

**Eco-profile of
high volume commodity
phthalate esters
(DEHP/DINP/DIDP)**

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Prepared for:

**The European Council
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Preface

Life Cycle Assessment (LCA) is a growing tool used by the industry, governments and environmental groups to help establish environment related strategies.

The initial phase of LCA is the collection of Life Cycle Inventory (LCI) data, which quantifies the material, energy, and emission data associated with a functional system. To date, methodologies for LCI calculation are relatively advanced and related ISO standards for LCI step have been finalised : ISO 14040 - LCA: Principles and framework, ISO 14041 - LCA: Goal and scope definition and inventory analysis. "Cradle-to-gate" life cycle inventory, from the extraction of raw materials from the ground to the gate of the factory where the product is manufactured, is also named eco-profile.

This report results of a study commissioned by the European Council for Plasticisers and Intermediates (ECPI), a sector Group of CEFIC. This study aimed at establishing the average European eco-profile of high volume commodity phthalate esters: Di-2-ethylhexyl phthalate (DEHP), Di-isononyl phthalate (DINP) and Di-isodecyl phthalate (DIDP).

By this study, ECPI and its member companies wish to respond to the general concern of the environmental impacts of these products (DEHP, DINP, DIDP) by providing industry-based information on them for further use.

This study has been carried out by ECOBILAN, an independent LCA expert, member company of PricewaterhouseCoopers, from October 1999 to October 2000.

This work involved 8 industrial companies or group of companies manufacturing intermediates and/or high commodity phthalate esters in Europe: BASF, BAYER, CELANESE Chemicals, ATOFINA, EXXONMOBIL Chemical, LONZA, NESTE OXO and OXENO Olefinchemie. These companies supplied their own industrial data but also actively participated, through their representatives, in the Eco-profile Expert Working Group that was created within ECPI for this study and that regularly met all along the study.

As one of the request of ECPI was to use the same format as the Association of Plastics Manufacturers in Europe (APME) eco-profiles' one, this work has been conducted with a methodology very close to the one followed for the APME eco-profiles. The aim was to facilitate the further use of this eco-profile all together with the APME eco-profiles of PVC, one of the main thermoplastics formulated with phthalate esters.

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Glossary of abbreviations

- **DEHP:** Di-2-ethylhexyl phthalate - $C_6H_4(COO-C_8H_{17})_2$

CAS number: 117-81-7

EINECS numbers: 204-211-0

- **DINP:** Di-isononyl phthalate - $C_6H_4(COO-C_9H_{19})_2$

CAS numbers: 28553-12-0, 68515-48-0,

EINECS numbers: 249-079-5, 271-090-9,

- **DIDP:** Di-isodecyl phthalate - $C_6H_4(COO-C_{10}H_{21})_2$

CAS numbers: 26761-40-0, 68515-49-1

EINECS number: 271-091-4

- **2-EH:** 2-Ethyl-hexyl alcohol - $C_8H_{17}OH$

- **INA:** Isononyl alcohol - $C_9H_{19}OH$

- **IDA:** Isodecyl alcohol - $C_{10}H_{21}OH$

- **PAN:** Phthalic anhydride - $C_8H_4O_3$

1 Goal, scope and functional unit

A life cycle inventory quantifies the total material and energy flows into and out of a studied system. This requires the collection of numerical data associated with these flows as well as the application of different calculation procedures. In order to collect the data relevant to the study, the goal and scope of the system under study have to be defined.¹ These elements are outlined below.

1.1 Goal of the study

The goal of the project was to provide ECPI and further users with:

- representative average “cradle-to-gate” life cycle inventory, or eco-profile, of high volume commodity phthalate esters (DEHP, DINP and DIDP) in Western Europe;
- the ability to identify main sources of environmental impacts in the high volume commodity phthalate esters production routes;
- the ability to extend this “cradle-to-gate” approach to build “cradle-to-grave” profiles, in the general framework of Life Cycle Assessment studies.

1.2 Scope of the study

The whole project consists in a “cradle to gate” life cycle inventory (LCI), from the extraction of raw materials “in earth” (the cradle) to the gate of the plant where high volume commodity phthalate esters are produced (the gate).

The geographical scope of the study is Western Europe².

In order to be able to calculate the final eco-profile of high volume commodity phthalate esters, specific data collection on site was required for the production of:

- 5 intermediates: Phthalic Anhydride (PAN), C₈ and C₉ olefins, n-Butyraldehyde and synthesis gas;
- 3 intermediate oxo alcohols: 2-Ethylhexanol (2-EH), Isononanol (INA) and Isodecanol (IDA);
- The 3 final phthalate esters under study: DEHP, DINP and DIDP.

8 different companies (or Group of companies) participated at the data collection step: BASF, BAYER, CELANESE Chemicals, ATOFINA, EXXONMOBIL Chemical, LONZA, NESTE OXO and OXENO Olefinchemie.

1.3 Functional unit

The functional unit of this study is:

“to produce one kilogram of high volume commodity phthalate esters”.

¹ The methodology used for this study has been formalised under the ISO 14 000 series of international standards. The standard ISO 14040: Life Cycle Assessment – Principles and Framework provides a definition of LCA and the standard ISO 14041: Life Cycle Assessment – Goal and Scope Definition and Inventory Analysis defines the methodology for compiling a Life Cycle Inventory (LCI).

² ECPI’s definition of Western Europe: France, Belgium & Luxembourg, The Netherlands, Germany, Italy, The United Kingdom, Ireland, Denmark, Spain/Portugal, Norway/Sweden/Finland, Switzerland & Austria, Greece, Turkey, Cyprus, Malta, Iceland.

2 High volume commodity phthalate esters

2.1 Introduction on plasticisers and high volume commodity phthalate esters

Plasticisers are inert, organic substances incorporated into a polymer to increase its flexibility and workability, thanks to a decrease in the glass transition temperature of the polymer. They are divided into 2 main groups: external and internal plasticisers, depending on whether the polymer is chemically modified by the plasticiser (internally plasticised) or not (externally plasticised). External plasticisers are the most common, as they allow the highest freedom in term of formulations and final flexibility at the lowest cost. After fillers, external plasticisers are the highest volume additives used in plastics.

The major chemical types of plasticisers are:

- Phthalate esters,
- Adipate esters,
- Trimellitates esters,
- Phosphate esters,
- Sebacate and azelate esters,
- Polyester plasticisers,
- Sulfonate esters,
- Citrate esters.

Phthalate esters are the most widely used plasticisers because they have excellent compatibility with vinyls and other polymers and a good balance of other properties. They represent more than 90 %³ of the Western European plasticisers market. The widespread use of phthalate esters and their position as leading plastics additives class has resulted in relatively close environmental scrutiny. Because their production and use represent a significant volume, regulations on water and air concentrations, disposal, and worker exposure criteria have been formulated for the most heavily used phthalates. Unlike many other additives which are considered to be specialty chemicals, the phthalate esters are classified as commodity chemicals.

The most important phthalate esters are Di-2-ethylhexyl phthalate (DEHP), also referred to as DOP (Di-octyl-phthalate) in trade, Di-isononyl phthalate (DINP) and Di-isodecyl phthalate (DIDP). These 3 phthalate esters, referred to as “high volume commodity phthalate esters” in this report, represent more than 85 %⁴ of the total phthalate esters produced in Western Europe. DEHP, which accounts for about 50 %⁵ of the production tonnages in Western Europe, has long been accepted as the industry standard general purpose primary plasticiser.

Other main phthalate esters are Butyl benzyl phthalate (BBP), Di-n-butyl phthalate (DBP) and some others.

In this study, only the high volume commodity phthalate esters - i.e. DEHP, DINP, DIDP- were studied. The average eco-profile published in this report corresponds to the average calculated by using the production tonnages of each individual phthalate esters for which data were collected within this study.

³ 1998 situation – Source: ECPI statistics

⁴ 1998 situation – Source: ECPI statistics

⁵ 1998 situation – Source: ECPI statistics

2.2 The chemical structure of high volume commodity phthalate esters

Phthalate esters are diesters of phthalic anhydride, with a common chemical structure shown in Figure 1. They are made by reacting phthalic anhydride (PAN) with oxo alcohols to form esters. They differ from the nature and length of the oxo alcohols (C_1 to C_{13}) they are made with.

Either alkyl or aryl functional groups may be added to the phthalic acid backbone to form the final ester. Chain branching and substitution add additional options. In general, as R increases, volatility, plasticating efficiency, processing ease, specific gravity and water extraction decreases, whereas oil extraction increases. Branching of the R group decreases the low temperature performance and the extent of oil extraction. The addition of aromatic functional groups tends to improve compatibility, but impairs the low temperature properties of the plasticiser.

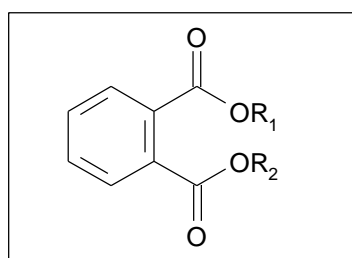


Figure 1: General chemical structure of phthalate esters

As already outlined, this study is only concerned with three phthalate esters, referred to as “high volume commodity phthalate esters” in this report (see Figure 2 for their detailed chemical structure):

1. **DEHP (Di-2-ethylhexyl phthalate)** - also known as Dioctyl phthalate (DOP) - is produced from PAN and 2-Ethylhexyl alcohol. This C_8 phthalate ester has been considered as the “workhorse” plasticiser for more than thirty years and is particularly adequate for many applications in the vinyl industry. DEHP presents good gelation characteristics, good plasticising efficiency and adequate viscosity properties in emulsion PVC pastes.
2. **DINP (Di-isononyl phthalate)** is produced from PAN and C_9 oxo alcohols (Isononyl alcohol) and has similar plasticising properties to DEHP. With a slightly higher molecular mass than DEHP, its plasticising efficiency is somewhat lower than DEHP, which requires a greater addition of plasticiser to impart an equivalent softness. At the same time, this higher molecular mass improves high temperature performance and resistance to extraction.
3. **DIDP (Di-isodecyl phthalate)** is produced from PAN and C_{10} oxo alcohols (Isodecyl alcohol). Due to its higher molecular mass (lower volatility), it has the best high temperature performance compared to DINP and DEHP but also lower plasticising efficiency, thus requiring greater plasticiser addition to impart the same softness to the final formulation.

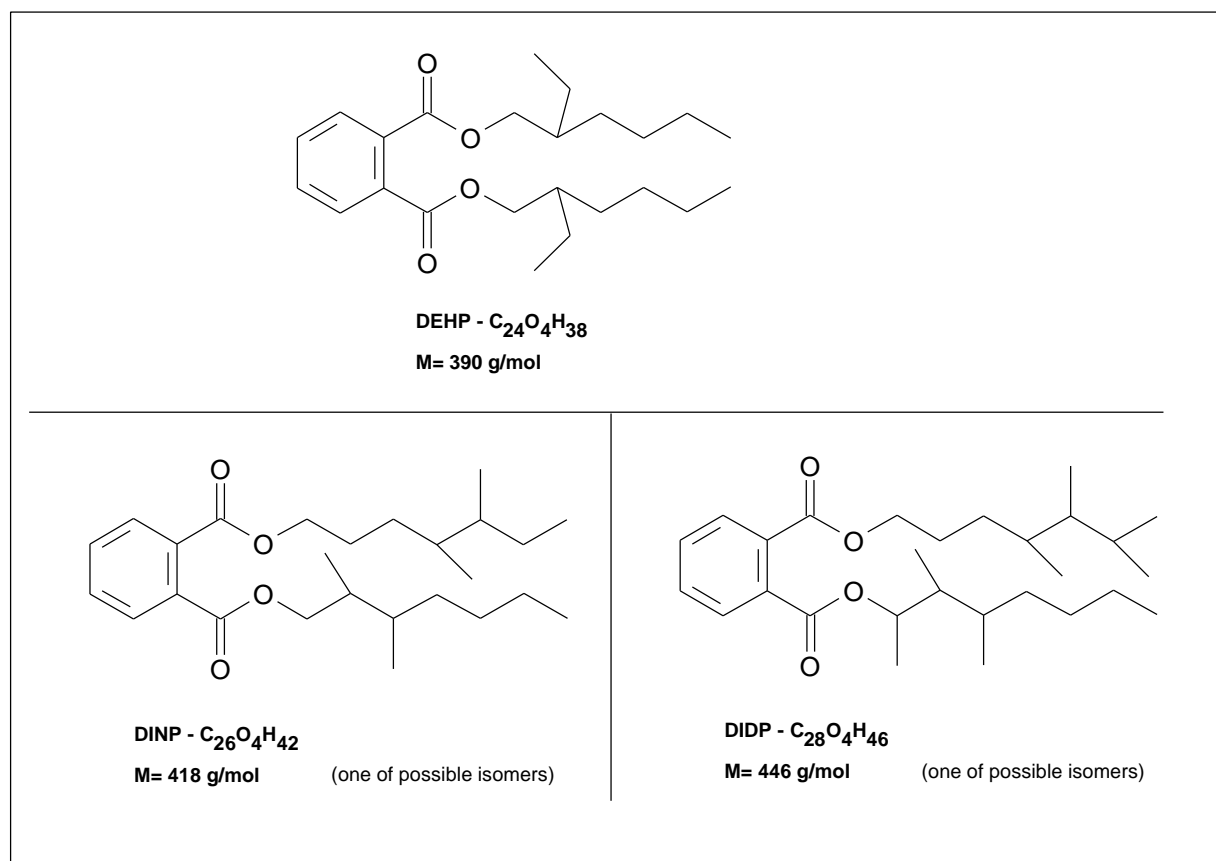


Figure 2: Chemical structure of DEHP, DINP, DIDP

High volume commodity phthalate esters are clear, oily liquids at room temperature. They are soluble in common organic solvents.

2.3 Production routes for phthalate esters under study (DEHP/DINP/DIDP)

High volume commodity phthalate esters are produced by a final esterification reaction consisting of 2 steps (see Figure 3): first, the alcoholysis of PAN to the monoester, second the conversion of the monoester to a diester (reversible reaction).

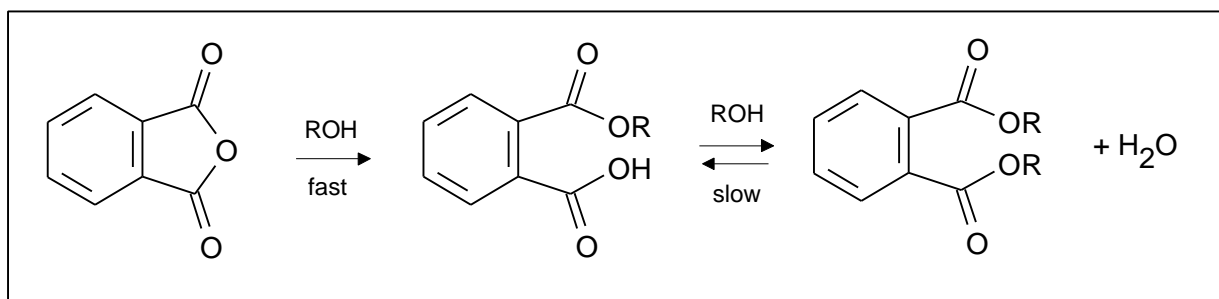


Figure 3: Final esterification reaction to produce phthalate esters

The rate of the overall reaction depends on the choice of the catalyst and the reaction temperature. In order to shift the equilibrium toward the diester, the water produced during the second step of the reaction is removed by distillation. Phthalate esters can be produced continuously or batchwise. A simplified flow chart for the final esterification step of phthalate esters is presented in Figure 4.

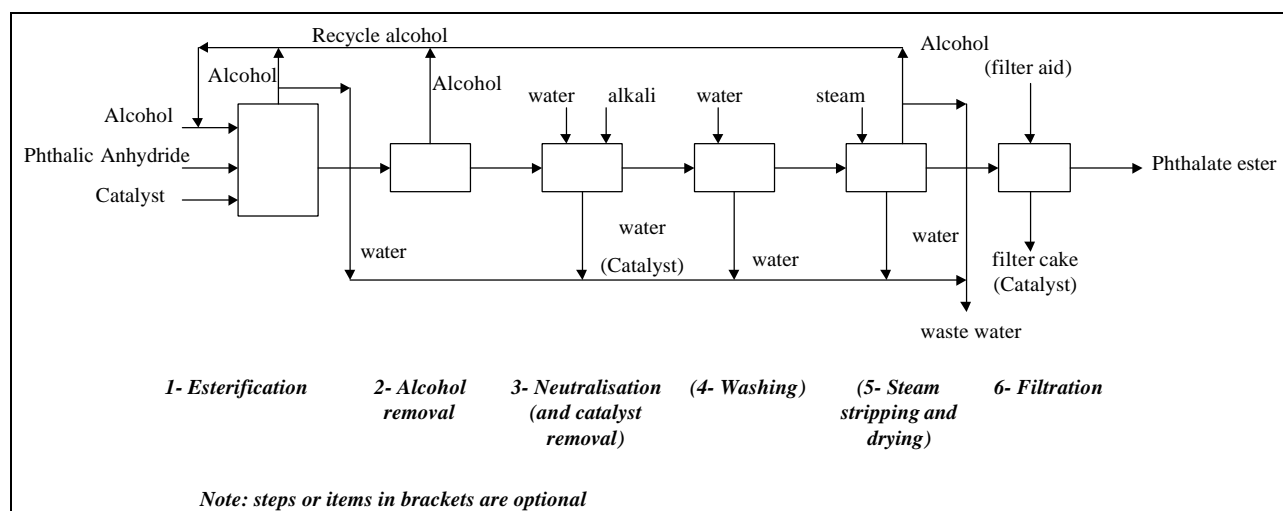


Figure 4: Simplified flow chart for the esterification final step of phthalate esters production

The overall production route of final phthalate esters can be split into the main following steps:

- manufacturing of Phthalic anhydride from *o*-Xylene by oxidation;
- manufacturing of C₈ olefins and C₉ olefins from Propene and Butenes in polygas or dimer units, produced in either steam cracking process or in petrochemical plants;
- manufacturing of the three different oxo alcohols: 2-Ethylhexanol from *n*-Butyraldehyde made by reacting Propene and Syngas, Isononyl alcohol from C₈ olefins and Syngas, and Isodecyl alcohol from C₉ olefins and Syngas;
- manufacturing of the three high volume commodity phthalate esters by esterification between the Phthalic anhydride and the corresponding oxo alcohol.

The respective production routes for DEHP on the one hand, and DINP - DIDP on the other hand, are displayed by Figure 5 and Figure 6.

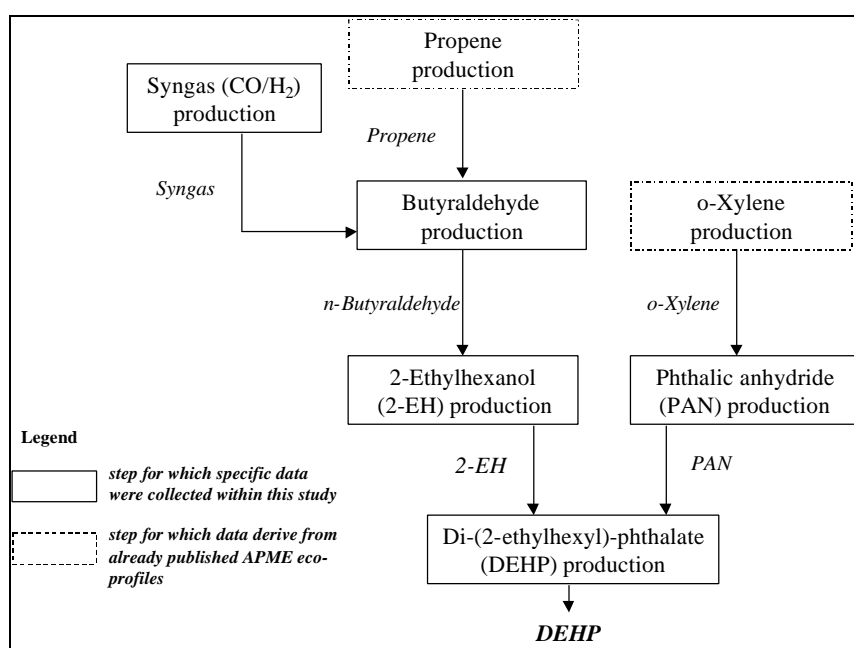


Figure 5: Schematic flow diagram for the production of DEHP

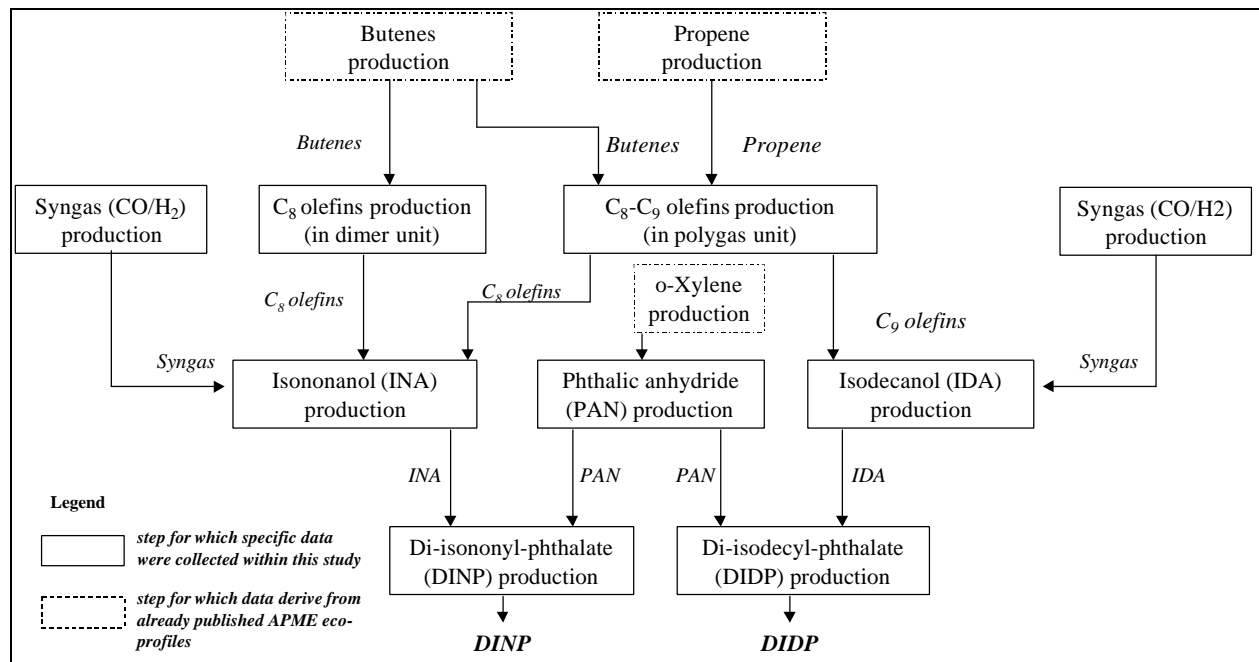


Figure 6: Schematic flow diagram for the production of DINP and DIDP

3 Data sources and quality

The data used for the calculation of the final eco-profile reported here can be split into 4 main categories:

1. Specific site data on intermediates and final phthalate esters (DEHP, DINP, DIDP);
2. Starting raw materials data (o-Xylene, Propene, Butenes, natural gas and naphtha);
3. Fuels and energy data;
4. Ancillary materials and transport.

3.1 Data on intermediates and final phthalate esters

Data sources

Information on the production of the 3 final phthalate esters - DEHP, DINP, DIDP - and on the main intermediates - PAN, C₈ olefins, C₉ olefins, Synthesis gas, n-Butyraldehyde, 2-Ethylhexanol, Isononyl alcohol and Isodecyl alcohol - was supplied by:

- **15 industrial plants** located in Belgium (1 plant), France (3 plants), Germany (4 plants), Italy (1 plant), Netherlands (2 plants), Spain (1 plant), Sweden (2 plants) and UK (1 plant) belonging to
- **8 industrial companies** or group of companies manufacturing intermediates and/or high commodity phthalate esters in Europe: **BASF, BAYER, CELANESE Chemicals, ATOFINA, EXXONMOBIL Chemical, LONZA, NESTE OXO** and **OXENO Olefinchemie**.

All the supplied site data refer to **year 1998**, with some exception of some site data referring to year 1999.

For the data collection step, the production routes of the three phthalate esters were broken down into independent process units or “modules”. Table 1 presents for each process step involving specific site data collection, the number of companies and sites which supplied the data within this study.

	PAN	C8-C9 olefins	SYNGAS	Butyraldehyde	OXO alcohols 2-EH/INA/IDA	Phthalate esters DEHP/DINP/DIDP
Total number of data sets per process step	7	4	7	6	12	12
Total number of sites per process step	7	4	7	6	8	8
Total number of companies per process step	6	3	5	5	6	7

Table 1: Detail of the data sources for the production of intermediates and final phthalate esters

Data collection procedure

The site data on phthalate esters and intermediates were directly collected by ECPI member companies on their plants with the help of a common electronic Excel questionnaire and a methodological guide, both prepared by ECOBILAN for this study. The methodological guide aimed at ensuring a homogeneous data collection step and at avoiding national and regional variations regarding data entry and terminology. The ECPI Eco-profile Expert Working Group was also briefed by ECOBILAN during a training session for the data collection step.

The electronic questionnaire was based on the APME data categories in order to match the APME format, as requested by ECPI. It essentially asked for all the flows that enter (inputs) and all the flows that exit (outputs) the system for a given process step.

The inputs include:

- Energy sources: electricity (grid and on site), steam, natural gas, heavy fuel oil..
- Raw materials/intermediates: Propene, Butenes, o-Xylene, H₂, Syngas...(depending on the synthesis step which is considered);
- Water: from public supply, river/canal, sea, well or with unspecified origin (with the distinction of cooling use and process use).

The outputs include:

- Valuable products: intermediates (PAN, C₈ olefins, C₉ olefins, Butyraldehyde and Syngas), oxo alcohols (2-EH, INA and IDA), final phthalate esters (DEHP, DINP, DIDP) or any valuable co-products;
- Energetic by-products;
- Waste, landfilled or incinerated without energy recovery on the site or out off the gate of the plant;
- By-products that are recovered internally or externally (material recycling or incineration with energy recovery);
- Air emissions (with the distinction of air emissions from process and from fuel use);
- Water effluents (with the distinction of water emissions from process and from fuel use).

Data quality

During the data collection step, plants were asked to qualify each data they were filling by using a quality coding on 3 parameters: source of the data, type of the data and year of the data.

- Three possible sources of data were defined:
 - L: Literature
 - P: Plant, i.e. site specific
 - O: Other: e.g. from other sites or suppliers
- Five types of data were defined:
 - M: Measured: the flow value comes from continuous measurement or daily measurements. For instance, the total electricity consumed is readily available from electricity meters. Coal consumption is continuously measured with weighbridges or other forms of stock accountability.
 - A: Averaged value: the flow value has been extrapolated from spot measurements. For instance, lead air emissions have been measured three times a year, one day each time: from these values the annual value is calculated.
 - C: Calculated: the flow value has been calculated using emission factors, regulation thresholds, mass balance or other indirect methods. For instance, SO_x emission may have been measured for several years, and an emission factor has been determined and used for the subsequent years. Another example is CO₂ air emission calculated from the carbon balance.
 - E: Estimated: the flow value estimation has been established based on approximations. For instance, the transportation distance of some raw material may be estimated because of lack of better information.
 - U: Unknown: This type is only available for data coming from a bibliographic source when the provided information is insufficient to classify the data in the previous types.
- The date of the data is the year which the data refers to (e.g. date of the actual measurement).

Beyond the procedure used for the data collection step (use of a common questionnaire with a specific methodological guide), basic checks on quality data such as mass or element balance, as well as comparison of orders of magnitude from different sites for a same process step, the quality and reliability of the data highly depend on the quality of the records and reporting performed by companies on plants.

Data representivity

The information regarding the representivity of the data collected within this project is summarised in Table 2.

	PAN	Oxo alcohols 2-EH/INA/IDA	Phthalate esters DEHP/DINP/DIDP
Total production covered by the data collection within this study (in ktpa)	360	1 565	840
Representivity within Western Europe	> 45 %	>95 %*	> 80 %

* ECPI estimation

Table 2: Information on the representivity of this eco-profile study

3.2 Starting materials: o-Xylene, Butenes, Propene...

Data on starting raw materials (o-Xylene, Butenes, Propene, naphtha, natural gas) used as feedstock for the process steps involved in the production route of phthalate esters (see Figure 5 and Figure 6, page 9) correspond to the last version of the eco-profiles published in 1999 by APME on its Web site (<http://lca.apme.org>).

3.3 Fuels and energy models

Fuels consumed by plants participating in the study

Except for natural gas, for which the used data correspond to the APME public data, all the information related to fuel production and supply have been derived from the data published in 1996 by the Federal Office for Energy located in Zürich (ETH⁶). These data were adapted by ECOBILAN in order to match the APME eco-profiles data categories and method of accounting energy as gross calorific values instead of net calorific values.

⁶ ETH, Eidgenössische Technische Hochschule, Federal Office of Energy based in Zürich - "Ökoinventare für Energie Systeme"

Grid electricity

Regarding the production of grid electricity, energy breakdowns used in each participating country have been derived from the data published in 2000 by the International Energy Agency⁷ (see details in Table 3) and correspond to the 1998 situation as this is the year the data collected on plants refer to.

% of fuel by country	Belgium	France*	Germany	Italy	Netherlands	Spain	Sweden	UK*	European Union for information
Hard coal	17.0	6.2	27.6	8.8	26.5	26.3	1.3	34.3	19.1
Lignite	0.0	0.3	25.1	0.1	0.0	5.3	0.0	0.0	7.4
Peat		0.0	0.0					0.0	0.3
Process gas (coke oven and blast furnace)	3.2	0.7	1.2	1.7	3.4	0.8	0.7	0.0	1.0
Heavy fuel oil	3.1	2.3	1.1	41.3	3.9	9.0	2.1	1.6	7.7
Natural gas	18.1	1.0	9.8	27.3	57.0	8.3	0.3	32.4	14.7
Nuclear	55.5	75.9	29.1	0.0	4.2	30.2	46.5	28.0	34.3
Hydro (including wind, tide...)	1.8	13.0	4.6	18.6	1.1	19.0	47.2	2.2	13.6
Free electricity (geothermal, solar, renewable fuels)	1.3	0.5	1.6	2.1	4.0	1.2	2.0	1.6	1.9
Distribution losses on the network (in %)	4.7	6.1	4.3	7.1	4.3	9.5	6.6	7.6	6.2

* means that a recycling scheme for used nuclear fuels has been considered

Table 3: Characteristics of grid electricity in 1998 from different fuels, for the countries involved in this study (source: International Energy Agency, July 2000)

Electricity efficiency, production, supply and combustion of each type of fuels, except for hydroelectricity and nuclear electricity, have been derived from data published in 1996 by the Federal Office for Energy (ETH⁸).

For hydroelectricity model, an efficiency of 90 % was applied to convert hydropower to primary energy.

For nuclear electricity, the data of the nuclear cycle and efficiency were derived from previous LCA studies performed by ECOBILAN for the nuclear sector. For UK and France, the existence of a partly recycling scheme of nuclear fuel after its use in powerplant was taken into account.

Important remark: the ECOBILAN models for nuclear electricity production explicitly account for uranium resource consumption and radioactive waste production. For exhaustiveness reason, the ECPI Eco-profile Expert Working Group decided to consider these new categories of flows in the eco-profile. As the APME published eco-profiles don't mention the uranium ore consumption nor the radioactive waste production data, and for consistency reasons, the APME eco-profiles used in this study (o-Xylene, Propene, Butenes...) were adapted by ECOBILAN in order to take into account these flow categories. The conversion factors applied to the APME nuclear energy indicator "Total Gross Primary Nuclear Energy" are presented in Table 4 for transparency reason but also to allow future users of this phthalate esters eco-profile, together with APME published eco-profiles, to adapt the latter with the same rules.

For 1 MJ of nuclear energy appearing in APME eco-profiles	
Uranium ore consumption (in mg)	2.5
Highly Radioactive Waste - from fuel production (in mg)	0.339
Low Radioactive Waste - from fuel production (in mg)	11.5

Table 4: Conversion factors applied to published APME eco-profiles in order to take into account the uranium ore consumption and radioactive waste production

⁷ International Energy Agency – "Energy Statistics of OECD countries –1997 and 1998 year", 2000 edition, published in July 2000

⁸ ETH, Eidgenössische Technische Hochschule, Federal Office of Energy based in Zürich - "Ökoinventare für Energie Systeme"

3.4 Ancillary products and transport data

Data related to transport have been mainly derived from the data published in 1996 by the Federal Office for Energy located in Zürich (ETH⁹). As for energy data, they were adapted by ECOBILAN in order to match the APME eco-profiles data categories and method of accounting energy as gross calorific values instead of net calorific values.

Data related to ancillary products (NaOH, KOH, H₂, sulphuric acid, N₂, O₂, ...) have been derived, whenever possible, from the last version of the APME published eco-profiles and, if not, from ECOBILAN own global LCI database named DEAM^{TM10}.

⁹ ETH, Eidgenössische Technische Hochschule, Federal Office of Energy based in Zürich - "Ökoinventare für Energie Systeme"

¹⁰ DEAMTM: Data for Environmental Analysis and Management. The DEAMTM database is the Ecobilan's vast base of LCI data stemming from its ten years of LCA practice. The DEAMTM LCI modules are constantly updated.

4 Main methodological assumptions

4.1 System boundaries

Definition of the system boundaries

One of the most important methodological steps of a life cycle inventory (LCI) study is the product system definition. The definition of the system considered in this study correspond to a “cradle-to-gate” system and is displayed by Figure 7.

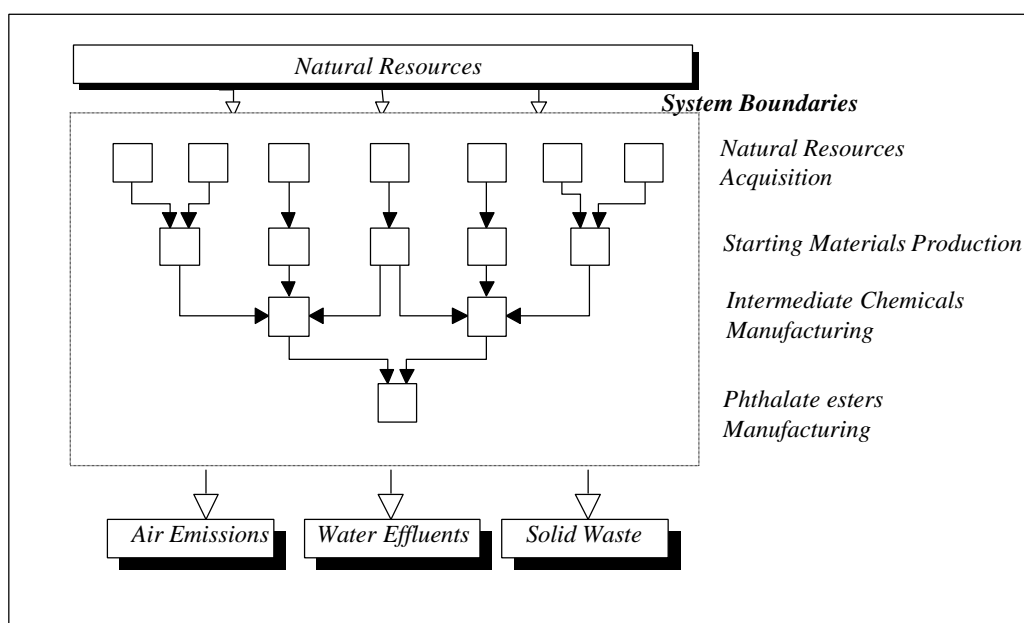


Figure 7: Boundaries of the ECPI system

Inputs

It is quite impossible and of little use to try to record all of the inputs of the process stages. Many inputs are consumed in such small quantities that their contribution to the final LCI can be negligible.

Decision rules have been established, as follows, to restrict data collection to significant inputs. Where data were available, the input flow were asked to be recorded. Where data were not readily available this material may have been omitted according to the following rules:

- 1) All energetic inputs, including energy data, electricity, steam, hot water, compressed air were requested to be recorded.
- 2) 99 % (w/w¹¹) of total process stage inputs were requested to be recorded except for catalysts and packaging inputs, as requested by the ECPI Eco-profile Expert Working Group in order to be consistent with the APME methodology.
- 3) the omitted inputs are considered not to have an important environment burden.

Concerning this third cut-off criteria for data collection, it is difficult to know a priori, whether the environmental burden of a material will contribute significantly to the final LCI result. However it is useful to include the flows that have a high potential environmental burden, should the model be expanded beyond its first scope. Typical criteria for the importance of environmental burden examine whether:

¹¹ w/w: weight/weight

- the material contains any highly toxic compounds such as cyanide, phenol, hexavalent chromium or any other significant hazardous compounds.
- the financial cost is high, since this can be used as an environmental burden indicator (high financial cost is often related to high energy consumption or to a scarcity of the resource).

Solid Waste and by-products

Waste and solid by-products for which the accumulated tonnage represented less than 5 % w/w of the total waste and by-product tonnage of a given process step could be left unrecorded by the plants, unless they contain highly toxic compounds.

Air and water emissions

The air and water emissions list for which plants were asked to supply data corresponds to the APME data categories. However, in order to take into account some specificity of the phthalate esters production route, data on air emissions of phthalic anhydride, alcohols and phthalate esters were also asked. On the contrary, air emissions which are currently considered to have neutral environmental impacts, such as oxygen (O₂), steam and nitrogen (N₂), were not included.

4.2 System modelling and calculation procedure

ECOBILAN built the model corresponding to the whole studied system by using its LCA software tool TEAM^{TM12}, to represent the three high volume commodity phthalate esters production routes. The data sheets from the Excel questionnaires filled by each company/plant were directly downloaded in a common database in TEAMTM, by using automatic procedures. Before this step, the data gathered on-site by companies were reviewed by ECOBILAN who performed some cross-checking operations like checking mass balance, element balances and comparing orders of magnitude. All the inventories were then calculated with the TEAMTM LCA software.

4.3 Averaging methods and data gaps

Intermediate averages

Whenever possible, vertical averaging method (see Figure 8) was used since this method better represents the actual industrial practices.

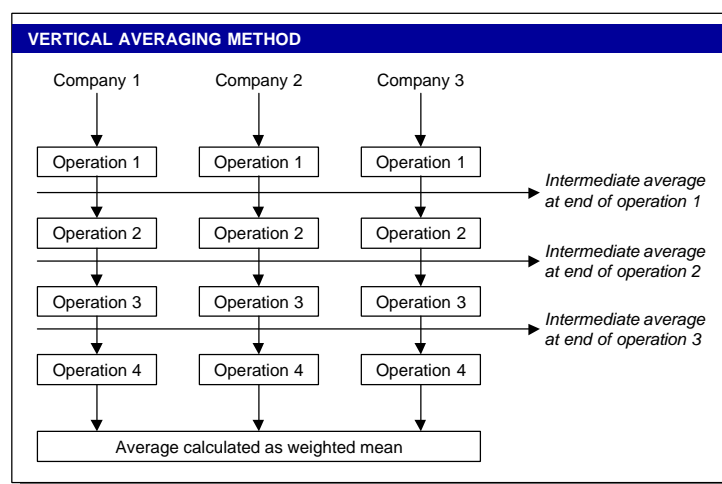


Figure 8: Vertical averaging method

¹² TEAMTM: Tool of Environmental Analysis and Management. Team is the modelling LCA software developed and used by ECOBILAN to describe physical operations. It allows in particular to build a large database and to calculate life cycle inventories for complex systems.

Horizontal averaging method (see Figure 9), based on the production tonnages for which data were supplied by each site, was used in the 2 following situations:

- whenever a company didn't produce an intermediate product necessary to produce the final phthalate ester (for instance, it was the case for some companies regarding PAN or 2-EH)
- whenever a company didn't supply data on common utilities like on-site electricity, on-site steam, compressed air or waste water treatment plant. For the latter, a "standard average" waste water treatment plant was defined in terms of consumption of electricity, COD (Chemical Oxygen Demand) emission and waste production, as well as in terms of degradation rates of main substances. Table 5 summarizes the standard degradation rates that were applied to intermediate water emissions, whenever a plant didn't supply any data regarding the efficiency of its own waste water treatment plant. These rates correspond to the average of the plants that supplied this kind of information.

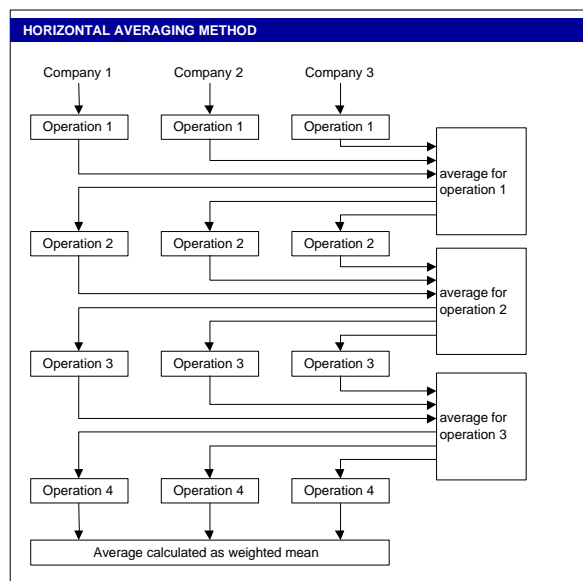


Figure 9: Horizontal averaging method

Type of substance released in water	Source	Average standard degradation rate applied
COD, dissolved organics, hydrocarbons, other organics...	7 plants	90 %
Ammonium and nitrogen matter	2 plants	confidential
Sulphates, sodium, chlorides, metals	By default	0 %

Table 5: Summary of average degradation rates applied within this study to data gaps regarding these parameters

Final average of high volume commodity phthalate esters

The final average corresponding to the eco-profile of high volume commodity phthalate esters was calculated by using the production tonnages of each individual phthalate ester for which data were collected within this study.

4.4 Allocation rules

Material co-products

Mass based allocation rules were applied whenever necessary, i.e. when a product considered in this study was produced all together with valuable products (for instance for n-Butyraldehyde produced all together with Iso-butyraldehyde).

Energy by-products

In the production route of phthalate esters, a few steps like the PAN unit, correspond to exothermic reactions and generate some steam which may be recovered by the site for other applications, included or not in the system boundaries of the study. In that case, the Eco-profile Expert Working Group chose to use the “avoided impacts” method, also referred to as the “credit” method or as a method consisting of an “expansion of the system boundaries”.

This method consists of subtracting the environmental impacts related to the production of the net quantity of steam produced by the system by using a “standard” model of steam production (see Figure 10). For the latter, the subtracted step used in this study corresponds to the on-site steam production model specific to each site whenever available, if not, to the average on-site steam model.

Important remark: this methodological choice is different from the standard APME methodology related to energetic by-products, since in the APME eco-profiles, the energy by-product produced by the system appears as itself in the final eco-profiles under the category “Recovered Energy”.

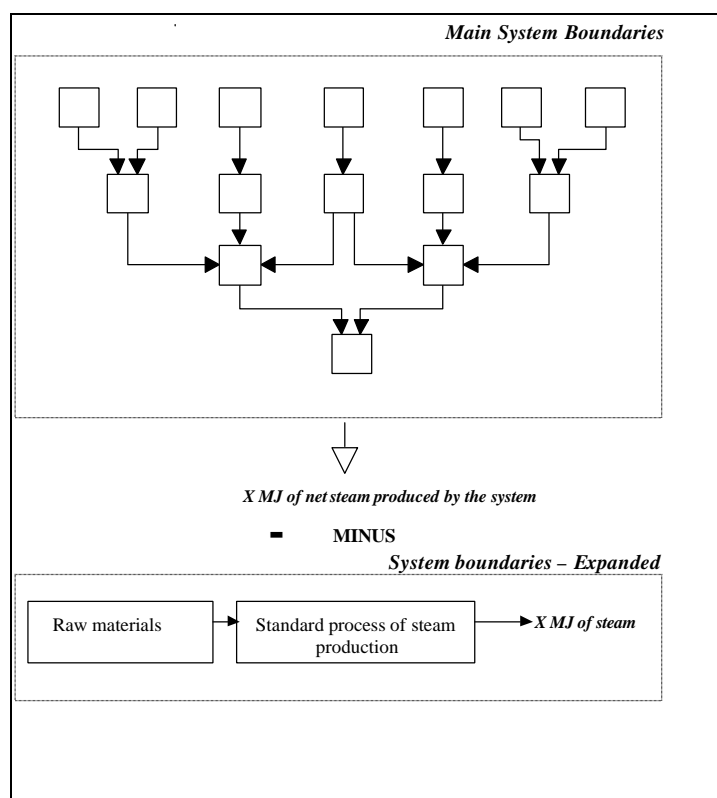


Figure 10: Principle of “avoided impact” method applied for steam by-products within this study

5 Format of the eco-profile results

The final results of the eco-profile presented in this report (section 6) are displayed in the format of eight tables, corresponding to the classical format of APME's eco-profiles, as requested by ECPI. For more information on this format, please refer to the standard APME methodology dealing with eco-profiles of plastics and related intermediates [3]. The main characteristics of these eight tables are described below.

- **Three tables on gross energy requirements.** All energy related calculations of this eco-profile are based on gross calorific values of fuels and feedstocks.
 - The first table (referred to as “energy data”) presents the repartition of energy between 3 groups of energy: electricity, oils and other types of energies. Furthermore, this table details the energy repartition between 4 contributions:
 1. Fuel production and delivery energy
 2. Energy content of delivered fuel
 3. Transport energy
 4. Feedstock energy
 - The second table (referred to as “fuels and feedstocks data”) displays the nature of energy (i.e. coal, oil, gas...), expressed in energetic units (i.e. in MJ). As the first one, this table details the energy repartition between 4 contributions:
 1. Fuel production and delivery energy
 2. Energy content of delivered fuel
 3. Transport energy
 4. Feedstock energy
 - The third table (referred to as “raw material inputs”) displays the mass of necessary energetic resources. As already explained p. 14 of this report, this table also presents the consumption of uranium ore, which is not covered by APME eco-profiles.

- **A table on raw materials consumption.** This table presents the consumption of non-energetic resources.

- **A table on gross water resources requirements.** This table distinguishes cooling water from processing water as well as 5 different categories in terms of water origin:
 1. Public supply
 2. River/canal
 3. Sea
 4. Well
 5. Unspecified origin

- **A table on air emissions,** corresponding to the APME categories. For each value, the total is split into the following sub-divisions:
 1. Fuel production and delivery
 2. Fuel use
 3. Transport

4. Process
5. Biomass

- **A table on water emissions**, corresponding to the APME categories. As for air emission, each value is split into the following sub-divisions:
 1. Fuel production and delivery
 2. Fuel use
 3. Transport
 4. Process
 5. Biomass

- **A table on solid waste production**, split into the APME categories, i.e. mineral, mixed industrial, slags/ash, inert chemical, regulated chemical, construction, metals, plastics, wood waste, waste to incinerator, waste to recycling and unspecified. Moreover, as already explained p. 14 of this report, this table also presents the quantity of radioactive waste which is produced, category which is not covered by the APME eco-profiles. 3 radioactive waste sub categories are distinguished: low radioactive, medium radioactive (produced when the nuclear fuel is recycled) and highly radioactive. As for air and water emissions, each value is split into the following sub-divisions:
 1. Fuel production and delivery
 2. Fuel use
 3. Transport
 4. Process
 5. Biomass

6 Final eco-profile tables

Note: totals may sometimes not agree due to rounding.

6.1 Energy data

Fuel Type	Fuel production and delivery energy (in MJ)	Energy content of delivered fuel (in MJ)	Energy use in transport (in MJ)	Feedstock energy (in MJ)	Total energy (in MJ)
Electricity	2.94	1.34	0.004	0.004	4.29
Oil fuels	0.67	7.86	0.20	24.10	32.84
Other fuels	1.96	10.86	0.05	21.89	34.76
Total	5.57	20.07	0.25	46.00	71.90

Table 6: Gross energy expressed in MJ required to produce 1 kg of high volume commodity phthalate esters

6.2 Fuels and feedstocks data

Fuel Type	Fuel production and delivery energy (in MJ)	Energy content of delivered fuel (in MJ)	Energy use in transport (in MJ)	Feedstock energy (in MJ)	Total energy (in MJ)
Coal	0.63	0.42	0.0005	0	1.06
Oil	0.84	7.97	0.20	24.11	33.11
Gas	2.81	10.73	0.05	22.60	36.19
Hydro	0.06	0.18	0.001	-	0.24
Nuclear	0.90	0.42	0.0002	-	1.32
Lignite	0.34	0.08	0.0002	-	0.42
Wood	0	-	0	0.0001	0.0001
Sulphur	0	0.0002	0.0001	0.022	0.02
Biomass	0.002	0.001	0.0001	0.0001	0.003
Hydrogen	0.0001	0.05	0.0001	-	0.05
Recovered energy	-	-1.64	-	-	-1.64
Unspecified	0.004	1.86	0.0001	-0.73	1.13
Peat	0.0002	0.0001	0.0001	-	0.0003
Total	5.57	20.07	0.25	46.00	71.90

Table 7: Gross primary fuels and feedstock expressed in MJ required to produce 1 kg of high volume commodity phthalate esters

Fuel Type	Input (in mg)
Crude oil	733 190
Gas/condensate	703 427
Coal	45 549
Metallurgical coal	149
Lignite	26 712
Peat	29
Wood	178
Biomass	326
Uranium ore*	3

* cf. § 3.3 , p. 14

Table 8: Gross primary fuels and feedstocks in mg to produce 1 kg of high volume commodity phthalate esters

6.3 Raw material and water inputs

Raw material	Input (in mg)
Air	1 446 800
Barytes (BaSO ₄)	33
Bauxite (Al ₂ O ₃)	477
Bentonite	114
Calcium Sulphate (CaSO ₄)	11
Chalk	0
Chromium	0
Clay	45
Dolomite	5
Feldspar	0
Ferromanganese	0
Fluorspar (CaF ₂)	0
Granite	0
Gravel	47
Iron (Fe)	572
Lead (Pb)	0
Limestone (CaCO ₃)	2 649
Nickel (Ni)	0
Nitrogen (N ₂)	37 256
Olivine	3
Oxygen (O ₂)	125 780
Phosphate (as P ₂ O ₅)	0
Potassium chloride (KCl)	343
Rutile (TiO ₂)	0
Sand	83
Shale	31
Sodium chloride (NaCl)	10 310
Sulphur (bonded)	0
Sulphur (elemental)	2 380
Zinc	0

Table 9: Gross raw materials in mg required to produce 1 kg of high volume commodity phthalate esters

Origin of water	Use for processing (in mg)	Use for cooling (in mg)	Total (in mg)
Public supply	2 048 400	1 280 272	3 328 672
River/canal	808 482	76 420 094	77 228 575
Sea	119 883	66 894 967	67 014 850
Unspecified	699 056	8 398 836	9 097 892
Well	77 845	318 429	396 274
Totals	3 753 666	153 312 597	157 066 263

Table 10: Gross water resources in mg required to produce 1 kg of high volume commodity phthalate esters

6.4 Air emissions data

Emission	From fuel production (in mg)	From fuel use (in mg)	From transport (in mg)	From process operations (in mg)	From biomass use (in mg)	Total (in mg)
Dust	500	174	6	32	-	712
CO	1 173	604	25	13 138	-	14 939
CO ₂	421 699	1 162 500	9 716	242 743	-357	1 836 300
SO _x	1 886	2 833	184	288	-	5 191
NO _x	3 055	2 713	137	153	-	6 058
N ₂ O	2	3.1E-01	1	1.0E-01	-	3
Hydrocarbons	748	243	20	1 306	-	2 317
Methane (CH ₄)	3 902	546	1	170	-	4 618
H ₂ S	1	-	-	2	-	3
HCl	37	1	-	1	-	38
Cl ₂	2.7E-06	-	-	1.2E-01	-	1.E-01
HF	1	2.5E-02	-	1.8E-02	-	1
Lead (Pb)	7.0E-02	6.4E-03	4.5E-04	6.3E-03	-	8.3E-02
Metals (unspecified)	64	2	3.3E-01	2.7E-02	-	66
F ₂	3.3E-05	-	-	6.2E-03	-	6.2E-03
Mercaptans	9.8E-09	6.2E-03	-	3.1E-02	-	3.7E-02
Organo Chlorine	8.0E-08	-	-	7.6E-03	-	7.6E-03
Aromatic hydrocarbons	4	-	2.3E-03	22	-	27
Polycyclic hydrocarbons	7.2E-03	-	8.3E-06	6.2E-03	-	1.3E-02
Other organics (unspecified)	45	-	-	85	-	130
CFC/HCFC	1.3E-02	-	-	4.0E-01	-	4.2E-01
Aldehydes (unspecified)	2.6E-01	-	-	3.0E-01	-	5.6E-01
HCN	1.5E-03	-	-	6.2E-03	-	7.6E-03
H ₂ SO ₄	-	-	-	6.2E-03	-	6.2E-03
Hydrogen (H ₂)	-	-	-	34	-	34
Mercury (Hg)	2.3E-03	-	1.9E-05	9.7E-02	-	9.9E-02
Ammonia (NH ₃)	1.2E-01	-	-	4.3E-01	-	5.5E-01
CS ₂	-	-	-	8.9E-02	-	8.9E-02
DCE	-	-	-	3.4E-08	-	3.4E-08
VCM	-	-	-	1.9E-08	-	1.9E-08
Alcohols (unspecified)	-	-	-	10	-	10
Organic acids (unspecified)	-	-	-	184	-	184
Phthalate esters (unspecified)	-	-	-	7.1E-03	-	7.1E-03
Phthalic anhydride	-	-	-	6	-	6

Table 11: Gross air emissions in mg from the production of 1 kg of high volume commodity phthalate esters

6.5 Water emissions data

Emission	From fuel production (in mg)	From fuel use (in mg)	From transport (in mg)	From process operations (in mg)	Total (in mg)
COD	4	-	-	485	490
BOD	1	-	-	39	40
Acid (H+)	2	-	-	85	87
Dissolved solids	166	-	-	249	415
Hydrocarbons	26	1.6E-01	-	46	72
NH4+	4	-	-	36	40
Suspended solids	29	-	-	251	280
Phenol	2	-	-	1	2
Aluminium (Al+++)	1	-	-	2.9E-01	1
Calcium (Ca++)	199	-	-	1	199
Copper (Cu+ / Cu++)	1.0E-02	-	-	2	2
Iron (Fe ++ / Fe+++)	43	-	-	6.8.E-02	43
Mercury (Hg+ / Hg++)	2.6.E-05	-	-	1.1E-02	1.1E-02
Lead (Pb++ / Pb +++)	4.9.E-02	-	-	2.9E-03	5.2E-02
Magnesium (Mg++)	5	-	-	3.7E-02	6
Sodium (Na+)	1 938	-	-	2 372	4 309
Potassium (K+)	27	-	-	12	39
Nickel (Ni++)	1.9E-02	-	-	5.6E-02	7.4E-02
Zinc (Zn++)	3.8.E-02	-	-	5.8.E-02	9.6E-02
Metals - unspecified	58	-	-	260	319
Nitrate (NO3-)	1	-	-	1	2
Other nitrogen	4	-	-	10	14
CrO3	4.0E-02	-	-	1.5E-02	5.5.E-02
Cl-	3 425	-	-	919	4 344
CN-	5.4E-02	-	-	4.5E-02	9.9E-02
F-	1.7E-01	-	-	9.2E-03	1.8.E-01
SO4--	275	-	-	3 767	4 043
CO3--	7.7E-02	-	-	580	580
Phosphate as P2O5	7.1E-02	-	-	2	2
Arsenic (As+++, As+++++)	3.9E-03	-	-	8.3E-05	4.0E-03
DCE	-	-	-	5.6E-11	5.6E-11
VCM	-	-	-	6.0E-25	6.0E-25
Detergent/oil	37	-	-	73	110
Dissolved Cl2	-	-	-	2.5E-02	2.5E-02
Organo-chlorine	3	-	-	7.4E-02	3
Dissolved organics	1	-	-	39	40
Other organics	2	-	-	49	51
Sulphur/sulphide	1.0E-01	-	-	1	1

Table 12: Gross water emissions in mg from the production of 1 kg of high volume commodity phthalate esters

6.6 Waste data

Waste type	From fuel production (in mg)	From fuel use (in mg)	From process operations (in mg)	Total (in mg)
Mineral waste	28 214	-	2 498	30 712
Mixed industrial waste	121	-	638	759
Slag/ash	2 680	83	1 530	4 293
Inert chemical waste	5	-	832	837
Regulated chemical waste	200	-	2 430	2 630
Unspecified waste	323	-	46	368
Construction waste	-	-	50	50
Metals waste	-	-	10	10
Waste to incinerator	40	-	4 971	5 011
Waste to recycling	18	-	6 702	6 720
Paper & board waste	-	-	-	-
Plastic waste	-	-	14	14
Wood waste	-	-	2.9E-01	2.9E-01
Highly radioactive waste*	3.8E-01	-	-	3.8E-01
Intermediate radioactive waste*	4.3E-01	-	-	4.3E-01
Low Radioactive waste*	53	-	-	53
Unspecified radioactive waste*	6	-	-	6

* cf. § 3.3 , p. 14

Table 13: Gross solid waste in mg from the production of 1 kg of high volume commodity phthalate esters

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