicity within 48 hours to Daphnia magna (less than1 mg/L). All concentrations, except of TBBPA, are measured with either ICP-AES or HPLC-MS/MS. TBBPA is tested nominally. The classification is based on the REACH criteria (European Union, 2006; European Union, 2008).
Some specific remarks must be added with respect to the results. Firstly, the nanoclay Cloisite was tested at a nominal concentration of 100 mg L-1, which caused 100% immobility. Since the exact chemical composition of this material is unknown, it was not possible to determine the actual exposure concentration, thereby preventing classification of this HFFR. For seven compounds ATH, BDP, RDP, MPP, MgOH2, ZS, and ZHS the EC50 is higher than their water solubility and therefore could not be established.

For compounds that have an EC50 above their water solubility, it is important to realise that effects may still be expected if effect concentrations (e.g. lowest observed effect concentration) of the compound are close to the water solubility. This is of particular relevance if such compounds have a low water solubility, such as ATH.

Chronic toxicity to Daphnia magna and Lumbriculus variegatus
Chronic toxicity tests were performed on Daphnia magna for water soluble FRs DOPO and Alpi (21 days), and on the benthic invertebrate Lumbriculus variegatus for RDP which is a hydrophobic compound associated to the sediment (28 days).

The most sensitive chronic endpoint of D. magna for Alpi was reproduction (cumulative reproductive output) with an EC50 of 2.3 mg L-1(95% CL: 1.8-2.9). The EC50 value for survival after 21 days is also classified as moderate toxicity indicating that toxicity increased with increasing exposure time, with an acute to chronic ratio (ACR) of 6.8. Chronic testing is more environmentally relevant as organisms are more likely to be exposed for longer periods of time in any ecosystem. Studying long term exposure in order to accurately assess toxicity is therefore considered crucial.

For DOPO the daphnids survived the concentration range tested. The EC50 for cumulative reproductive output and for population growth rate (r) was higher than 10 mg L-1 and therefore classified as low

The benthic toxicity test with L. variegatus showed alow EC50 value greater than 100mg kg-1 dry weight sediment. Currently, to our knowledge no classification system for sediment toxicity exists. As it is unlikely that concentrations as high as 100 mg kg-1 sediment occur in the environment, the toxicity of RDP is estimated to be low.

Cytotoxicity
Cytotoxicity of organic and inorganic HFFRs was studied in rat liver cells using MTT and LDH leakage assays. Cells were exposed to 10 µM of the organic FRs and compounds with low solubility were tested at the maximum solubility in water. The results showed that no effects were observed for the FRs on rat liver cell viability. Cell respiration assays were performed to assess effects of FRs on bacterial viability and cellular respiration processes. The results indicate that at high concentrations (100 µM) TBBPA, DOPO and to a lesser extent TPP, RDP and BDP induce a limited reduction in cell respiration. At up to 10 µM, none

of the organic FRs tested had any effect on cell respiration, with the exception of TBBPA that already inhibited cell respiration at 1 µM.

Endocrine disruption and mutagenicity

As some brominated FRs are powerful disruptors of the thyroid hormone axis, the organic HFFRs were tested for their potency to displace T4 from the T4 carrier protein transthyretin (TTR). Of the BFRs that were able to displace T4, TBBPA being more potent (IC50 = 26 nM) than DecaBDE (IC50 greater than 25 µM), but all organic HFFRs had no effect.

In vitro bioassay tests for estrogenic and androgenic activity showed that TPP, RDP and BDP are weakly estrogenic, and RDP is a weak anti-androgenic compound. It was found that the by-products (e.g. TPP) in the technical products of RDP and BDP were not responsible for the estrogenic and anti-androgenic activity but that the pure substance of RDP and BDP were responsible. A two-generation reproduction toxicity with rats, available at the ECHA database, showed no reproduction effects for RDP, and RDP could be classified as not toxic to reproduction.

The mutagenic test (AMES II) showed that none of the HFFRs showed mutagenicity. All HFFRs showed also no dioxin-like toxicity.

Neurotoxicity

For risk assessment purposes, chemicals are often classified according to the different categories of potential harm that they may cause. An example of a widely used CLP classification classify existing data on specific endpoints in relation to potential risks during their use by the European Union (European Union, 2006; European Union, 2008), which is based on LD50 (half maximal lethal dose) or EC50 (half maximal effective concentration) values. However, as complete concentration-response curves are often absent for in vitro tests used in ENFIRO, e.g. because of low solubility of the test compounds of many HFFRs, a rank ordering of the tested HFFRs based on the lowest observed effect concentration (LOEC, potency) and maximal effect size per tested endpoint was made. These combined results were used to make an overall assessment of the in vitro neurotoxic potencies of the selected HFFRs.

In the first phase hazard characterization tests, cytotoxicity of FRs was assessed in pheochromocytoma (PC12) and B35 neuroblastoma cells using a combined Alamar Blue and Neutral Red test. Most HFFRs did not induce overt cytotoxicity, though ZHS and ZS evoked moderate cytotoxicity at low concentrations comparable to the TBBPA-induced cytotoxicity. These results thus indicate that the observed acute flame retardant-induced neurotoxic effects in the second phase tests are in general not confounded by acute cytotoxicity. Next, effects of the selected compounds on the production of reactive oxygen species (ROS) was determined. Oxidative stress occurs when ROS levels in the cell increase, potentially resulting in significant damage to cell structures. In line with the observed cytotoxic effects, TBBPA and ZS showed a significant increase in ROS production.

In the second phase of the hazard characterisation, the underlying mechanisms were studied by investigating changes in the intracellular calcium concentration ([Ca2+]i) using single cell fluorescent microscopy as a prolonged increase in [Ca2+]i is an important trigger for apoptosis. TBBPA, ATH, MMT, ZHS and ZS were able to disturb basal Ca2+ homeostasis. Changes in [Ca2+]i also play an essential role in intra- and intercellular signaling pathways, including neurotransmission. Therefore, the effects of BFRs and HFFRs on depolarization-evoked increases in [Ca2+]i in PC12 cells were also determined. This proved to be a sensitive endpoint since 10 of 16 tested compounds were able to inhibit depolarization-evoked calcium influx.

In another step in the in vitro screening studies, effects of the selected compounds on the function of human a4í2 nicotinic acetylcholine (nACh) receptors, expressed in Xenopus oocytes, were measured using the two-electrode voltage-clamp technique. Although the results demonstrate that none of the tested flame retardants acts as agonist of the human nACh receptor, TBBPA, TPP, ATH and nano-MMT were able to inhibit the ACh-evoked current.

The inhibition of acetylcholine esterase (AChE) activity for the BFRs and organic HFFRs was also studied showing that TBBPA had a 20% inhibition of AChE activity at high concentration. No AChE inhibition was found for TPP, BPS, DOPO (MIG and S&S) and decaBDE at the highest concentration. RDP and BDP showed AChE activity, and showed different inhibition kinetics compared to the reference compound dichlorovos. Additional work showed that the observed inhibition was not competitive for RDP and BDP. The observed inhibition of AChE in vitro is confirmed by two non-public in vivo studies found in the ECHA database that reported RDP effects on cholinesterase. However, no effects were observed in male rats.

As a final step in the health hazard characterization, the neurodevelopmental effects of TBBPA as positive control, Alpi and ZS were investigated in the ex vivo validation experiments with mice. Long-term potentiation (LTP), which requires proper function of both pre- and postsynaptic mechanisms, was measured using extracellular field recordings in hippocampal slices from neonatally-exposed (on post natal day 10) mice. The preliminary results indicate that synaptic function and plasticity are not affected to a relevant extent by a single oral exposure at PND10 to TBBPA, Alpi or ZS. This suggests that these compounds are not neurotoxic. However, these findings need to be treated with caution as protein analysis and determination of internal dose are ongoing and the exposure paradigm is not realistic for human exposure.

Summary hazard characterisation
Based on literature information, databases, and the ENFIRO hazard assessment seven of the selected HFFRs showed to have less issues of toxicity concern (APP, Alpi, ATH, MPP, DOPO, ZS, ZHS), with the remark that Alpi showed moderate chronic aquatic toxicity, than some BFRs. Two HFFRs (RDP and BDP) are of some concern as these show varying results between aquatic toxicity studies in the literature (moderate-low and high-low toxicity, respectively). This variation may be due to the amount of TPP present in the technical products; TPP is a by-product and known to be very toxic for aquatic organims (classified as H400, H410 (M = 1) by nearly all notifiers). In addition, BDP is a persistent compound. Another compound that is of concern and needs further study is the nanoclay (nano-MMT) that showed a strong in vitro neurotoxicity effect. Also the fate (leaching) of nanoclay from polymers needs further study.

Exposure, fate and modelling (WP4)
The major objectives were i) to collect physical-chemical property information for the selected HFFRs, ii) perform modelling of these to produce initial and updated environmental exposure assessments, iii) identify the most important knowledge gaps, carry out experiments to fill these gaps (determine water solubilities of the organic HFFRs, study

leaching of HFFRs from polymers to water and emissions from polymers to air), iv) to perform persistency tests, and v) to collect samples for the field monitoring study and analyse these.

Modelling and exposure assessments
The literature was first mined for information relevant to the sources, physical-chemical properties, degradation rates, environmental occurrence and environmental behaviour of six selected organic HFFRs being considered for the case-study. Gaps in data for key physical-chemical properties and degradation half-lives were estimated using available structure-property relationships. The information for the organic compounds was then synthesized using existing multimedia fate modelling tools to produce an initial environmental exposure assessment. In a next step, physical-chemical properties of the three organic HFFRs included in the case study (DOPO, RDP, BDP) were updated and their environmental fates were reassessed. Two fugacity-based multimedia models were adopted, i.e., the equilibrium criterion (EQC) model (version 2.80.1), TaPL3 model (version 3.00) and Low Resolution Multi-Species (LoResMS; version 1.0) model for the reassessment. Model predictions indicate that the emission mode (environmental media receiving emission) has a large influence on fate and distribution in the environment. Comparison of model results from the previous and updated study suggested that the updated changes in physical-chemical properties (particularly predicted water solubility) largely altered the predicted environmental fate and distribution of two of the three selected organophosphorus FRs, i.e., BDP and DOPO. New evidence suggested that DOPO is a weak acid and ionisable under environmental conditions.

A short review of available modelling tools for inorganic chemicals was discussed. Due to limited information on physical-chemical properties, chemical-specific speciation and geochemical conditions, it is extremely challenging to model these compounds. The expected environmental fates and distributions of the six selected inorganic FRs were evaluated based on current knowledge of inorganic environmental chemistry. It is expected that environmental levels of the selected six inorganic FRs will be highest close to point sources. However, due to their ionic nature and propensity to dissociate, these inorganic FRs are neither expected to be persistent in the environment nor to have high potential for long-range transport in air and water.

Persistency tests
In a first step, a ready biodegradability experiment was performed based on the OECD 301 guideline. An automated respirometer was used to study the mineralisation of Alpi, BDP, DOPO, RDP, MPP, TPP and TBBPA. Full degradation was monitored by measuring CO2 with the respirometer hourly for 28 days. The compounds were added to diluted sewage sludge at concentrations of about 100 mg L-1. None of these compounds fulfilled the ready biodegradability criteria (greater than 60% degradation in 10 days after start of mineralisation) at these concentrations. In the vitality control, activity of the sludge microorganisms was confirmed by rapid mineralisation (ready biodegradability) of glucose. However, toxicity controls revealed toxicity to the microorganisms at 100 mg L-1, as limited CO2 production was observed in these vessels. This should have been the same rapid mineralisation as in the vitality controls. Due to a limitation of the set-up, the flame retardant responsible for the observed toxicity could not be elucidated. Therefore the conclusion of these experiments was that Alpi, BDP, DOPO, RDP, MPP, TPP and TBBPA are

not ready biodegradable or one of them is/they are all toxic at 100 mg L-1 to the microorganisms of the waste water treatment plant.

In a second step, aerobic biodegradation studies were performed for BDP, RDP and DOPO. The experiments were carried out in diluted waste water treatment sludge or mineral medium (blanks) and the parent compounds were monitored over 28 days. High losses to the glass flasks were observed during the experiment for RDP, BDP and DOPO, causing a large drop from the nominal concentration at the first measured time point. RDP showed slight biodegradation, but mostly losses occurred due to adsorption to the sludge and abiotic degradation. Diphenyl phosphate (DPP) was measured solely in the biodegradation samples indicating (slow) biodegradation. BDP does not seem to disappear over time and therefore did not seem to degrade, which is in agreement with the ECHA database which states that BDP is not readily biodegradable. DOPO disappears by adsorption but also seems to degrade abiotically. Based on these results, BDP appeared to be most persistent, whereas RDP and DOPO might be degradable, but more research is needed to study their degradability and breakdown products.

Air emission and leaching to water

The results of the initial assessment identified the need for measurement of chemical release to indoor air from the application (FR-treated plastics or textiles) at elevated temperatures to be expected from electronic equipment in use or in a car sitting in sunlight. Due to widely varying water solubilities for DOPO, RDP and BDP predicted from the modelling studies, it was determined that these should be determined experimentally. There was also a need to measure the leaching of FRs from materials to the outdoor environment (water) as it is difficult to identify and trace back the inorganic FRs in the environment due to the non-specific character of metals (e.g. Al, Zn or Sn can have many different sources).

For air emissions, the flame-retarded polymer to be studied was placed in a glass petri dish that was then placed at the bottom of a metal can. A pre-cleaned polyurethane foam (PUF) disc was suspended in the opening of the can using a collar of aluminium foil and the lid of the can replaced to form an airtight seal. The can was then placed either in a laboratory at room temperature or in a constant-temperature oven at a precise temperature for different lengths of time. At the end of each time period, the cans were removed from the oven and the PUFs were extracted and analysed. In a first step, the flame-retarded plastics were tested at a high temperature (80 oC) to see if there was any emission at all of FRs. After 7 d at 80 oC, measurable amounts of DOPO, RDP and decaBDE were found in the PUFs. The emission rates for the HFFRs and decaBDE were similar, ranging from less than0.5 to 2.0 pg/cm2/d. To simulate a more realistic situation, polymer plates were then tested at 40 oC for 3, 10, 15, 29 and 58 d, and at room temperature (22 oC) for 58 d. No DOPO, RDP or BDP was detected in PUFs after 58 d at 40 oC or 22 oC. However, TBBPA was detected in PUFs in the experiments performed at 40 oC (emission rate of 1.2-2.2 pg/cm2/d) as well as at 22 oC (emission rate of 0.03 pg/cm2/d). Thus, the HFFRs present lower risk for emissions to air from polymers compared to TBBPA.

Saturated water solutions of DOPO, RDP and BDP were prepared in sealed glass test tubes. The test tubes with DOPO were rotated for 9 days, and then allowed to stand for 4 months and the test tubes with RDP and BDP were rotated for 3.5 months and allowed to stand for another 3.5 months at room temperature until analysis. For DOPO, the experimentally obtained water solubility compared well with the modeled water solubility but both RDP and BDP were found to be considerably more water soluble than predicted (2-4 orders of magnitude).

An overview of leaching tests of chemicals from materials to the water phase were collected and showed that no standardized method exists. Therefore, a worst case (TLCP) and a conservative (DIN) leaching method were selected. During the first screening study, moulded plates were compared with pellets. Based on the outcome of the screening study it was decided to focus only on the moulded plates because they represent the actual product instead of focusing on the pellets (raw material). The leaching properties of different HFFRs were compared with BFRs using the TCLP leaching protocol. Five different polymers were selected containing HFFRs that could replace the BFRs, choosing formulations that exceeded the V-0 fire performance criteria. The concentration of the BFRs and HFFRs leaching from the material was performed at different time points (18h, 2.5d, 5d, 10d, 20d and 30d). In general, it was found that the polymer type is the main parameter determining leaching behaviour, and the more porous the more FRs can be released. Three polymers (PBT, PA6.6 and epoxy resin encapsulates) showed the highest leaching properties. Almost no FR leaches from the PPE/HIPS and PC/ABS polymers. The porosity of the materials has a high influence on the leaching behaviour of the flame retardants. Differences were also observed between the leaching behaviour of the BFRs compared to the HFFRs. In the PA6.6, PBT and epoxy resin encapsulates, the alternative FRs leach more than the BFRs, mainly due to the insolubility of polymeric-based brominated polystyrene in water. For the PHB and PCA polymers no differences were observed in leaching between the HFFRs and BFRs. In general, the leaching method developed can be used to compare the leaching behaviour of BFRs and HFFRs from different types of polymer materials.

Field monitoring of HFFRs

Based on the results from the updated environmental exposure assessment, key environmental media to be sampled for the field monitoring campaign were identified for the three organic HFFRs (RDP, BDP, DOPO). Due to their water solubilities and predicted behaviour in the modelling exercise, these included sewage sludge, sediments, STP effluent water, house dust and indoor air. Monitoring of the inorganic HFFRs in the outdoor environment was not carried out due to the difficulty to identify the source of the non-specific character of the metals. Based on this information sampling campaigns in several European countries were carried out for the organic HFFRs only.

RDP and BDP were found in most sediment samples collected from rivers and estuaries in the Netherlands, Germany, Belgium, Norway and France, with RDP usually present in similar or higher concentrations than BDP. For Norway, the concentrations for RDP range from less thanLOQ to 2.2 ng/g, and for BDP less thanLOQ to 1.4 ng/g. In the more central European sediments, the range for RDP was less thanLOQ-0.5 ng/g and for BDP, 0.05-0.2 ng/g. The highest concentrations were found in the Oslofjord (Norway). Sewage sludge samples from the Netherlands had similar concentrations of RDP and BDP, 0.70-3.37 ng/g and 1.6-10.3 ng/g, respectively. For effluent water samples from two sewage treatment plants in Sweden and four in the Netherlands were investigated. RDP was detected in measurable concentrations in one Swedish sample and BDP in one Dutch sample. These results indicate that sewage treatment plants could be a source of RDP and BDP to the outdoor environment.

In order to determine possible routes of exposure for humans to the organic HFFRs, DOPO, RDP and BDP were analysed in indoor dust samples collected from around furniture and electronics in homes, stores and cars in Sweden, the Netherlands and Greece. RDP and BDP were detected in most dust samples. BDP was usually the most predominant FR in the dust samples and the highest concentrations (up to 700 000 ng/g) were found on electronic equipment (game console, flat screen TVs, PCs, laptops). The RDP and BDP levels observed in the dust samples from Greece are similar to the levels found in Sweden. The higher concentrations found in houses in the Netherlands may have to do with differences in the electronic equipment sampled compared to Sweden and Greece. RDP and BDP are relatively ubiquitous in dust samples from various indoor environments in Sweden, the Netherlands and Greece, and this implies that Europeans will be exposed to these compounds via dust inhalation and dust ingestion. DOPO was found in one dust sample, and dust may be an exposure source for this as well. Note that people are probably also exposed to the inorganic FRs.

To determine if organic HFFRs are present in indoor air, samples were collected from the same localities in Sweden where dust samples were collected. No DOPO was detected in the air samples with a detection limit of 2 pg/m3. It was not possible to quantify RDP or BDP in air samples, as they were found to bind irreversibly to the glass fiber filter of the air sampler and could not be extracted.

Risk assessment (WP7)

An environmental (ERA) and a human risk assessment (RA) were carried out for a selected number of HFFRs. The risk assessment consisted of four major steps, i) hazard identification, ii) effect assessment, iii) exposure assessment and iv) risk characterization. The hazard identification and effect assessment were based on (eco)toxicity data from the literature, ECHA, and the ENFIRO hazard characterization.

For the ERA Predicted No Effect Concentrations (PNEC) for water (PNECaqua) and sediment (PNECsediment) were taken from ECHA, but also calculated for water using the latest ecotoxicity information resulting in an ENFIRO PNECaqua. For the exposure assessment the Predicted Environmental Concentration (PEC) was calculated based on i) the leaching data of HFFRs to water, and ii) measured concentrations of RDP and BDP in sediment and STP effluent. The sediment and water data is limited to organic HFFRs only, but the leaching data is available for all selected HFFRs. PECs were calculated for water and sediment at the local and regional scale. For the local scale it is assumed that the discharge of effluent from STPs is the main source for environmental exposure of HFFRs. It is assumed that HFRRs will mainly enter the environment by leaching and volatilization from plastics during the end-user, product use or waste phase and finally entering the environment via STPs effluent or by air. It is assumed that the emissions at the production phase are low compared to the other life cycle phases. For the regional scale a worst case scenario was used assuming that all polymers with HFFRs occurring in the STP effluent will reach the fresh and marine environment.

The ENFIRO leaching experiments have shown that the non-reactive flame retardants can leach from the polymer material. The flame retardants have two main pathways to enter the environment, i) by the waste phase of products (e.g. computers, TVs), and ii) the use phase of products that emits flame retardants by volatilization, wearing or abrasion and ends up in indoor dust and finally in STPs. If a landfill is managed properly most of the chemicals will not enter into the environment. The ENFIRO LCA end of life scenario showed that landfill had the lowest total impact, and therefore was of minor importance for the risk assessment. However, STP effluents have been found to be a source of flame retardant emission. ENFIRO showed that the alternative FRs RDP and BDP occur in STP effluent and sewage sludge (other HFFRs were not determined but probably also occur).

In the risk characterization phase the ratio of the PEC, at the local and regional spatial scale, was compared to the PNECaqua or PNECsediment. If the PEC/PNEC ratio is higher than one there is a need for further information, testing or the risk should be reduced. A PEC/PNEC ratio equal or lower than one needs no action. The ERA showed that for the ENFIRO selected HFFRs none of the PECaqua/PNECaqua ratio was higher than 1. This indicates that the HFFRs pose no risk for organisms in the water phase. For RDP and BDP the PECsed/PNECsed ratio was estimated for sediment at the local and regional scale. These estimates showed also a PEC/PNEC ratio below 1, and therefore no risk for the benthic organisms is expected for these compounds. The current status showed that there is no need for risk reduction measures of the selected HFFRs. However, it should be stressed that the leaching experiments showed that HFFRs can leach to the environment and some polymer types leach more HFFRs than BFRs. Therefore, new flame retardant systems should be developed that reduce leaching to the environment. In addition, the PEC estimates are based on a limited set of monitoring data.

The human risk assessment focussed on the exposure route of five HFFRs (DOPO, RDP, BDP, ZS, ZHS). The risk assessment was limited to RDP, BDP, ZHS and ZS as the hazard characterization showed some hazards for these compounds. For this risk assessment only house dust as a possible source of exposure to two groups, toddlers and adults was used. Any exposure via e.g. dust in shops or cars was not taken into consideration. Based on earlier studies with e.g. BFRs it became obvious that toddlers would be the major potential risk group compared with adults. Besides potential uptake from food, house dust was found to be the major exposure pathway of BFRs to toddlers and infants. However, in the case of these four selected non-brominated flame retardants the exposure via food can very likely be neglected. HFFRs are considered not to bioaccumulate in the human food chain. Oral uptake of house dust was assumed to be either 50 or 20 mg/day for respectively toddlers and adults, and 100% bioavailability. It is assumed that toddlers are spending most of their time on the house floor between 6 and 24 months. House dust monitoring data for DOPO, RDP, and BDP were available for three countries (Sweden, The Netherlands, Greece). In general, the highest concentrations were found in dust collected on the electronic equipment, and these were used for the risk assessment. Therefore the risk assessment is a worst case scenario. In general, the concentrations decreased with distance from the electronics. Mainly, RDP and BDP were found at relative high levels in dust on electronic equipment. The daily exposure calculations showed that toddlers were about 25 times higher exposed to the organic HFFRs than adults. The maximum daily intake for toddlers for DOPO was in the low ng/kg body weight/d, for RDP in the hundreds of ng/bw/d, and BDP in the low µg/bw/d.

The hazard quotients (HQ) of RDP, BDP, ZS, and ZHS were determined for the toddler and adult based on house dust exposure. A HQ of greater than 1 indicates no immediate concern. Depending on the FR used HQs were calculated in the range from 103 to 108. The HQ for RDP was 2.5*104 to 6*105, for BDP was 2*103 to 5*104, and for ZHS and ZS 1*107 - 3*108. These HQ values will provide more than sufficient safety for the use of RDP, BDP, ZS and ZHS in house-holds. Even if the use of these three FRs will increase in the near future with a factor 10 to 100, their risks in households for the toddler should still be considered negligible.

Impact Assessment Studies (WP8)

The impact assessment studies comprise an environmental, social and economical component. The environmental component is most developed while methods for economical and social impact assessment studies are in general not yet well developed. The ENFIRO project contributed substantially to the development of the Social LCA along the UNEP/SETAC guidelines.

The Env-LCA (LCA) has been conducted according to the procedures described in ISO14044. Each Life-Cycle Impact assessment study is divided into 4 phases:

1. The goal and scope phase, in which the purpose of the study is stated, the level of detail and study boundaries are defined, and methodological choices are made.
2. The life cycle inventory phase (LCI phase) results in an inventory of input/output data with regard to the system being studied. It involves the collection of the data necessary to meet the goals of the defined study.
3. The life cycle impact assessment phase (LCIA) has the purpose to transform the large body of data on inputs and outputs from the LCI into a limited number of environmental effect scores.
4. In the Life cycle interpretation phase, the results of the LCIA are summarized and discussed as a basis for conclusions and recommendations, in accordance with the goal and scope definition. In addition, the robustness and validity of the data and results are checked by performing sensitivity analyses.

Environmental impact assessment

The Env LCA findings have lead to the following conclusions.

- In most phases of the life cycle of FRs, fossil energy use related impact categories dominate the LCA score: Climate change, Fossil depletion and Particulate matter formation.
- The life cycle phases in which human toxicity and ecotoxicity play the largest role are:
- Export of WEEE followed by improper waste treatment. In this waste scenario, the formation of dioxins during improper incineration of BFR containing plastics has the largest contribution to human toxicity.
- Emissions of FRs during volatilization (or wearing/abrasion) in the use phase have LCA scores only in the toxicity impact categories. Emission factors of FRs are considered to be low.
- During accidental fire, emission of ATO to air has a relatively high score for terrestrial ecotoxicity. However, when considering the complete life cycle, only a small fraction of the laptops will end up in an accidental fire, and therefore accidental fire has only a small contribution to the total score.
- For the waste scenarios MSWI incineration and landfill, contributions to the toxicity impact categories come from both FR related (ATO, bromine, ZHS, ATH and Alpi) and non-FR related emissions (heavy metals).
- The environmental impact in the production phase of FRs (cradle-to-gate, per kg) varies considerably. The highest impacts are found for ZS, ZHS and ATO. Lower total impacts are found for decaBDE, RDP, BDP, DOPO

and Alpi, with differences in total scores within 20%. Then followed by TBBPA, MPP and BPS, and the lowest impact is found for the production of ATH. For the three FRs with the highest environmental impact (ZHS, ZS, ATO), the raw material mining phase has a high contribution to the total score.

- For the production of flame retarded polymers (cradle-to-gate, per kg), differences in environmental impact between BFR and HFFR are not very large, with maximum differences of 16%.
- Emission of FRs in the use phase through volatilization, wearing or abrasion cause the highest impact on human toxicity and freshwater ecotoxicity for the BFR scenario, and the highest impact on terrestrial and marine ecotoxicity for the HFFR scenario. In the overall score, the BFR scenario has the highest score, through the contribution of human toxicity.

The emissions of FRs in this phase have only a small contribution to the overall impact over the complete life cycle, but this phase is still likely to be the most important exposure route for humans.

- In the case of accidental fire, the BFR scenario has a higher overall impact than the HFFR scenario due to a higher rate of smoke formation and a higher terrestrial ecotoxicity score. In the HFFR scenario, the score for Climate change is higher than in the BFR scenario due to higher CO2 emissions (more complete combustion).
- Of the four End-of-Life scenarios for WEEE, the option 'export followed by improper treatment' has the highest environmental impact for both the BFR and HFFR scenarios. In the BFR scenario, this high impact is mainly caused by the formation of (brominated) dioxins during improper WEEE incineration. The high LCA score for improper WEEE treatment in the HFFR as well as the BFR scenario shows that even when BFRs are substituted by HFFRs, these practices are still quite harmful, as there is a range of toxic emissions during improper treatment, including lead, arsenic, hydrogen fluoride, (chlorinated) dioxins and PAHs.
- The main differences between the two full life cycle scenarios of the laptop with BFRs and with HFFRs are found in the scores for the impact categories human toxicity, freshwater, marine and terrestrial ecotoxicity and metal depletion. For these five impact categories, the impact is lower in the HFFR scenario. For the other impact categories, the scores of both full life cycle scenarios are almost equal.

The Env-LCA study shows that for improvements of the life cycle environmental performance of FRs, the waste treatment phase is critical. Export and improper treatment of WEEE has the highest impact of all waste treatment options for both the BFRs and HFFR scenarios, and efforts should continue (or be intensified) to reduce the amount of European WEEE ending up in this scenario.

Recycling of WEEE is the key to closing the material cycles of electronic products. Currently, the focus is mainly on recycling the precious metals in electronics but this needs to be expanded to more efforts in recycling of plastics.

The Env-LCA study shows that processes which are often ignored in LCA studies can have an important contribution to the environmental performance of a product (in this case the improper WEEE treatment phase). It is therefore recommended to broaden the scope and system boundaries of future LCA studies to include unofficial or illegal scenario options (specifically in the End-of-Life phase) to provide a more complete description of the full environmental impact of a product's life cycle, and thereby contribute to relevant discussions in society and policy.

Social impact assessment

No fully fledged out S-LCA methods are available yet and the field is still in its infancy. In this project the UNEP/SETAC guidelines were followed and the method developed in a study carried out by Ciroth and Franze (2011) was substantially improved by a further developing of the social life-cycle data inventory and the impact assessment methodology. Because of these challenges and the limitation of the study undertaken, results presented here should be cautiously interpreted. But although much work remains, the present research does show that by using the UNEP/SETAC S-LCA guidelines, social hotspots for a complete life cycle can in principle be determined and compared between different product alternatives.

The primary aim of this study was to compare social hotspots between brominated and halogen free flame retardants over the complete life cycle. The results suggest that for both laptop alternatives concerns regarding social issues are present in all life cycle stages and affect all of the included stakeholders (workers, local communities and society). However, in both the laptop containing HFFRs and the BFR laptop the social hotspots were predominantly found for the extraction of raw materials and the improper treatment of e-waste in developing countries. In general the well-being of workers and the local community seems to be adversely affected by the highest number of social hotspots. The lowest number of social hotspots was identified for the HFFR production phase. When taking the complete life cycle into account, findings show no clear differences in the total number of social hotspots found between the two scenarios.

An analysis of the characteristics of social hotspots influencing stakeholders tentatively shows that in both laptop scenarios and throughout the life cycle the well- being of workers is compromised mainly by the risk of infringements to the right to associate and collectively bargain and the risk of not being provided with adequate social benefits. Dangers to health and safety were mostly associated with mining and the improper treatment of e-waste, while receiving a salary that covers the cost of living seems the most problematic an issue for the improper treatment of e-waste. In addition, evidence was found for the presence of child labor occurring for bauxite mining in Guinea (limited) and the improper treatment of e-waste in China.

The dominant social issues for the stakeholder local community were the risk of not having access to material resources (land use conflicts for example) and immaterial resources (limited efforts by companies to support education or community service programs), and seemingly limited efforts by companies to include stakeholders in the decision process. This was the case for both the HFFR and BFR scenario and all investigated life cycle steps except the production of HFFRs. Additionally there were compromises to community safety and health, whereby pollution and a lack of efforts by companies to reduce it were found on multiple occasions in most life cycle stages.

For the stakeholder group society substantial similarities were found in social hotspots between the HFFR and BFR laptop in most life cycle stages. The most prominent were a lack of commitment by companies to sustainable issues (lacking quantified sustainability related targets and reporting progress) and a risk of corruption particularly in developing countries. Efforts by companies to prevent and mitigate conflicts were often perceived to be inadequate. This was the case for all investigated life cycles but less so for the mining in the BFR scenario and HFFR production.

When overall severity of social impacts was compared for both HFFR and BFR scenarios, relatively small differences in impact scores were found for the extraction and production phase. Especially uncertainties regarding the locations where unit processes take place (lack of traceability) and the unavailability of (good quality) data were important limitations for the current study.

Economical Impact assessment

The economical impact is mainly governed by the market price of the raw materials. The market for FRs keeps on growing mainly due to increased fire safety regulations. However, the growth is unevenly distributed. The market of brominated flame retardants in the EU is declining due to both restrictions, economical and social factors. Consequently the HFFR market will mainly benefit from this growth.

For almost all polymer applications used in E&E products marketed HFFR options are available and some of them are already cheaper to apply than their BFR alternative. The price of some FRs is highly volatile, some of them depend on the availability of resources and some of them may have international trade restrictions. For example the declining market relevance of ATO can be explained by its volatile price changes and current restrictions on the export from the main raw material producer China. Its price has increased in Europe from $2/kg in 2002 to $5-6.50 in 2007 and to around $15 in 2011. Such a vast increase in price will increase the price of FR systems where ATO is used. This may drive substitution processes for ATO alone or for complete new FR systems.

In most E&E products, price differences between polymer systems with BFRs and HFFRs are small or even absent. Therefore it is unlikely that any price differences of end-products where these FRs are used are caused by differences in the applied FR systems.

Differences in EU and LCA impact assessment studies

In the ENFIRO impact assessment on BFR substitution, several assessment methods were used: a qualitative assessment using questionnaires (based on the EU guidelines for impact assessment), an environmental LCA, a social LCA and a market study. The impact assessment methods differed in methodology, system boundaries and level of detail. The EU guidelines are developed to assess the impact of policy changes on the sectors involved. The EU guidelines consist of large questionnaires divided into categories. However, most of these categories are also found in the LCA-approach. The questionnaires were sent to members of the ENFIRO Stakeholder Forum at the start of the project. The outcomes were then compared to the results of the LCA assessment methodology.

The environmental issues found to be of relevance in the Env-LCA were also mentioned by (some of) the questionnaire respondents. The quantitative and structured nature of the LCA method gives a lot of additional insight into which environmental impacts are relevant in which phases of the life cycle. A number of social issues that were found to be relevant in the S-LCA study were not found in the qualitative assessment.

This is partly related to the type of results of an S-LCA: besides a direct comparison of scenarios, a list of social hotspots along the life cycle is delivered as one of the main results of the assessment. In addition, the EU guidelines focus on Europe while the S-LCA looks at the product chain. The market study showed that several of the economic concerns expressed in the qualitative assessment are not likely to be of actual relevance in BFR substitution. Initial concerns over price increases, competitiveness and trade barriers were found in the more detailed interviews and market study to be of no significant consequence or not to occur at all.

Summary ENFIRO Science and Technology (S&T) results

The Project Approach

- ENFIRO showed that viable alternative flame retardants are available with similar fire performance and technical application capabilities as some BFRs, and confirmed that some are environmentally friendly alternatives to brominated fire retardants and pose less risk for the environment and humans.
- ENFIRO followed a practical approach in which HFFRs were evaluated and compared to BFRs regarding their flame retardant properties, their influence on the function of products once incorporated, and their environmental and toxicological properties.
- The ENFIRO approach is based on the chemical substitution cycle which consists of four major elements: i) prioritization and selection of alternatives, ii) technical, toxicological, and exposure assessment, iii) risk assessment, and iv) impact assessment.
- ENFIRO showed that it is important to follow the completed substitution chain based on the four above elements, in contrast to most substitution programs which focus on the first two elements only.
- ENFIRO followed a unique approach to assess data at three levels, i) the flame retardants (hazard, exposure, risk), ii) the material (fire performance, technical applicability, leaching and air emissions), and iii) the product (impact assessment including LCA).
- ENFIRO showed that all of the selected alternative halogen free flame retardants do fulfil the regulatory fire test.

Results for Target Applications

- A simple method was developed for characterizing the fire performance and fire toxicity of FR/polymers and to compare alternative FRs with BFRs.
- An important finding was that halogen free systems have clear benefits as demonstrated, e.g. less visible smoke, in some cases lower peak heat release rate with halogen free products, and less toxic components in smoke.
- There is no single drop-in replacement for BFRs by HFFRs available for the polymer systems. However, for all polymer systems investigated a HFFR option was found that was commercially available and fulfils the fire requirements.
- For the polymer blends (PC/ABS, PPE/HIPS) the HFFRs do meet the fire performance requirements but performs less well than the material with BFRs for which it has been formulated, and there are some concerns on the environmental hazard. Additional work is needed to search for other alternative FRs for the polymer blend systems.
- Both polymers with brominated and nonbrominated FR showed similar loss in mechanical properties compared to the polymer alone.
- All formulations (both HFFR and BFR) showed equal or better performance regarding processability for injection moulding.

- An important part of the project was the input received from the Stakeholder forum on formulations.
- The results for the PCBs with the HFFRs where as good as or better compared to the reference PCBs produced using BFRs.
- A novel intumescent coating system was developed for pure HIPS, which is difficult to flame retard without halogen, that was efficient and makes HIPS fulfill the fire regulatory tests as well as the industry fire standards relevant to the electronics industry.

Hazard and Risk Assessments
- From the initial selection of 14 alternative flame retardants seven (APP, Alpi, ATH, DOPO, MPP, ZS, ZHS) were found to be of less concern.
- Bioaccumulation of the inorganics HFFRs is probably not a concern, but BDP is persistent.
- Environmental fate models predicted that the organic HFFRs would be found primarily in soils, sediments and dust and to a lesser extent in water and air.
- Controlled air emission experiments showed that all organic HFFRs emitted from polymers at elevated temperature but not at lower temperatures.
- The used leaching methods are suitable to provide a measure for the leaching of FRs to the outdoor environment.
- Leaching experiments showed that HFFRs and BFRs can leach to water. For some polymers no differences in leaching behaviour between BFRs and HFFRs were found, but for some the HFFRs systems had higher leaching properties than the BFR (e.g. polymeric based FRs). The type of polymer and the porosity are the main parameters determining the leaching behaviour.
- Analysis of dust samples from microenvironments where these organic HFFRs might be used showed highest concentrations on and around electronic equipment, such as flat-screen television sets. Lower, but measurable concentrations were also found around other electronics, furniture, car seats and in apartments.
- Some of the organic HFFRs were also found in the environment (STP effluents, sewage sludge and sediment).
- Based on these results, it is clear that humans can be exposed to HFFRs via dust ingestion and organisms via sediment and STP emissions.
- The risk assessments showed that some HFFRs show less risk for the environment and human health. The lower risk is mainly due to the lower hazards of the HFFRs, and probably not due to a lower exposure.
- Leaching of flame retardants from polymers should be further reduced to reduce the human and environmental exposure.

Life Cycle Assessments and Socio-economic considerations
- The Env-LCA study showed that for improvements of the life cycle environmental performance of FRs, the waste treatment phase is critical. Export and improper treatment of WEEE has the highest impact of all waste treatment options for both the BFRs and HFFR scenarios, and efforts should continue (or be intensified) to reduce the amount of European WEEE ending up in this scenario.
- The social hotspots were predominantly found for the extraction of raw materials (health and safety issues) and the improper treatment of e-waste in developing countries (fair salary, social security, health and safety issues).
- For the overall severity of social impacts between HFFRs and BFRs small differences in impact scores were found, mainly for the extraction and production phase.
- From an economic viewpoint price differences between polymer systems with BFRs or HFFRs are small and should be no obstacle.

- The most viable alternative HFFR/polymer combinations from a fire performance.
- For the substitution of chemicals a complete substitution cycle is needed: technical/application performances, hazard, exposure, and impact assessments. Such an assessment can only be performed with a group of experts from different disciplines (material experts, fire safety researchers, toxicologist, chemist, social scientist, life-cycle experts etc).

Overall it can be said, that the approach adopted by ENFIRO was very successful and can be used for similar substitution studies, e.g. REACH.

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Potential Impact:

Dissemination
The major activities of the ENFIRO dissemination was the launch of the Website, logo, flyer, newsletters, presentations, publications, organisation of the mid-term and final workshop, the establishment and meetings with the ENFIRO Stakeholder Forum (ESF), and the ENFIRO film. Press releases in English, Dutch and Swedish were released to inform the project start. A large number of presentations were given about ENFIRO in national and international symposia by several partners. For 2013 several presentations are planned to further disseminate the work at conference, workshops and publications. ENFIRO was presented at special sessions on chemical alternative assessments at conferences of SETAC North America 2010, BFR2010, SETAC Milano 2011, SETAC Berlin 2012, BFR2013, and SETAC Glasgow 2013. ENFIRO was also presented at the Going Green Care Innovation conference visited by a wide range of experts from industry, academia, NGOs and policy.

The ESF was established consisting of 17 companies/institutes; 7 FR producers, 6 formulators, and 4 others (e.g. NGOs, waste recycling). Yearly ESF meetings with the ENFIRO consortium were established. The ESF functioned as a reference group for the identification, elaboration and evaluation of the drivers and barriers connected to the FR substitution process. Beside the drivers and barriers inventory, the input of the ESF in the ENFIRO project guaranteed a broad dissemination of the feasibility of successful substitution, and assures their active involvement and commitment to the required substitution process. At the first ESF meeting the ENFIRO approach, concepts, and the selected set of HFFRs was presented and discussed. The ESF members provided feedback on the selected HFFRs, i.e. 3 HFFRs were added, and additional information on physical-chemical properties and toxicity were provided. At the second meeting information of the HFFRs on fire performance, application, toxicity, and impact assessment was provided, and information for the impact assessment studies was exchanged. At the third meeting the main outcomes of the project were discussed and additional information for the impact studies were requested for specific flame retardants and polymers. The ESF was invited for the mid-term and final ENFIRO workshops.

Other international projects/networks were approaches to disseminate ENFIRO (e.g. INFLAME, ChemSec, NORMAN network, UK POP network), and FR producers were visited to discuss the exchange of information. The integration of producers, formulators, end-users was established in an early start by presenting ENFIRO at the Phosphorous, Inorganic and Nitrogen Flame Retardant Association (Pinfa) at four workshops and general assembly meetings, which was also participated by NGOs and policy-related institutes. Intensive exchange of information was set-up between ENFIRO and the U.S. EPA Design for the Environment (DfE) projects on decaBDE alternatives assessment partnership, and the substitution program of HBCD. The DfE decaBDE program started in the same time frame as ENFIRO therefore, ENFIRO was presented at the kick-off meeting of the DfE project. Regular updates of the results of ENFIRO and the DfE decaBDE projects were discussed between the coordinators of both projects, which were a great benefit for both projects, and not to duplicate studies and gain as much information as possible. Further contacts have been established between the programs on the substitution of BFRs at Environment Canada and University of British Columbia. In addition, contacts were set-up on the life cycle and alternative assessment of HBCD in products carried out by the Yokohama University which was carried out for the Ministry of the Environment, Japan. The main outcomes of ENFIRO and the ENFIRO film will also be presented at a workshop on flame retardants at Yokohama University. Recently several Civil Society Organisations (CSOs) have developed schemes to enhance the substitution of certain BFR-systems. The Green Screen, a chemical screening method to move to greener and safer chemicals, the yearly produced Guide to Greener Electronics of Greenpeace are examples of CSO schemes specifically developed to improve the green image of electronic equipment. These schemes are implemented by several large companies producing electronic equipment. ENFIRO was involved in Green Screens of Clean Production Action of HFFRs and the results of the Green Screen are available for ENFIRO.

ENFIRO results have also contributed to the recently increased scientific and public interest in plastics in the environment. On several symposia and conferences (e.g. SETAC2010&2011, 'Plastic forever?'-symposium) the relevance of plastics additives (such as flame retardants) for the environmental fate and effects of plastics was addressed.

On 15th March 2011 the ENFIRO mid-term workshop was organised with the title "From Hazard to Product Evaluation - How can we make chemical substitution work - Case study flame retardants substitution?" in Amsterdam, The Netherlands. The main objective of the workshop was to bring together people that are working in the field of chemical substitution, in particular for flame retardants. Due to their persistent nature and toxicity some brominated flame retardants (BFRs), applied in a wide range of commercial products, need to be substituted by non-toxic substitutes. The workshop focussed on the substitution process chain starting with the prioritization and selection of viable flame retardants, to hazard characterization, fire and product performance and finally to impact assessment. The workshop presented and discussed findings obtained by the ENFIRO. Beside six ENFIRO presentations five speakers outside the consortium were invited (e.g. US EPA, iNEMI). About 60 participants discussed issues related to the substitution of flame retardants to fire and applications performance to hazard, exposure and life cycle assessment, including bio-based polymers as flame retardants, and other alternative decaBDE substitution programs. The workshop was visited by many participants from industry. One major conclusion of the workshop was that flame retardants need to be tailored to their end application, be it different polymers or textiles or other materials. Substitution is generally feasible but usually requires some effort and resources and furthermore, should take not only chemical hazard information into account but also full life cycle aspects.

Burning Questions was the final workshop organised by the ENFIRO project on 7-8 November 2012 in Brussels to disseminate the highlights of the project. About 90 participants from industry, research organisations, policy organisations, NGOs and EU officers were present. Beside 14 presentations showing an overview and insights of the ENFIRO results other projects were presented by scientists outside the consortium as well. A lively discussion about the challenges and opportunities for alternative flame retardants concluded the last ENFIRO workshop in Brussels. Underlined was the amount of stakeholders present at the workshop, marking the use of ENFIRO. The political dimension that was added through the social LCA impressed some participants. It was mentioned that the ENFIRO approach should be implemented in the consumer chain. There was a need for the inclusion of social scientists in substitution projects to bring that element of sustainability into the alternative assessment chain. The closing remarks called for the reduction of the exposure to flame retardants for instance by the development of novel flame retardant systems using reactive or polymer based FRs, or recycling. A highlight in the evening program was the premiere of the ENFIRO film BURNING QUESTIONS.

The film BURNING QUESTIONS was produced to show the project highlights including shots of the experimental work (2000 copies have been produced). The film showed the background on some BFRs, the importance of fire safety and how to conduct an alternative substitution process. The film starts with an introduction on the background of some brominated flame retardants, followed by the ENFIRO approach on the search for alternative flame retardants, and presentations of the highlights of the ENFIRO project by the researchers with strong visual impressions from their experimental work. The film was shot at various European locations and is presented by broadcaster Kate McIntyre and features laboratory sequences and interviews with experts. The film is distributed on DVD and sent to potentially interested parties such as authorities, producers, users, NGO's, international organization, etc. The film is already shown at various conferences, workshops, and trade shows (e.g. Dioxin2012, ERA Technology - Electrical and Electronic Equipment and the Environment, NORMAN workshop Emerging chemicals, 8th Congress of Turkish Society of Toxicology). It will also be possible to use the film for educational purposes, e.g. during university courses. At a later stage the film will be made available on the web. Beside the film, a film trailer was made and shown at the ENFIRO website. A poster, press release, and photo material was prepared which can be downloaded from the ENFIRO site.

Economical and social impact

The economical impact is mainly governed by the market price of the raw materials. The market for FRs keeps on growing mainly due to increased fire safety regulations. However, the growth is unevenly distributed. The market of brominated flame retardants in the EU is declining due to both restrictions, economical and social factors. Consequently the HFFR market will mainly benefit from this growth. For almost all polymer applications used in E&E products marketed HFFR options are available and some of them are already cheaper to apply than their BFR alternative. Furthermore some of the HFFRs possess at least an equivalent market relevance as its BFR option. The price of some FRs is highly volatile, some of them depend on the availability of resources and some of them may have international trade restrictions. For example the declining market relevance of ATO can be explained by its volatile price changes and current restrictions on the export from the main raw material producer China. In most E&E products, price differences between polymer systems with BFRs and HFFRs are small or even absent. Therefore it is unlikely that any price differences of end-products where these FRs are used are caused by differences in the applied FR systems.

For the Social Life-Cycle Impact Assessment study S-LCIA the results suggest that there are concerns regarding social issues in all life cycle stages and affect all of the included stakeholders (workers, local communities and society) for both the HFFRs as BFRs. However, in both the HFFRs and the BFR laptop the social hotspots were predominantly found for the extraction of raw materials and the improper treatment of e-waste in developing countries. These social hotspots are specifically related to the location of a specific step in the Life-Cycle of the product. Consequently a proper tracking system of the same material from another location may lead to a better social LCIA. Since the first full development of a S-LCIA methodology in this project lacks the application of such a tracking system findings show no clear differences in the total number of social hotspots found between the applied BFR and HFFR scenarios. ENFIRO showed the importance of an S-LCIA as part of the impact assessment studies as additional information to the Env-LCIA is provided. This is an important to provide information on the risk and benefits of the substitution process.

Risk assessment and REACH
The ENFIRO project indicates that a full risk assessment (RA) for each HFFR-alternative is not feasible due to data gaps. However, a full RA may not be required since for substitution of the substance only a comparison between potential health and environmental risks must be made. This comparison can be based on the precautionary approach by establishing concern levels rather than hazard levels. In this case screening tests, as used in ENFIRO, are useful tools to establish quickly concern levels and defining the best screening methodology in a substitution process is then important. Screening tests were used in the ENFIRO project to quickly compare relevant hazard endpoints. The results do not lead to a chemical safety assessment (CSA) as outlined in the REACH but quickly indicates at least a health or environmental concern level of the alternatives in relation to the BFR used in the system. Therefore screening tests and assays can fulfill a crucial role in this comparison when dealing with substitution issues.

Currently the RA methodology is hazard driven rather than exposure driven. However there is a tendency to switch to an exposure driven RA methodology. The exposure experiments conducted in ENFIRO shows that certain alternative FR-systems are already widely present in the environment and as such have a higher level of concern. Attention can then be given to assess whether these alternatives are indeed an improvement of the health and environmental profile of the substitute and could become a potential concern again. Therefore just substituting the undesired substance does not imply automatically a lower risk.

The potential release for example by leaching is practically non-existent for reactive FR-systems. From a point of view of the risk assessment the FRs linked to the polymer chain thus have a lower risk than when an additive type of FR is used. However, while the RA methodology leads to a lower risk in this case, the Env-LCIA study shows that such a reactive system may lead to similar impacts in the waste phase when an additive BFR-system is substituted by its reactive one. Still the development of polymer-based or reactive FR systems should be stimulated to reduce the environmental and human exposure. From the viewpoint of waste proper waste treatment and recycling should be high on the agenda.

The relevant data required in the RA of the alternative FR selected in the ENFIRO project indicates not only the lack of data for many relevant parameters but also that many relevant data cannot be estimated with reasonable accuracy. This is caused by the fact that most of these estimation methods are developed for organic substances and are not valid for inorganic or organometallic ones. It is recommended to develop estimations tools for exposure of inorganic compounds. In ENFIRO about 40% of the studied flame retardants were inorganic or organometallic based.

Impact assessment studies

The Life-Cycle impact assessment studies should be based on a realistic life-cycle of the product. ENFIRO included a number of processes in the Env-LCA that are often not addressed, such as illegal waste scenarios (improper WEEE treatment), which significantly contributed to the environmental perfomance of the products. Future LCA studies should increasingly include these issues, because ignoring them may result in an incomplete description of the full environmental impact of a product's life cycle. Other issues that were included in the Env-LCA study that are normally left out, are indoor human exposure via dust (local impact), human exposure to FRs in Asia (and not only in Europe) when burning electronics waste in open fires to recycle the metals (occupational health issue) and fire occurrence (incident). Therefore the different life-cycle assessment studies should be based on the real life-cycle including illegal and local aspects that are relevant in the impact assessment study. Env-LCA studies on a part of the complete life-cycle may obscure relevant impacts. It is recommended to broaden the scope of LCA studies.

Alternative assessments

Currently the assessment of alternatives is often simply based on substitution of the undesired substance by another one without taking into consideration if the alternative possesses an improved health and/or environmental profile. This dilemma was the basis for the EU to establish a specific call to assess the health and environmental risk and impact of alternative FR-systems . ENFIRO developed an alternative strategy based on four elements of the chemical substitution cycle combined with a unique assessment approach of the data. The data was assessed at three levels the chemical (flame retardant), the material, and the product. This approach was very successful and could be used for similar substitution studies (e.g. REACH). Current chemicals policy does not require a pre-assessment of alternatives although REACH indirectly solves at least a part of this aspect if the substance must be registered under this regulation. In that case a summary of the registration report will be published and the different registration reports can be compared to each other.

Alternative assessments can also include other ways to increase the safety of the product. The ENFIRO project did not pay attention for example to possible improvement of the fire retardancy by indicating new ways of design of products, which may not require flame retardants at all, as this was not the scope of the project.

Gender issues

Despite substantial progress towards equality between women and men achieved by equal treatment legislation, gender mainstreaming, specific measures for the advancement of women, the social dialogue and the dialogue with the civil society, this has not led to the desired gender balance in the EU workforce. In the ENFIRO project, a platform was created for awareness raising and exchange of ideas through presentations by the gender officer and invited speakers that initiated and stimulated lively discussions within the project group. A valuable source of information on the current status of women representation in the EU was the "She Figures 2009 - Statistics and Indicators on Gender Equality in Science", that revealed that the figures are encouraging but the gender imbalance is not self-correcting. The various aspects of the implementation of quotas for women representation in company boards was presented inspired by "Women on Board – The Norwegian Experience" (Aagoth Storvik and Mari Teigen, (Friedrich Ebert Stiftung), 2010). Guidelines for improvement of the quality of selection procedures for the appointment of professors with special emphasis on equal opportunities for women were highlighted, derived from the PhD thesis “Behind the Scenes of Science – Gender practices in the recruitment and selection of professors in the Netherlands (2010)” by M. van den Brink. More general, world-wide information was derived from the “Global Gender Gap Report 2010”, a publication of the World Economic Forum. In addition, Johanna Andersson, Gender Coordinator at Chalmers University (Goteborg, Sweden) and Sara Hunter, Head of Equality and Diversity Services of the University of Ulster (Belfast, UK) were invited to present the initiatives and strategies implemented to address gender mainstreaming at these respective universities.

List of Websites:
http://www.enfiro.eu