Non-surfactant Organic Ingredients and Zeolite-based Detergents

Final Report

prepared for the European Commission

RPA

June 2006

NON-SURFACTANT ORGANIC INGREDIENTS AND ZEOLITE-BASED DETERGENTS

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by

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EXECUTIVE SUMMARY

Background

During the 1970s and 1980s, there was concern that the use of detergents containing sodium tripolyphosphate (STPP) was contributing to the problems of eutrophication. As a consequence, there was a move towards non-phosphate (or ‘phosphate free’) detergents. This resulted in a large increase in the use of zeolite based detergents (together with the associated necessary co-builders) from the mid-1980s to the mid-1990s.

Although the Scientific Committee on Toxicity, Ecotoxicity and the Environment concluded that the use of zeolites would not lead to any toxicological or ecotoxicological problems, it recommended that consideration should be given to the health and environmental risks associated with the co-builders. More generally, there are concerns over the potential impacts on the environment associated with the wide range of chemicals substances added to detergents. Although considerable progress has been made in relation to surfactants, culminating in the recently implemented Detergents Regulation, there remains some concern over other chemicals with particular reference to organic compounds.

As a consequence, DG Enterprise contracted Risk & Policy Analysts Ltd (RPA) to review these issues and the findings are presented in this report.

Detergents

The overall consumption of detergents in the EU-25 is probably of the order of six million tonnes per year. Most detergents are used in the household (especially for laundry and dish washing).

Modern detergents may contain 30 or more ingredients. The main ingredients are surfactants which perform the cleaning process through surface chemical reactions. The environmental behaviour and fate of surfactants has been the subject of extensive research which has led, most recently, to the Detergents Regulation, which regulates the nature of surfactants used in detergents with particular regard to their biodegradability.

Builders are another important group of ingredients which assist the cleaning process by removing calcium and magnesium ions. Historically, many detergents contained sodium tripolyphosphate (STPP) but moves towards non-phosphate laundry detergents resulted in a large increase in the use of zeolite based detergents (together with the associated necessary co-builders) from the mid-1980s to the mid-1990s. However, it is important to note that detergents used in dishwashers are still generally phosphate-based.

The focus of this study is on the current use of organic co-builders and other organic non-surfactant ingredients and associated implications in terms of risks to people and to the environment. It was the intention that this would build on earlier research undertaken for the Commission and take into account of the views of the Scientific Committee on Toxicity, Ecotoxicity and the Environment. Furthermore, it was hoped that the analysis would facilitate comparison of the costs and benefits of moving from phosphate to zeolite based detergents.

Identifying Ingredients of Potential Concern

For this study, a list of 50 non-surfactant ingredients (both organic and inorganic) was derived with a focus on those used in household laundry and dish washing detergents. This list was based on those ingredients identified in the Specification with additional ingredients identified in detergent products. It is, of course, accepted that, in recent months, companies have taken further steps to provide comprehensive listings of ingredients in their products as well as associated data sheets (as required by the Detergents Regulation). Furthermore, it is accepted that some of the ingredients (including fragrances) which are now listed (in the public domain) as being present in detergents are not considered in this report.

For each of these ingredients, a one-page summary of key properties (physico-chemical, toxicological and environmental) was prepared. These summaries provided a basis for determining whether or not a particular ingredient was likely to be of potential concern. Particular attention was given to those organic ingredients which were not readily biodegradable or had other properties of particular concern. In relation to inorganic ingredients, the only one of concern was sodium perborate which is widely used (in various forms) in detergents as a bleaching agent. The issue is over the potential classification of sodium perborate as Toxic to Reproduction Category 2.

Based on a review of the ingredient properties, eleven groups of detergent ingredients were identified as being of potential concern comprising:

- phosphonates;
- polycarboxylates;
- EDTA and EDTA tetrasodium salt;
- nitrilotriacetic acid (NTA);
- detergent dyes;
- dye transfer inhibitors with particular reference to polyvinylpyrrolidone (PVP);
- fluorescent whitening agent FWA-5;
- foam regulators with particular reference to paraffins (assumed to be C_{10}-C_{16} *n*-paraffins) and polydimethyl siloxane (PDMS);
- formulation aids with particular reference to the use of polyetheylene glycols (PEG) with higher molecular weights (greater than, say, 2000);
- anti-redeposition agents with particular reference to the use of carboxymethyl-cellulose (CMC) and other polymers; and
- solvents with particular reference to the use of 1-decanol and triethanolamine.

At the outset of this study, it was envisaged that the moving from phosphate to zeolite based detergents would involve replacing the phosphate with zeolites together with a number of other necessary ingredients (termed co-builders). In practice, it has been found that many of these co-builders, such as phosphonates and polycarboxylates, are used in both types of detergents. In other cases, notably EDTA and NTA, their use in household detergents is limited and the overall consumption has not changed significantly with the move (in some countries) to phosphate-free detergents.

Further Analysis of the Ingredients of Potential Concern

For each group of ingredients of potential concern (as listed above), further analysis involved:

- a review of (published) risk assessments;
- a review of monitoring data (with particular emphasis on waste water treatment and surface waters);
- further discussion on degradation pathways; and
- determining whether further work was required.

It is important to stress that comprehensive data on the identified groups are not available - with particular reference to monitoring data. Nevertheless, for some ingredients, such as EDTA, there are detailed risk assessments and extensive monitoring data from a few countries. For other ingredients, notably dyes, there is a lack of published information on which to comment. A summary of the analysis is presented in the table below. The entries highlighted in bold are those where there is potential concern (including those for which there are considerable data uncertainties).

Summary of Further Analysis of Ingredients of Potential Concern

Ingredient	**Conclusion from Analysis**
Phosphonates	**There is a broad consensus that phosphonates degrade slowly and may present a risk to the environment with concern being focused on the potential aquatic chronic toxicity of HEDP (and its salts) to *Daphnia*. It is of note that there appears to be no monitoring data on HEDP (and/or its salts). Although most of the phosphonates (used in household detergents) will end up in sewage sludge of which some is applied to agricultural land, available data indicate that the terrestrial toxicity of phosphonates is very low. On this basis, the presence of phosphonates in sewage sludge does not present a significant risk.**
Polycarboxylates	Although polycarboxylates do not readily biodegrade, it is unlikely that their use in detergents would lead to significant risks to consumers or to the environment due to their low toxicity and ecotoxicity. However, there are no available monitoring data and concentrations in sludge-treated soils may be significant.
EDTA and EDTA tetrasodium salt	**Available data indicate that EDTA and its salts may be of concern to the environment with regard to their use in industrial and institutional (I&I) cleaning - but not for household detergents (where their use is limited). Apart from the direct risk, there is the potential for the (soluble) EDTA to mobilise metals from sediments and soils leading to contamination of surface and ground waters. However, the EDTA RAR notes that the associated risk is not expected to be significant.**
Nitrilotriacetic acid (NTA)	**Although NTA appears not to be of concern to the environment, its presence in a detergent (as for EDTA) excludes the award of an eco-label due to its potential carcinogenicity. NTA, trisodium salt has recently been classified as a Category 3 Carcinogen with an R40 label. Further discussions (at EU level) on the results of the (as yet unpublished) human health risk assessment are imminent.**
Detergent dyes	**At this stage, it is not possible to conclude that dyes do not present any human or environmental risks. However, on the other hand, no evidence has been identified to suggest that dyes present a potential problem.**
Dye transfer inhibitors: polyvinyl-pyrrolidone (PVP)	PVP is ‘safe’ for human use and there appears to be a general consensus that PVP is of limited environmental concern. Nevertheless, further data would be desirable to demonstrate that PVP presents no significant environmental risks.

Summary of Further Analysis of Ingredients of Potential Concern	
Ingredient	**Conclusion from Analysis**
Fluorescent whitening agent FWA-5	**The reported concentrations of FWA-5 in the environment are more than an order of magnitude below the PNEC. On this basis, FWA-5 is unlikely to present a significant risk to people or to the environment. However, there remains the possibility that the degradation products are of potential concern.**
Foam regulators: paraffins (assumed to be C10-C16 *n*-paraffins) and polydimethyl siloxane (PDMS)	In relation to *n*-paraffins, it is unlikely that significant amounts will reach the environment due to a combination of rapid biodegradation and waste water treatment. Nevertheless, available data on properties such as aquatic toxicity and bioaccumulation are highly uncertain which make it difficult to conclude with confidence that the risks to the environment are of no concern. The use of PDMS in detergents contributes to its presence in soils and sediments. Although considered persistent, PDMS degrades in the environment - particularly in dry, clay soils. Furthermore, there are few concerns over the risks associated with the higher molecular weight PDMS compounds as used in detergents.
Detergent formulation aids:- polyetheylene glycols (PEG)	Due to its high solubility, low bioaccumulation potential and low toxicity, there is little to suggest that PEG presents any significant risk to the environment - even allowing for the fact that higher molecular weight PEGs are not readily biodegradable.
Anti-redeposition agents: carboxy-methylcellulose (CMC)	It is unlikely that the use of CMC in detergents presents significant risks to people or to the environment due, primarily, to its low toxicity. However, further data on levels found in the environment would provide further substantiation of this view.
Solvents: 1-decanol and **triethanolamine**	It is unlikely that the use of 1-decanol in detergents presents significant risks to people or to the environment due, primarily, to its rapid biodegradation. **Further data are required to reach a conclusion on whether triethanolamine is likely to be of concern.**

With reference to the above table, there are three key observations:

- many detergents contain ingredients which may be of concern in relation to the associated risks, primarily, to the environment;
- for many of the ingredients, there remains considerable uncertainty as to their environmental fate (based on available published information); and
- although the rate of biodegradation is a significant factor, there is little doubt as to whether a particular ingredient readily biodegrades or not.

Benefits of Moving to Zeolite Detergents

The key benefit associated with moving from phosphate to zeolite detergents is reducing the phosphorus load to the environment which, in turn, will reduce problems of eutrophication. In qualitative terms, the greatest benefits would accrue in those countries with a high phosphate detergent use, a low provision of tertiary treatment (resulting in significant phosphorus loads being discharged directly to rivers/lakes/seas) and existing severe problems of eutrophication. On the other hand, countries with limited phosphate detergent use would obtain few benefits from any future requirement to move to zeolite (or other phosphate-free) detergents.

These three parameters (phosphate detergent use, provision of tertiary treatment, problems of eutrophication) were assessed for each of the EU-25 countries using a simple scoring system and the results are summarised in the table below.

Benefits of Moving to Phosphate-Free Detergents		
Score	**Description**	**Countries**
>10	Maximum Benefits	Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal, Slovakia
5-10	Some Benefits	Greece, Cyprus, Estonia, UK, Luxembourg, Hungary, Belgium, France
1-5	Few Benefits	Denmark, Finland, Austria, Sweden, Ireland, Slovenia, Italy, Netherlands, Germany
0	No Benefits	Malta

Whilst it is acknowledged that the approach is fairly simplistic, it does demonstrate that the (potential) benefits associated with moving to phosphate-free detergents vary significantly from country to country. As already indicated, in those countries which are already ‘phosphate-free’ or have no eutrophication issues (i.e. Malta), there are generally few benefits to be obtained. However, there could be significant benefits in some countries (notably Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal and Slovakia).

Although determining economic values for such benefits is complex, there is another benefit of reducing the costs of phosphorous removal. Based on consideration of the UK, an upper bound estimate (for the EU-25) of €2bn was derived. Clearly, this is an estimate which is open to debate on several grounds. By way of example, under the Urban Waste Water Directive, tertiary plants will be required for larger population centres so that associated (capital) costs cannot be avoided. Similarly, reduction in phosphate loads (through moving to zeolite detergents) may not remove the need to provide additional tertiary treatment under the Water Framework Directive (or indeed, under the Habitats Directive) due to the phosphate load from human excretia.

Costs of Moving to Zeolite Detergents

Disruption of Phosphate Supply Chain

It is reported that there are six EU manufacturers of STPP which clearly would be affected in the event of a further move towards zeolite detergents. However, such losses would be offset, to a greater or lesser extent, by an expansion of activities within the EU-based zeolite producers.

Reformulation and Rebranding

Although it might be expected that some of the larger formulators would find it relatively easy to substitute one phosphate detergent with a comparable zeolite detergent currently marketed elsewhere, the situation becomes more complex where there are smaller formulators (which are likely to include SMEs) serving only the domestic market with phosphate detergents. A change in formulation may well place such formulators at a disadvantage leading to a loss of their market share to the large international companies - particularly in those countries with limited experience of zeolite detergent formulation (such as Poland). The average costs of reformulation (with particular regard to costs associated with performance testing) have been assumed to be

€20k per formulation. For 1,000 formulations, this could lead to reformulations costs of €20m or more.

It is worth noting that the current co-existence of phosphate and zeolite detergents in many countries suggests that there would a limited impact on the costs of detergent products to consumers. In other words, there is not a significant price differential between phosphate and zeolite detergents.

Increase in Risks to People and the Environment

Based on the discussion presented above, it is unlikely that a move from phosphate to zeolite based detergents would lead to a significant increase in risks to people and the environment. However, further confirmatory evidence of this would be desirable.

Additional Costs for Testing

Biodegradation testing is relatively inexpensive. An indicative screening test may cost as little as €500 although a comprehensive test with a full report for submission to regulators will cost several thousand euros (or more depending on the test selected).

More generally, however, the analysis presented in this report suggests that the issue of biodegradation testing is unlikely to be a key issue since most of the ingredients studied have been shown to be either clearly persistent or readily biodegradable. It is accepted that, in some cases, further testing will be required under REACH irrespective of whether the ingredient is destined for zeolite and/or phosphate detergents. It is important to stress that, under the current proposals, the requirements of REACH do not extend to polymers and, of course, vary with different tonnage bands.

Even where extensive data on properties exist, it is likely that there will be a need for further assessments of the risks in some cases. Clearly, this process has progressed significantly in recent years through the industry-led HERA project assessments and the ESR assessments being undertaken by the Competent Authorities.

Summary of Costs and Benefits

Based on the analysis presented above, it would appear that there would be significant benefits in moving from phosphate to zeolite based detergents. The benefits would be greatest amongst some of the new Member States (Czech Republic, Poland, Latvia, Lithuania and Slovakia) as well as Spain and Portugal.

However, the necessity for reformulation of detergents would also impact most upon smaller companies (SMEs) producing detergents for the domestic market in these countries. There may also be costs in terms of increased risks to people and to the environment associated with the increased use of those ingredients used in zeolite based detergents. Although there appear to be few such concerns in those countries which are now phosphate-free, uncertainties remain as highlighted above.

Discussion of the Way Forward and Recommendations

Detergents are used extensively throughout the European Union. From a chemical risk management perspective, they may be characterised as having a wide dispersive use and as being used in high volumes. It is therefore desirable to ensure that detergent ingredients do not present risks to human health or to the environment.

The use of sodium tripolyphosphate (STPP) as the main builder in detergents contributes to the phosphorous load in the environment which, in turn, contributes to problems of eutrophication. Although moves to phosphate-free laundry detergents have reduced this load, it is important to note that most detergents for dishwashing machines are phosphate-based.

Recommendation 1): the detergents industry should be encouraged to develop phosphate-free detergents for dishwashing machines.

Although the development of phosphate-free detergents involves the development of new products or reformulation of existing phosphate-based products, this study has found that many of the 50 ingredients found in leading household detergents may be used in both phosphate and phosphate-free detergents. It is important to note that the overall number of ingredients used in detergents (including cleaning products more generally) within the EU-25 will be significantly greater than these 50 identified ingredients. The Detergents Regulation now requires information on these ingredients to be made more widely available.

Although no evidence has been found to suggest that ingredients used in detergents (whether or not phosphate-based) are, in practice, particularly harmful to people or to the environment, there a number of ingredients over which there remain uncertainties on their properties, environmental fate and associated risks.

It is recognised that, for some of these substances, the requirements of REACH will ensure that more comprehensive data on basic properties and associated health and environmental effects are collated and published. However, REACH does not currently extend to polymers.

Recommendation 2): discussions should be held with the detergents industry to agree a data set (on properties, health and environmental effects) which could be collated and published for the various polymers used in detergents.

It is recognised that whether or not a particular ingredient may be classified as ‘readily biodegradable’ provides a useful screening tool. However, the analysis presented in this report suggests that, even for persistent ingredients, there may be no associated risks (i.e. the PEC/PNEC ratio is less than one) due to environmental degradation and/or low environmental toxicity. Given the range of current detergent ingredients which are not readily biodegradable, it is not considered practicable to impose a ready biodegradation criterion (in a similar manner as for surfactants under the Detergents Regulation). However, there is a need for an analysis of the associated risks which takes account of the life-cycle of the ingredient. By way of example, such an assessment would consider not only the degradation of the ingredient but also the rate of degradation of the metabolites and their associated risks. Similarly, if a particular ingredient was found to be removed in waste water treatment by adsorption to the sludge, further information on the potential effects of adding such sludge to agricultural soil should be obtained. It is of course accepted that such studies have been undertaken for many of the ingredients considered in this report by Competent Authorities (under the ESR programme), the industry-led HERA programme and other industry groups (such as the CEEP study on PDMS).

It may be the case that where detergent ingredients have been studied and that the associated risk assessments demonstrate that there are no risks, then these ingredients could be declared 'no risk'. This, in turn, creates the possibility of formulating detergents with 'no risk' ingredients.

Although further moves to phosphate-free detergents would reduce the phosphorous load on the environment, the relative importance of the various sources of phosphorous and their associated contributions to eutrophication at a regional level have yet to be fully established. As such, there remains a degree of uncertainty over the benefits of moving to phosphate-free detergents, as well as the over the risks, depending on the ingredients used.

Recommendation 3): the use of phosphate-free detergents should not be encouraged unless all the ingredients can be demonstrated to present no risks to people or to the environment.

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1. INTRODUCTION

1.1 Background

During the 1970s and 1980s, there was concern that the use of detergents containing sodium tripolyphosphate (STPP) was contributing to the problems of eutrophication. As a consequence, there was a move towards non-phosphate (or 'phosphate free') detergents. This resulted in a large increase in the use of zeolite based detergents (together with the associated necessary co-builders) from the mid-1980s to the mid-1990s.

Although the Scientific Committee on Toxicity, Ecotoxicity and the Environment[1] concluded (CSTEE, 2003a) that the use of zeolites would not lead to any toxicological or ecotoxicological problems, it recommended that consideration should be given to the health and environmental risks associated with the co-builders.

More generally, there are concerns over the potential impacts on the environment associated with the wide range of chemicals substances added to detergents. Although considerable progress has been made in relation to surfactants, culminating in the recently implemented Detergents Regulation[2], there remains some concern over other chemicals with particular reference to organic compounds.

As a consequence, DG Enterprise contracted Risk & Policy Analysts Ltd (RPA) to review these issues and the findings are presented in this report.

1.2 Objectives of this Study

The full Specification for this study is attached as Annex 1. In summary, the study involves two parts - Part I relates to non-surfactant (organic) chemicals and Part II relates to zeolites.

More specifically, the objectives of Part I are to:

- collate available data on use and properties for a representative range of non-surfactant organic chemicals;
- review available test methods for determining biodegradation;
- collate available information on environmental impacts (and associated assessments); and
- assess costs and benefits of imposing biodegradation requirements (for non-surfactant organic chemicals) on the detergents industry.

And, in summary, the objectives of Part II are to:

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[1] Now the Scientific Committee on Health and Environmental Risks (SCHER).

[2] Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents (OJ L104, 8/4/2004, p1).

- collate available data on use and properties of STPP and zeolite-based detergents;
- evaluate the associated health and environmental risks; and
- assess costs and benefits of switching from STPP to zeolite-based detergents.

As became clear during the course of the study, there is considerable overlap between the two parts and, for this reason, this report attempts to address the various objectives within a single coherent report.

1.3 Structure of Report

Section 2 provides an overview of the use of detergents (and other cleaning products) across the EU-25. Particular consideration is given to the relative proportions of phosphate and zeolite based detergents being used in different countries. Further consideration is given to the typical make-up of zeolite based detergents with particular reference to the nature and composition of zeolites and the co-builders being marketed.

Section 3 outlines the relevant properties of the key constituents of phosphate and zeolite based detergents drawn from a representative list of 50 non-surfactant chemicals. Section 3 also provides an initial screening of the hazard potential of each of the chemicals with particular emphasis on biodegradation issues.

Section 4 discusses in more detail previous assessments and monitoring data relevant to those chemicals which merit further consideration.

Section 5 provides a commentary on the likely implications upon the environment (and human health) associated with the move from phosphate to zeolite based detergents, including a qualitative review of the likely ‘costs’ and ‘benefits’.

The overall findings of the study are summarised in Section 6. Given the wide range of chemicals considered in this report, much of the information has been presented in Annexes to minimise the length of the main report.

2. USE OF DETERGENTS

2.1 Overall Consumption

2.1.1 Overview

Article 1 of the Detergents Regulation defines a detergent as:

> *any substance or preparation containing soaps and/or other surfactants intended for washing and cleaning processes. Detergents may be in any form (liquid, powder, paste, bar, cake, moulded piece, shape, etc.) and marketed for or used in household, or institutional or industrial purposes.*

The overall consumption of detergents across the EU-25 is probably of the order of six million tonnes/year with a market value approaching €30bn (AISE, undated).

Most of these detergents are used for laundry (and dishwashers). Although the per capita consumption varies from country to country, there is a general consensus that the average annual consumption of detergents (for laundry/dishwashers) is about 10 kg per person which equates to an annual EU-25 consumption of about 4.5 million tonnes (since there are now over 450 million people in the 25 Member States of the European Union (Eurostat, 2004)). The European household detergent market, with a value of over €23bn, is dominated by three large companies (Proctor & Gamble, Henkel and Unilever (Lever Faberge)). Dishwashing detergents account for about €3bn of this market with an approximately equal split between detergents for hand and machine washing. Additional major companies in this field include Reckitt Benckiser and Colgate Palmolive (Mintel, 2006).

The smaller non-household (usually referred to as industrial and institutional (I&I)) detergent market, with a value of over €6bn, is more fragmented with two large companies (Ecolab-Henkel and JohnsonDiversey) accounting for, perhaps, 40% of the market with the remainder dominated by SMEs providing specialist products across a wide range of applications (AISE, undated; Johnson *et al*, 2005).

The focus of this report is on the use of phosphate and zeolite based household detergents and associated ingredients (although reference is also made to their use in I&I products). Although the chemical composition of (phosphate and non-phosphate) detergents is continually being refined to maximise washing efficiency, the main ingredients have remained relatively constant over the last 20 years. However, in parallel, the physical form has also evolved from regular powders of the 1980s to the compact powders of the 1990s to the dense tablets of the 2000s. This process of evolution has resulted in smaller quantities of detergents being required to achieve the same washing efficiency.

Apart from technological and cultural reasons, the other key reason for variability in consumption is water hardness. In broad terms, water is harder in the southern Member States resulting in higher rates of detergent consumption that in northern Member States where water tends to be soft.

2.1.2 Use of Phosphate-Based Detergents

For this study, there is particular interest in the use of phosphate-based detergents and of their alternatives. The two main uses of phosphate-based detergents are in laundry detergents and in dishwashing machines (i.e. dishwashers).

As already indicated, there was a move to phosphate-free detergents from the mid-1980s to the mid-1990s as shown in Table 2.1. However, it is important to stress that this applies only to laundry detergents. Although there are a few phosphate-free detergents for dishwashers, the leading brands are all phosphate-based.

Table 2.1: Degree to which EU25 countries are Phosphate-Free (Laundry Detergents)

Country	**Population[1] (millions)**	**%Phosphate-Free[2,3]**
Belgium	10.4	100%
Czech Republic[4]	10.2	35%
Denmark	5.4	80%
Germany	82.5	100%
Estonia	1.3	20%
Greece	11.0	50%
Spain	42.2	40%
France	59.9	50%
Ireland	4.0	100%
Italy	57.8	100%
Cyprus	0.7	***20%***
Latvia	2.3	***20%***
Lithuania	3.4	***20%***
Luxembourg	0.4	***100%***
Hungary	10.1	30%
Malta	0.4	***20%***
Netherlands	16.2	100%
Austria	8.1	100%
Poland	38.2	15%
Portugal	10.4	30%
Slovenia	2.0	95%
Slovakia	5.4	***20%***
Finland	5.2	90%
Sweden	9.0	85%
United Kingdom	59.5	55%
EU-25	**456.0**	**66%**

Notes:
1) *Population data taken from Eurostat (2004).*
2) *Percentage figures taken from ZeoDet (2000) and WRc (2002).*
3) *Figures in* ***bold italics*** *are RPA estimates in the absence of further data.*
4) *It is understood that the Czech Republic has recently taken steps to become 'phosphate-free'.*

2.1.3 Use of Laundry Detergents

Various estimates can be found which provide an indication of the per capita consumption of detergents in EU countries. Two authoritative estimates are summarised in Table 2.2.

Table 2.2: Per Capita Consumption (kg/yr) of Laundry Detergents across the EU-25 Countries

Country	**Data from WRc (2002)**	**Data from IBM (2002)**	**%Phosphate -Free[1]**	**Mean Consumption (kg/yr)**	
				Phosphate Detergents	**P-free Detergents**
Belgium	7.6	9.7	100%	0.0	8.7
Czech Republic	1.7		35%	1.1	0.6
Denmark	5.8	5.2	80%	1.1	4.4
Germany	6.0	7.7	100%	0.0	6.8
Estonia			20%		
Greece	5.9	9.8	50%	3.9	3.9
Spain	6.1	11.4	40%	5.3	3.5
France	7.7	9.9	50%	4.4	4.4
Ireland	11.4	9.0	100%	0.0	10.2
Italy	7.2	11.7	100%	0.0	9.5
Cyprus			***20%***		
Latvia			***20%***		
Lithuania			***20%***		
Luxembourg		9.7	***100%***	0.0	9.7
Hungary	3.9		30%	2.7	1.2
Malta			***20%***		
Netherlands	6.5	7.3	100%	0.0	6.9
Austria	7.3	6.9	100%	0.0	7.1
Poland	9.6		15%	8.2	1.4
Portugal	4.3	11.3	30%	5.5	2.3
Slovenia			95%		
Slovakia			***20%***		
Finland	6.3	4.2	90%	0.5	4.7
Sweden	5.0	4.5	85%	0.7	4.1
United Kingdom	9.7	8.3	55%	4.1	5.0

Notes:

1) *From Table 2.1.*

A further source of data is the extensive work undertaken into eutrophication of the Danube basin (BUA, 2003) which includes estimates of the use of phosphates in laundry detergents as summarised in Table 2.3.

Table 2.3: Consumption (kg/yr/person) of Phosphate Laundry Detergents in the Danube Basin

Country	**Table 2.2 Estimate**	**Based on[1] BUA (2003)**	**Comment**
Czech Republic	1.1	4.3	BUA figure likely to be more robust and carried forward in the analysis.
Germany	0.0	0.0	In agreement
Hungary	2.7	3.5	Reasonable agreement but higher BUA figure carried forward in the analysis
Austria	0.0	0.0	In agreement
Slovenia	no data	0.9	BUA figure suggests that Slovenia is perhaps 90% (rather than 95%) phosphate-free
Slovakia	no data	2.4	BUA figure carried forward in the analysis

Notes:

1) *Figures in BUA (2003) presented as consumption of Phosphorous and have been increased by a factor of 16 (since sodium tripolyphosphate (STPP) contains about 25% Phosphorous and phosphate detergents contain about 25% STPP).*

2.1.4 Use of Detergents for Dishwashing

There are two broad types of dishwashing detergents:

- phosphate detergents used in dishwashing machines (dishwashers); and
- liquid detergents (based on fatty acids) used for washing dishes by hand.

In broad terms, the quantity of detergent used per unit of dishwashing is similar whether washed by machine or by hand. Although the precise quantity of detergents used in dishwashers does vary from country to country[3], for simplicity an average value of 30g per dishwasher use will be used in the analysis. Data on social indicators (including dishwasher ownership) from the late 1990s for the EU-25 countries have been presented by the European Commission (2004). Estimates of more recent ownership have been derived from consideration of recent market research data (Mintel, 2006).

Recent market research data indicate that the average dishwasher usage in the EU is about 4.5 times/week (Mintel, 2006). This, in turn, suggests an annual consumption of 7.0 kg of phosphate-based detergents per dishwasher owning household and, by implication, an annual consumption of 7.0 kg of washing-up liquid detergents per household without a dishwasher[4].

Detailed analysis of dishwashing practices (Stamminger *et al*, 2004) suggests that the amount of dishwashing liquid does vary significantly by country (due to water hardness and cultural reasons). Data for nine countries have been used to generate a usage factor for all EU-25 countries.

The above factors were used to estimate the overall consumption of phosphate-based detergents in dishwashers as shown in Table 2.4. For completeness, the corresponding figures presented in WRc (2002) and BUA (2003) have been included.

Table 2.4: Consumption of Dishwasher Detergents across the EU-25 Countries

Country	**Pop'n[1] (millions)**	**No. of Hsehlds[2] (millions)**	**%Hsehlds with Dish Washer[3]**	**Consumption (kt/yr)**		**Per capita (kg/yr)**	
				RPA[4]	**WRc (2002)**	**RPA**	**BUA (2003)**
Belgium	10.4	4.3	44%	13.5	*15.0*	1.3	
Czech Republic	10.2	4.2	6%	1.8	*0.0*	0.2	*0.2*
Denmark	5.4	2.4	49%	8.4	*10.0*	1.6	
Germany	82.5	38.5	52%	141.1	*158.0*	1.7	*1.3*
Estonia	1.3	0.6	1%	0.1		0.0	
Greece	11.0	4.0	36%	10.0	*9.0*	0.9	
Spain	42.2	14.5	34%	34.9	*25.0*	0.8	
France	59.9	24.6	49%	84.2	*168.0*	1.4	

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[3] By way of example, tablet sizes of leading brands in the UK are less than 25g whereas those in Spain are closer to 40g.

[4] It is, of course, accepted that dishwashing by hand will also occur in households with a dishwasher. As such, the household consumption will be slightly lower in households without dishwasher than that assumed.

Table 2.4: Consumption of Dishwasher Detergents across the EU-25 Countries

Country	Pop'n[1] (millions)	No. of Hsehlds[2] (millions)	%Hsehlds with Dish Washer[3]	Consumption (kt/yr)		Per capita (kg/yr)	
				RPA[4]	WRc (2002)	RPA	BUA (2003)
Ireland	4.0	1.3	39%	3.7	*3.0*	0.9	
Italy	57.8	22.0	38%	58.3	*36.0*	1.0	
Cyprus	0.7	0.2	36%	0.5		0.7	
Latvia	2.3	0.8	0%	0.0		0.0	
Lithuania	3.4	1.3	4%	0.3		0.1	
Luxembourg	0.4	0.2	54%	0.6		1.5	
Hungary	10.1	3.9	3%	0.8	*1.0*	0.1	*0.1*
Malta	0.4	0.2	6%	0.1		0.2	
Netherlands	16.2	7.0	42%	20.5	*21.0*	1.3	
Austria	8.1	3.3	54%	12.5	*13.0*	1.5	*1.3*
Poland	38.2	13.2	3%	2.7	*6.0*	0.1	
Portugal	10.4	3.6	36%	9.1	*2.0*	0.9	
Slovenia	2.0	0.7	32%	1.5		0.8	*1.4*
Slovakia	5.4	1.7	3%	0.3		0.1	*0.1*
Finland	5.2	2.4	51%	8.5	*7.0*	1.6	
Sweden	9.0	4.5	51%	15.9	*9.0*	1.8	
United Kingdom	59.5	25.1	36%	63.2	*85.0*	1.1	
EU-25	**456.0**	**184.3**	**38%**	**492.5**		**1.1**	

Notes:

1) Population data taken from Eurostat (2004).

2) No. of households derived from Eurostat census data.

3) Percentage figures based on dishwasher ownership figures (as percentage of households) presented in European Commission (2004) and updated using data from Mintel (2006).

4) Household consumption based on 7 kg/yr for dishwasher owning households.

As can be seen, there is a reasonably good agreement between the RPA derived figures and those previously presented in WRc (2002) although that previously presented for France seems unusually high. Similarly, there is reasonably good agreement between the figures derived by RPA and those presented in BUA (2003). With these points in mind, the RPA figures will be carried forward in the analysis.

Similar calculations were undertaken to derive the consumption of detergents used in dishwashing by hand as summarised in Table 2.5.

Table 2.5: Consumption of Hand Dishwashing Detergents across the EU-25 Countries

Country	Pop'n[1] (millions)	No. of Hsehlds[1] (millions)	% with No Dish Washer[2]	Usage Factor[3]	Consumption	
					kt/yr[4]	per capita (kg/yr)
Belgium	10.4	4.3	56%	0.7	11.8	1.1
Czech Republic	10.2	4.2	94%	**0.7**	19.1	1.9
Denmark	5.4	2.4	51%	0.7	6.0	1.1
Germany	82.5	38.5	48%	**0.7**	90.0	1.1
Estonia	1.3	0.6	99%	0.7	2.7	2.0
Greece	11.0	4.0	64%	1.4	25.5	2.3
Spain	42.2	14.5	66%	**1.2**	79.8	1.9
France	59.9	24.6	51%	**1.3**	114.0	1.9
Ireland	4.0	1.3	61%	**0.9**	5.2	1.3

Table 2.5: Consumption of Hand Dishwashing Detergents across the EU-25 Countries

Country	Pop'n[1] (millions)	No. of Hsehlds[1] (millions)	% with No Dish Washer[2]	Usage Factor[3]	Consumption	
					kt/yr[4]	per capita (kg/yr)
Italy	57.8	22.0	62%	**2.0**	191.7	3.3
Cyprus	0.7	0.2	64%	1.4	1.3	1.8
Latvia	2.3	0.8	100%	0.7	3.8	1.7
Lithuania	3.4	1.3	96%	0.7	5.9	1.7
Luxembourg	0.4	0.2	46%	0.7	0.4	0.9
Hungary	10.1	3.9	97%	0.7	18.6	1.8
Malta	0.4	0.2	94%	1.4	1.4	3.6
Netherlands	16.2	7.0	58%	0.7	20.0	1.2
Austria	8.1	3.3	46%	0.7	7.6	0.9
Poland	38.2	13.2	97%	**0.7**	62.6	1.6
Portugal	10.4	3.6	64%	**1.2**	19.7	1.9
Slovenia	2.0	0.7	68%	1.4	4.5	2.3
Slovakia	5.4	1.7	97%	0.7	7.9	1.5
Finland	5.2	2.4	49%	0.7	5.7	1.1
Sweden	9.0	4.5	49%	0.7	10.9	1.2
United Kingdom	59.5	25.1	64%	**0.9**	101.2	1.7
EU-25	**456.0**	**184.3**	**62%**		**817.1**	**1.8**

Notes:

1) *Population/household data as in Table 2.4.*
2) *Percentage figures based on those presented in Table 2.4.*
3) *Usage factors derived from Stamminger (2004). Those in bold are reported values (although that for Italy has been slightly reduced) and other values have been interpolated by RPA.*
4) *Household consumption based on 7 kg/yr for non-dishwasher owning households as corrected by the 'usage factor'.*

2.1.5 Summary of Laundry and Dishwashing (L&D) Detergent Consumption

Combining the data presented in Tables 2.2 to 2.5 enables the overall consumption of detergents in laundry and dishwashing to be determined as indicated in Table 2.6.

Table 2.6: Per Capita Consumption of Laundry and Dishwashing Detergents

Country	Laundry[1]		Dishwashing[2]		L&D Detergents
	P-based	P-free	P-based	P-free	
Belgium	0.0	8.7	1.3	1.1	11.1
Czech Republic	4.3	2.3	0.2	1.9	8.6
Denmark	1.1	4.4	1.6	1.1	8.2
Germany	0.0	6.8	1.7	1.1	9.6
Estonia	??	??	0.0	2.0	??
Greece	3.9	3.9	0.9	2.3	11.1
Spain	5.3	3.5	0.8	1.9	11.5
France	4.4	4.4	1.4	1.9	12.1
Ireland	0.0	10.2	0.9	1.3	12.4
Italy	0.0	9.5	1.0	3.3	13.8
Cyprus	??	??	0.7	1.8	??
Latvia	??	??	0.0	1.7	??
Lithuania	??	??	0.1	1.7	??
Luxembourg	0.0	9.7	1.5	0.9	12.1
Hungary	3.5	1.5	0.1	1.8	6.9

Table 2.6: Per Capita Consumption of Laundry and Dishwashing Detergents

Country	Laundry[1]		Dishwashing[2]		L&D Detergents
	P-based	P-free	P-based	P-free	
Malta	??	??	0.2	3.6	??
Netherlands	0.0	6.9	1.3	1.2	9.3
Austria	0.0	7.1	1.5	0.9	9.6
Poland	8.2	1.4	0.1	1.6	11.3
Portugal	5.5	2.3	0.9	1.9	10.6
Slovenia	0.9	8.3	0.8	2.3	12.3
Slovakia	2.4	0.6	0.1	1.5	4.5
Finland	0.5	4.7	1.6	1.1	8.0
Sweden	0.7	4.1	1.8	1.2	7.8
United Kingdom	4.1	5.0	1.1	1.7	11.8

Notes:

1) *Figures from Table 2.2 with revisions to figures for Czech Republic, Hungary, Slovenia and Slovakia as indicated in Table 2.3. Note that P-free detergents are generally zeolite-based detergents.*
2) *Figures from Tables 2.4 and 2.5. Note that P-based detergents are used in dishwashers and P-free detergents are generally fatty acid based as used for dishwashing by hand.*

2.1.6 Household Detergent Consumption

Within the home, detergents are mainly used for laundry and dishwashing. A relatively small amount of detergents is also used for cleaning purposes. Some estimates of the overall consumption of household detergents have been located and these are summarised in Table 2.7, together with estimates of the L&D consumption derived in Table 2.6.

Table 2.7: Per Capita Consumption (kg/yr) of Detergents across the EU-25 Countries

Country	L&D Detergents[1]	Household Detergents[2]	Household Detergents[3]
Belgium	11.1	10.6	
Czech Republic	8.6		
Denmark	8.2	6.4	
Germany	9.6	8.1	
Estonia	??		
Greece	11.1	10.2	11.3
Spain	11.5	12.4	11.4
France	12.1	11.7	11.4
Ireland	12.4	9.6	
Italy	13.8	12.6	11.2
Cyprus	??		12.8
Latvia	??		
Lithuania	??		
Luxembourg	12.1	10.6	
Hungary	6.9		
Malta	??		11.2
Netherlands	9.3	7.4	
Austria	9.6	7.7	
Poland	11.3		
Portugal	10.6	12.1	11.3
Slovenia	12.3		11.2
Slovakia	4.5		

Table 2.7: Per Capita Consumption (kg/yr) of Detergents across the EU-25 Countries

Country	**L&D Detergents**[1]	**Household Detergents**[2]	**Household Detergents**[3]
Finland	8.0	3.8	
Sweden	7.8	4.5	
United Kingdom	11.8	10.0	

Notes:
1) From Table 2.6.
2) HERA data for consumption of 'household detergents' as outlined in Fox (2001).
3) Estimates of (household?) detergent consumption from UNEP (2002) based on AISE data.

Although there is reasonable agreement for most countries, it is clear that deriving the consumption of 'other' household detergents by taking the difference between two larger values (one for 'total' consumption and one for 'laundry and dishwashing') with their associated uncertainties is not possible.

By inspection of Table 2.7, it was considered that some further assumptions could be made to fill the gaps in the RPA derived figures:

- the L&D consumption figures for Malta and Cyprus are likely to be about 11.0 and 12.5 kg/year respectively; and
- in the absence of reliable data, the L&D consumption figures for Estonia, Latvia and Lithuania have all been taken as 5.5 kg/yr.

These assumptions were used to revise the figures in Table 2.6 as shown in Table 2.8.

Table 2.8: Per Capita Consumption of Laundry and Dishwashing Detergents

Country	**Laundry**[1]		**Dishwashing**		**L&D Detergents**[1]
	P-based	**P-free**	**P-based**	**P-free**	
Belgium	0.0	8.7	1.3	1.1	11.1
Czech Republic	4.3	2.3	0.2	1.9	8.6
Denmark	1.1	4.4	1.6	1.1	8.2
Germany	0.0	6.8	1.7	1.1	9.6
Estonia	***2.7***	***0.7***	0.0	2.0	***5.5***
Greece	3.9	3.9	0.9	2.3	11.1
Spain	5.3	3.5	0.8	1.9	11.5
France	4.4	4.4	1.4	1.9	12.1
Ireland	0.0	10.2	0.9	1.3	12.4
Italy	0.0	9.5	1.0	3.3	13.8
Cyprus	***8.0***	***2.0***	0.7	1.8	***12.5***
Latvia	***3.1***	***0.8***	0.0	1.7	***5.5***
Lithuania	***2.9***	***0.7***	0.1	1.7	***5.5***
Luxembourg	0.0	9.7	1.5	0.9	12.1
Hungary	3.5	1.5	0.1	1.8	6.9
Malta	***5.8***	***1.5***	0.2	3.6	***11.0***
Netherlands	0.0	6.9	1.3	1.2	9.3
Austria	0.0	7.1	1.5	0.9	9.6
Poland	8.2	1.4	0.1	1.6	11.3
Portugal	5.5	2.3	0.9	1.9	10.6
Slovenia	0.9	8.3	0.8	2.3	12.3
Slovakia	2.4	0.6	0.1	1.5	4.5

Table 2.8: Per Capita Consumption of Laundry and Dishwashing Detergents

Country	Laundry[1]		Dishwashing		L&D Detergents[1]
	P-based	P-free	P-based	P-free	
Finland	0.5	4.7	1.6	1.1	8.0
Sweden	0.7	4.1	1.8	1.2	7.8
United Kingdom	4.1	5.0	1.1	1.7	11.8
EU-25	**2.8**	**5.2**	**1.1**	**1.8**	**10.9**

Notes:
1) Figures in bold italics have been derived from assumptions presented above.

By inspection of Table 2.8, the per capita consumption of (laundry and dishwashing) detergents varies from about 4.5 kg/yr (Slovakia) to 13.8 kg/yr (Italy) with a mean EU-25 value of 10.9 kg/year. Furthermore, in general, southern countries use more detergents than northern ones. It is important to note that dishwashers account for over 25% of the total phosphate detergent consumption.

2.1.7 Quantities of Detergents Used

By combining the per capita figures with population numbers, it was possible to estimate the quantities of phosphate, zeolite and fatty acid based detergents used on an annual basis. Since there are concerns over the use of phosphate-based detergents, Table 2.9 ranks the EU-25 countries by their use.

Table 2.9: Consumption of Laundry and Dishwashing Detergents (kt/year)

Country	P-based	Zeolite	Fatty acid	Totals
France	347	263	114	724
Poland	316	55	63	433
United Kingdom	305	295	101	701
Spain	257	148	80	485
Germany	141	564	90	795
Portugal	66	24	20	110
Italy	58	547	192	796
Greece	53	43	25	122
Czech Republic	45	23	19	88
Hungary	36	15	19	70
Sweden	22	36	11	70
Netherlands	21	111	20	151
Denmark	14	24	6	44
Belgium	13	90	12	116
Slovakia	13	3	8	25
Austria	12	58	8	78
Finland	11	25	6	42
Lithuania	10	2	6	19
Latvia	7	2	4	13
Cyprus	6	1	1	9
Ireland	4	41	5	50
Estonia	4	1	3	7
Slovenia	3	17	5	25
Malta	2	1	1	4
Luxembourg	1	4	0	5
EU-25	**1769**	**2393**	**817**	**4979**

Table 2.9 shows that across the EU-25 nearly 1.8 million tonnes of phosphate-based detergents are used per year for laundry and dishwashers. Four countries (France, Poland, UK and Spain) account for 70% of this consumption. Although Germany is 'phosphate-free' with respect to laundry detergents, it is the fifth largest consumer of phosphate detergents due to their use in dishwashers.

The annual consumption of zeolite laundry detergents is nearly 2.4 million tonnes with the Germany and Italy each accounting for over 20% of the total consumption. The annual consumption of fatty acids (as used for hand dishwashing) is about 0.8 million tonnes with Italy as the largest consumer.

2.2 Overview of Detergents

Broadly speaking, all detergents comprise a range of chemicals which may be grouped according to their function. The key groups of chemicals are surfactants, builders, solvents, bleaches, performance additives and water. Three of the main groups of detergents are those based on fatty acids (such as washing up liquids), phosphates (especially for laundry and dishwashers) and phosphate-free detergents based on zeolites.

Typical compositions are illustrated in Table 2.10.

Table 2.10: Indicative Composition of Detergent Types

Group	Fatty Acid	Phosphate	Zeolite
Surfactants	35%	15%	20%
Builders	12%	50%	47%
Solvents	12%	n/a	n/a
Bleaches	n/a	20%	20%
Performance Additives	1%	5%	8%
Water	40%	10%	5%

Sources: MFG (1996), WRc (2002)

A key aspect of this study is to compare detergents based on phosphates and on zeolites. The main difference between these two types of detergents is the main 'builder' as shown in Table 2.11 although zeolite detergents use additional co-builders with particular reference to polycarboxylates. However, it is important to note that some phosphate detergents also use polycarboxylates[5].

Table 2.11: Typical Builders by Detergent Types

Detergent Type	Main Builder	Typical Co-builders
Phosphate	Sodium Tripolyphosphate (STPP)	Sodium Silicate[1], Sodium Carbonate
Zeolite	Zeolite	Sodium Silicate[1], Citric Acid, Sodium Carbonate, Polycarboxylates

Note 1): Sodium silicate is also a corrosion inhibitor (which is important for machine washing).
Sources: MFG (1996), WRc (2002)

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[5] By way of example, one of the leading UK phosphate-based dishwashing tablets contains 5-15% polycarboxylates.

2.3 Use of Phosphate Detergents

2.3.1 Overview of Consumption

Sodium tripolyphosphate (STPP) was the main builder used in (powder) detergents from the late 1940s to the 1980s. Phosphate-free detergents based on zeolites were introduced in the mid-1980s and progressively replaced STPP-based detergents through to the mid-1990s when the markets stabilised. With an assumed concentration of around 25% STPP in phosphate detergents, the peak consumption (in the early 1980s) was probably in excess of 1 million tonnes of STPP/year (equivalent to 0.25 million t (as P)/year) which has now more than halved due to the introduction of zeolites[6].

Within the EU-25, the major use of phosphates is in fertilisers with an estimated consumption of around 3.5 million t (as P_2O_5)/year (equivalent to around than 1.5 million t (as P)/year) (IFA, 2004; EFMA, 2005). On this basis, it appears that, currently, STPP-based detergents account for less than 10% of the phosphates used in fertilisers.

2.3.2 Composition of STPP Detergents

Although there are numerous formulations of phosphate detergents, Table 2.12 provides an indication of the typical compositions of the main product types used in laundry detergents. It is interesting to note that, to some extent, the inclusion of compact powders is somewhat academic since, for all practical considerations, all compact laundry detergents introduced in the 1990s were zeolite-based (Smulders, 2002).

Table 2.12: Indicative Composition of STPP (Laundry) Detergents

Physical Form:	**Conventional Powder**	**Compact Powders**	**Tablets**
Period of Growth:	**pre-1990**	**1990s**	**2000s**
Surfactants	12%	14%	15-18%
Builders			
- STPP	20-25%	50%	25-47%
- Polycarboxylates	0%	0%	2%
- Phosphonates	0-0.2%	0%	0%
- Sodium Silicate	6%	5%	0%
- Sodium Carbonate	5%	4%	0%
Bleaches			
- Sodium Perborate (and/ or Percarbonate)	14%	10%	12-16%
- Activators	0-2%	3%	4-7%
Performance Additives	12-35%	6%	2-15%
Water	Balance	Balance	0%

Sources: WRc (2002), Smulders (2002)

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[6] With reference to Table 2.9, the current consumption of phosphate detergents is estimated to be about 1.8 million tonnes per year which equates to about 450,000 t/year of STPP. This is comparable with a recent industry estimate of 300,000 t/year for Western Europe (CEEP, 2005). Since the phosphorous content of STPP is 25%, these figures indicate a current consumption of about 100,000 tP/year.

2.4 Use of Zeolite Detergents and Co-Builders

2.4.1 Overview of Consumption

Zeolite A appeared in reduced phosphate detergents in 1976 and in phosphate-free detergents in 1983 (ZeoDet, 2000). Over the next decade, sales of zeolite detergents increased dramatically to take over 60% of the market share from phosphate detergents - a situation which has now stabilised.

Although new zeolites (such as Zeolites P and X) have been introduced, the dominant builder remains Zeolite A (and the development of zeolites is discussed further in Annex 2).

2.4.2 Composition of Zeolite Based Detergents

As for phosphate detergents, there are numerous formulations of zeolite detergents. Table 2.13 provides an indication of the typical compositions of the main product types used in laundry detergents.

Table 2.13: Indicative Composition of Zeolite (Laundry) Detergents

Physical Form:	**Conventional Powder**	**Compact Powders**	**Tablets**
Period of Growth:	**pre-1990**	**1990s**	**2000s**
Surfactants	13%	15%	19%
Builders			
- Zeolite A	25%	25%	25%
- Polycarboxylates	4%	5%	3%
- Phosphonates	0.4%	0.2%	0%
- Sodium Silicate	4%	3%	3%
- Sodium Carbonate	12%	15%	3%
Bleaches			
- Sodium Perborate (and/ or Percarbonate)	24%	15%	15%
- Activators	2%	5%	5%
Performance Additives	1.5%	1%	7-15%
Water	Balance	Balance	0%

Sources: ZeoDet (2000), WRc (2002), Smulders (2002)

Perhaps the most striking feature that emerges from a comparison of Tables 2.12 and 2.13 is that the main difference in the composition of modern-day high density tablets is the choice of the main builder. This is different from the situation previously in that moving from phosphate to zeolites involved changing both the main builder and the associated ingredients. In other words, for tablets, the ingredients used are very similar whether using STPP or Zeolite A as the main builder. Indeed, some of the leading brands of tablets contain both phosphates and zeolites as the primary ingredients.

With these points in mind, it may become increasingly difficult to differentiate between phosphate and zeolite detergents on the basis of the risks associated with the co-builders and with the other ingredients.

3. NON-SURFACTANT CHEMICALS

3.1 Introduction

Apart from the main builders (such as STPP or zeolite), detergents contain numerous ingredients. Table 3.1 lists the main groups of non-surfactant chemicals (as listed in the Specification) together with an outline of their role in detergents.

Table 3.1: Detergent Ingredients

Chemical Ingredient	Purpose
Acids and bases	To ensure optimal pH of wash water
Bleaching agents, activators and stabilisers	Enhanced cleaning
Builders, complexing agents and ion exchangers	To maximise cleaning efficiency (i.e. removing dirt and keeping in suspension)
Corrosion inhibitors	To prevent corrosion of washing machines
Dyes	To add colour to detergents
Dye transfer inhibitors	To prevent loss of garment dyes
Enzymes	'Biological' cleaning
Fluorescent whitening agents	Optical brightening
Foam regulators	To limit foam generation (machine washing)
Formulation aids	To improve detergent performance
Soil repellents/anti-redeposition agents	To prevent re-deposition of dirt during washing
Solvents	To keep ingredients in solution (particularly in liquid detergents)

The next step was to derive a representative list of the main ingredients for each group of chemicals. The starting point was the list of chemicals identified in the Specification which had been developed by DG Enterprise in consultation with industry. However, numerous other ingredients were identified from labels on detergent boxes and from information sheets available from manufacturers on the major brands in different Member States. Further potential ingredients were identified from published HERA[7] reports and other sources.

Although it had been hoped that the implementation of the Detergents Regulation (on 8 October 2005) would facilitate the provision of information by industry as to the precise contents of detergents currently on the market[8], such information was not forthcoming. As a consequence, the Consultants prepared a 'composite' list of 50 specific ingredients identified in the Specification and/or in major brands. This composite list was accepted by both DG Enterprise and industry as being representative of those ingredients currently on the market within the EU-25 and this forms the basis of the analysis which follows.

It is, of course, accepted that, in recent months, companies have taken further steps to provide comprehensive listings of ingredients in their products as well as associated data

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[7] Human & Environmental Risk Assessment on ingredients of European household cleaning products (HERA) is an ongoing industry-led programme which has produced numerous reports (www.hera.org).

[8] As specified in Annex VII (to the Detergents Regulation), data on ingredients including names, CAS numbers and an indication of concentrations are required in the form of data sheets available on the Internet.

sheets. Furthermore, it is accepted that some of the ingredients (including fragrances) which are now listed (in the public domain) as being present in detergents are not considered in this report.

For each of the ingredients on the composite list, a brief overview of its use and associated properties is presented below. In addition, Annex 3 provides a one-page summary (for each ingredient) of physicochemical, human/mammalian and environmental toxicity properties. These properties are drawn from various published sources including IUCLID[9], industry reports (with particular regard to those from the HERA project) and ESR[10] risk assessments.

The structure of the Annex 3 one-page summaries follows the requirements proposed under REACH[11]. It is important to stress that these summaries are **not** intended to be definitive nor authoritative but, rather, they are intended to provide an indication of whether data are readily available and, if so, whether particular properties (such as biodegradation or aquatic toxicity) are likely to be of concern. Based on the identified properties, consideration has also been given as to whether the various ingredients might be classified as PBT (persistent, bioaccumulative and toxic) and/or vPvB (very persistent and very bioaccumulative) substances using the characteristics[12] shown in Table 3.2.

Table 3.2: Proposed PBT and vPvB Criteria (from Annex XII, REACH Proposal)

Criterion	**PBT criteria**	**vPvB criteria**
P (persistent)	Half-life > 60 d in marine water or > 40 d in fresh/estuarine water or > 180 d in marine sediment or > 120 d in fresh/estuarine water sediment or > 120d in soil	Half-life > 60 d in marine or fresh/estuarine water or >180 d in marine or fresh/ estuarine water sediment or >180d in soil
B (bioaccumulative)	BCF > 2,000 (measured value)	BCF > 5,000
T (toxic)	Chronic NOEC < 0.01 mg/l or CMR or there is other evidence of chronic toxicity, as identified by the classifications: T, R48, or Xn, R48 according to Directive 67/548/EEC	Not applicable

For completeness, CMRs are substances which are carcinogenic, mutagenic, or toxic for reproduction and the classification T, R48 is defined as: Toxic - danger of serious damage to health by prolonged exposure; and Xn, R48 as: Harmful - danger of serious damage to health by prolonged exposure.

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[9] International Uniform Chemical Information Database. IUCLID reports dated 18/19 February 2000 for many HPV chemicals (those produced in quantities of >1,000 t/year by a single manufacturer) are available from the ECB's European chemical Substances Information System (ESIS) on http://ecb.jrc.it

[10] Existing Substances Regulation (Council Regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances (OJ, L84, 5/4/1993, p1)).

[11] As set out in Annexes V to VIII in the Proposals for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (COM(2003), 644 final dated 29/10/2003).

[12] It should be noted that the characteristics proposed under REACH are essentially the same as used in the Technical Guidance Document for undertaking ESR Risk Assessments (EC, 2003).

3.2 Acids and Bases

3.2.1 Identified Chemicals

Table 3.3 lists those acids and bases identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.3: Acids and Bases

No.	Substance Group	Substance	CAS No.	Identified in Specification[1]	Identified in Major Brands[2]
1	Acid	Acetic acid	64-19-7	y	
2	Acid	Citric acid	77-92-9	y	y
3	Acid	Adipic acid	124-04-9		y
4	Base	Sodium hydroxide	1310-73-2		y

Notes:

1) As discussed in Section 3.1, these ingredients are those identified in the Specification (see Annex 1).

2) As discussed in Section 3.1, these ingredients are those identified by the Consultants as being present in major brands on the market (based on inspection of product labels and from information available from detergent manufacturers).

3.2.2 Commentary

Acids and bases are present in relatively low concentrations within many detergents, particularly citric acid. HERA (2005) estimates that the total consumption of citric acid (and citrates) to be about 100,000 t/year (in household cleaning products).

All four ingredients are ‘high production volume’ (HPV) chemicals and data (on most parameters) are readily available. They are not considered to present significant risks at low concentrations to people or to the environment.

3.2.3 Biodegradation

Sodium hydroxide is an inorganic chemical and biodegradation is of no relevance. The three organic acids are all readily biodegradable using the range of standard tests. For these (and subsequent) ingredients, the following simple scoring system was used for biodegradation in the one-page summaries (as presented in Annex 3):

1. Not biodegradable;
2. Inherently biodegradable (in other words, some biodegradation observed but not sufficient to be classified as ‘readily biodegradable’);
3. Insufficient data to classify;
4. Readily biodegradable (using ‘standard’ tests); and
5. Not applicable (i.e. inorganic compounds).

3.3 Bleaching Agents, Activators and Stabilisers

3.3.1 Identified Chemicals

Table 3.4 (overleaf) lists those bleaching agents, activators and stabilisers identified in detergents and summaries of their properties are presented in Annex 3.

3.3.2 Commentary

Bleaches, bleaching agents and activators typically make up 20% of detergents and, as such, the annual consumption across the EU-25 is approaching one million tonnes

Most detergents use an inorganic bleaching agent - either sodium percarbonate or some form of sodium perborate. Sodium percarbonate is not considered to be of concern (HERA, 2002) and various risk assessments on perborates (and boron) have been undertaken which have concluded that the associated risks are very low (SDA, 1998; HERA, 2002a; Umweltbundesamt, 2003).

Table 3.4: Bleaching Agents, Activators and Stabilisers

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
5	Active substances	Sodium perborate	11138-47-9	y	
6	Active substances	Sodium metaborate	7775-19-1		y
7	Active substances	Sodium perborate monohydrate	10332-33-9		y
8	Active substances	Sodium perborate tetrahydrate	10486-00-7		y
9	Activators	TAED	10543-57-4	y	
10	Active substances	Sodium percarbonate	15630-89-4		y

Note: Sodium perborate (entry 5) is essentially a mixture of the monohydrate (entry 7) and the tetrahydrate (entry 8)

However, there are some toxicity concerns over the use of sodium perborate with particular regard to the reproductive toxicity effects of boron at low concentrations (CSTEE, 2004; US EPA, 2004; EFSA, 2004). Such concerns led the Austrian Competent Authority to propose in February 2005 that sodium perborate be classified as Toxic to Reproduction Category 2. Such a classification would lead sodium perborate to be a designated CMR substance which, in turn, could mean that it would no longer be used in detergents[13]. This proposal (and, indeed, other proposed classifications) for sodium perborate are being resisted by industry[14]. Although these issues have yet to be resolved, the main focus of this report is on organic rather than inorganic compounds.

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[13] Under the European Parliament and Council Directive 94/60/EC of 20 December 1994 amending for the 14th time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (OJ L365, 31/12/1994, p1), CMR (Category 1 and 2) substances and preparations containing them should not be placed on the market for use by the general public. However, in determining whether particular substances or preparations should not be placed on the market, consideration will be given to the associated risks and benefits.

[14] See, for example, various papers submitted by CEFIC's Peroxygens Sector Group and discussed at the ECB Technical Committee Classification and Labelling Meeting, 15-18 March 2005.

TAED (tetra acetyl ethylene diamine) is a bleach activator and is an HPV compound with an estimated consumption in detergents of over 60,000 t/year (HERA, 2002b). TAED is not considered to be of concern based on its low toxicity.

3.3.3 Biodegradation

For the inorganic bleaching agents, biodegradation is of no relevance. TAED is readily biodegradable using the range of standard tests. When used in detergents, TAED is rapidly converted to DAED (di acetyl ethylene diamine) during the wash cycle. DAED also has low toxicity and is readily biodegradable (HERA, 2002b).

3.4 Builders, Complexing Agents and Ion Exchangers

3.4.1 Identified Chemicals

Table 3.5 lists those builders, complexing agents and ion exchangers identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.5: Builders, Complexing Agents and Ion Exchangers

No.	Substance Group[1]	Substance	CAS No.	Identified in Specification	Identified in Major Brands
11	Phosphonates	HEDP	2809-21-4	y	
12	Phosphonates	HEDP-4Na	3794-83-0		y
13	Phosphonates	ATMP	6419-19-8	y	
14	Phosphonates	DTPMP-xNa	22042-96-2		y
15	Polycarboxylates	Sodium polyacrylate	9003-04-7	y	
16	Polycarboxylates	Polyacrylic acid	9003-01-4	y	
17	Polycarboxylates	2-propenoic acid, polymer with 2,5 furandion, sodium salt	52255-49-9	y	y
18	Polycarboxylates	2-butenedioic acid (Z), polymer with 2-propenoic acid	29132-58-9		y
19	Polycarboxylates	MW 3000-4000 (Unspecified)		y	
20	Polycarboxylates	MW 1000-70000 (Unspecified)		y	
21	Citrates	Disodium citrate	144-33-2	y	
22	Citrates	Trisodium citrate	68-04-2	y	
23	EDTA & Salts	EDTA	60-00-4	y	
24	EDTA & Salts	EDTA tetrasodium salt	64-02-8	y	
25	NTA	Trisodiumnitrilo-triacetate	139-13-9	y	
26	Carbonates	Sodium carbonate	497-19-8		y

Note 1): Although silicates may be classified as co-builders, they are considered in the next section (Section 3.5) as 'corrosion inhibitors'.

3.4.2 Phosphonates

Commentary

Phosphonates are used in laundry detergents as additives providing a range of properties such as sequestration/complexation, anti-redeposition and dispersion. Phosphonates are also used in laundry detergents as perborate and percarbonate stabilisers, preventing decomposition by transition metals, in automatic dish washing products and in hard surface cleaners.

There are three broad groups of phosphonates which have been categorised under the OECD/ICCA HPV programme as follows:

- Group 1 compounds based on ATMP (amino tris(methylene phosphonic acid));
- Group 2 compounds based on HEDP (1-hydroxy-ethane-1,1-diphosphonic acid); and
- Group 3 compounds based on DTPMP (diethylene triamine penta(methylene phosphonic acid)).

Table 3.6 presents details on the uses of the most significant phosphonates in the detergents/cleaning products industry.

Table 3.6: Household Applications and Finished Product Concentrations of Major Phosphonates

Application area	Phosphonates used	Typical content in finished product
Regular laundry detergents	HEDP, DTPMP	0.05-0.71%
Compact laundry detergents	HEDP, DTPMP	0.05-1.6%
Fabric conditioners	HEDP, DTPMP	0.03-0.05%
Laundry additives	HEDP, DTPMP	0.12-0.34%
Hand dishwashing detergents	HEDP, DTPMP	0.02%
Machine dishwashing detergents	HEDP, DTPMP	0.20-1.5%
Surface cleaners	HEDP, DTPMP, ATMP	0.18-0.5%
Carpet cleaners	HEDP, DTPMP	2%
Toilet cleaners	HEDP, DTPMP	0.05%

Source: HERA, 2004

It has been estimated that the European consumption of phosphonates (primarily HEDP and DTPMP) in detergents is over 12,000 t/year (HERA, 2004) as summarised in Table 3.7.

Table 3.7: Consumption of Phosphonates in Detergent Formulation

Substance	Consumption by six HERA companies	Extrapolated consumption for the EU	Application areas
ATMP	44 t/yr	53 t/yr	Cleaners
HEDP	7,067 t/yr	8,480 t/yr	All
DTPMP	3,412 t/yr	4,094 t/yr	All
Total	***10,523 t/yr***	***12,627 t/yr***	

Source: HERA, 2004

Although actual data are lacking, the HERA risk assessment for phosphonates estimates that a further 15,000 t/year are used in non-detergent applications. The major non-detergent use of phosphonates is as a scale inhibitor in water treatment of cooling and boiler water. Other applications include reverse osmosis water treatment, the photographic industry, the paper and pulp industry and the textile industry. Phosphonates are further used as stabilisers for hydrogen peroxide solutions and formulations.

Under the HPV programme, draft SIDS documents (ICCA 2004, 2004a and 2004b) were submitted in 2003 and reviewed at SIAM 18 (in April 2004). Although 30 phosphonates were considered in these documents, variation of properties within each ‘group’ was limited. As such, the four phosphonates considered here (i.e. entries 11-14 of Table 3.5) are assumed to be fairly representative of those currently in use (and which may be used in the near future).

Phosphonates are soluble and, generally, have low toxicity as well relatively low bioconcentration potentials. However, as discussed further in Section 4.2, they may affect algae at relatively low concentrations (c10 mg/L) due to removal of nutrients and, for HEDP, there are concerns over chronic toxicity to *Daphnia*. Further consideration was given to the human and environmental risks in a HERA assessment (HERA, 2004) which concluded that the associated risks were not significant.

Biodegradation

Extensive information on biodegradation suggests that phosphonates are inherently biodegradable but could, in some cases, be classified as persistent.

3.4.3 Polycarboxylates

Commentary

As indicated in Section 2, polycarboxylates are primarily used in zeolite-based detergents (powders and tablets) and in phosphate-based detergent tablets at concentrations of a few percent. The overall EU consumption of polycarboxylates in detergents is estimated to be about 50,000 t/year with the greatest national consumption in Germany (large population and phosphate-free detergents).

Polycarboxylates used in detergents are mainly water-soluble linear polymers. Polycarboxylates inhibit the crystal growth of inorganic precipitates so that these salts remain in suspension and do not precipitate onto textile fabrics (Danish EPA, 2001).

Polycarboxylates used in washing powders are produced industrially by free radical polymerisation of the monomeric acrylic acid (CH_2=CHCOOH) alone or in a mixture with maleic acid to produce P(AA) and P(AA-MA). Polycarboxylates used in washing powders are generally sodium salts with a molecular weight in the range 1,000 to 100,000.

With reference to Table 3.5, P(AA) polycarboxylates tend to have lower molecular weights, typically 4,000 and are represented by entries 15 and 16. P(AA-MA) polycarboxylates tend to have higher molecular weights, typically 70,000 and are represented by entries 17 and 18. Although entries 19 and 20 have been reproduced from the Specification, they have been taken as P(AA) and P(AA-MA) respectively with their general properties derived from consideration of entries 15 to 18.

As for phosphonates considered above, polycarboxylates are soluble with limited toxicity although algae and crustaceans appear to be more sensitive. Due to the relatively high molecular weights, bioaccumulation is not considered to be significant.

Biodegradation

ECETOC (1993) reports that, as for phosphonates, polycarboxylates do not readily biodegrade. It is worth noting that there has been considerable research effort into developing biodegradable polycarboxylates but with limited success (Swift, 2003).

3.4.4 Citrates

Commentary

As noted in S3.2.2, HERA (2005) estimates that the total consumption of citric acid and citrates in detergents to be about 100,000 t/year. Although citrates are generally not present in household detergents, they are used in commercial/industrial detergents at concentrations of up to 30% (see, for example, Clariant (undated)).

Although references can be found to trisodium citrate (entry 22 in Table 3.5) and to the general term ‘sodium citrate’, there are very few references to disodium citrate (entry 21 in Table 3.5) which suggests that its use in detergents is limited.

As for citric acid, citrates are not considered to present significant risks at low concentrations to people or to the environment. It is worth noting that sodium citrates (monosodium, disodium and trisodium) are EU approved food additives (E331).

Biodegradation

Sodium citrates acids are readily biodegradable using the range of standard tests.

3.4.5 EDTA and Salts

Commentary

Comprehensive ESR risk assessment reports (RARs) on EDTA and EDTA tetrasodium salt have been prepared (ECB, 2004; ECB, 2004a). The RARs report that over 10,000 t/year (EDTA and salts) were used in industrial/institutional detergents and over 2,500 t/year were used in household detergents in Western Europe in 1999[15] (together accounting for nearly 40% of the total use). More recent estimates suggest that for 2003, 11,600 and 1,800 t/year were used in industrial/institutional detergents and household detergents respectively[16].

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[15] Corresponding figures for 1987/88 were 8,500 and 7,000 t/year for industrial/institutional cleaning and household detergents respectively (Wolf & Gilbert, 1992).

[16] Figures provided by the European Amino-Carboxylates Producers Committee (EAC).

The main purpose of EDTA is as a chelating agent to keep metal ions in solution. Although a desirable property in detergents, there are concerns that such a property may adversely affect water quality - particularly since EDTA is not substantially removed by municipal waste water treatment (as discussed further in Section 4.4). However, the EDTA RAR notes that: "*a risk for the aquatic environment due to the influence of EDTA on the mobility of heavy metals is not expected*" (ECB, 2004).

EDTA (and sodium salts) are very soluble, not generally toxic and do not bio-accumulate. Although not particularly toxic to fish and crustacea, they are found to be toxic to algae (with an EC50 of 1 mg/L) in standard tests. However, as discussed in the RARs, this can be associated with the chelating action of the ETDA in removing metal ions essential to algal growth from the test solutions. In the natural environment, there are sufficient metal ions present to overcome this issue and, as a consequence, the RARs recommend use of a higher end-point (22 mg/L for *Daphnia*) in addressing aquatic toxicity.

Detergents containing EDTA (and/or salts) do not qualify for an eco-label under the current guidelines due to their hazard classification. Steps have been taken in various countries to limit EDTA in detergents. In the UK, there is voluntary agreement not to use EDTA in household detergents and its use is limited by law in France (WRc, 2002). In Sweden, concerns over EDTA led to its near elimination from household detergents during the early 1990s (Svenska Naturskyddsföreningen, 1999). In Germany, the issue of EDTA (from all sources) has been the subject of extensive debate which resulted in a voluntary agreement in 1991 to significantly reduce EDTA levels in the environment (Conrad, 2000).

Biodegradation

Using standard tests, EDTA (and salts) are found not to be readily biodegradable and may be classified as persistent (P) or very persistent (vP). However, EDTA (as a chelating agent) readily forms complexes with metal ions present in waste water and surface waters. As a consequence, some degradation will occur through the photodegradation of the Fe(III)-EDTA complex (as discussed further in Section 4.4).

3.4.6 NTA

Commentary

NTA is nitriloacetic acid which is used directly or as a trisodium salt in detergents (these compounds are often collectively referred to as NTA). NTA trisodium salt has been the subject of an environmental ESR RAR (ECB, 2005) which concluded that the environmental risks were not significant.

However, due to concerns over its toxicity (and potential carcinogenicity (IARC, 1999)) and ability to remobilise heavy metals in river sediments, NTA is hardly used as a builder in EU detergents (Smulders, 2002; WRc, 2002). In the UK, there is a voluntary agreement not to use NTA in household detergents and its use is prohibited by law in France (WRc, 2002). In Sweden, as for EDTA, concerns over NTA led to its near elimination from household detergents during the early 1990s (Svenska

Naturskyddsföreningen, 1999). However, in Germany, the authorities recommend the use of NTA as an alternative to EDTA (Conrad, 2000).

Although the use of NTA in household detergents is limited (less than 1,000 t/year[17]), its use in other 'cleaning agents' (i.e. I&I applications) is extensive. The RAR reports that nearly 18,000 t/year were used in cleaning agents in Western Europe in 2000 (rising to 19,000 t/year in 2003[18]). It is likely that many of these products will now be covered by the new Detergents Regulation given the broader definition of 'detergent' (see Section 2.1).

Biodegradation

NTA is readily biodegradable using standard tests (and is removed to a significant extent by waste water treatment) although NTA-metal complexes may not be as discussed further in Section 4.5.

3.4.7 Sodium Carbonate

Commentary

Sodium carbonate (soda ash) is used as a builder in detergent powders and tablets for water softening in the washing process and as a source of alkaline reserve (AELA, 2004). Sodium carbonate is also used in laundry additives, machine dishwashing products, surface cleaners, toilet cleaners and other household cleaning products. For most products, the typical sodium carbonate content is less than 30%, but maximum concentrations can be higher - up to 90% (HERA, 2002c).

Sodium carbonate is used in most household detergents with generally higher concentrations in zeolite-based detergents than in STPP-based detergents. The highest concentrations tend to be found in zeolite-based compact powders with typical concentrations of 15%. The amount of sodium carbonate, which was used in household cleaning products in Europe, was estimated to be 550,000 tonnes in 1999 (HERA, 2002c).

Sodium carbonate has been the subject of a detailed risk assessment (HERA, 2002c). This assessment concluded that the sodium, which originates from the use of sodium carbonate in household cleaning products, has a negligible effect on the aquatic ecosystems. Moreover, due to effluent treatment, the carbonate present in the household cleaning products, will not be discharged to the aquatic ecosystems but will be neutralised. Furthermore, based on the available data, the use of sodium carbonate in household cleaning products has no adverse effect on consumers.

Biodegradation

Sodium carbonate is an inorganic chemical and biodegradation is of no relevance.

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[17] NTA quantities as tonnes of NTA trisodium salt per year.

[18] Figure provided by the European Amino-Carboxylates Producers Committee (EAC).

3.5 Corrosion Inhibitors

3.5.1 Identified Chemicals

Table 3.8 lists those corrosion inhibitors identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.8: Corrosion Inhibitors

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
27	Silicates	Sodium metasilicate, anhydrous	6834-92-0		y
28	Silicates	Sodium silicate	1344-09-8	y	y
29	Silicates	Disodium disilicate	13870-28-5		y

3.5.2 Commentary

Sodium silicates are used in detergents primarily for their corrosion inhibiting properties and ability to maintain a substantially constant pH value during the wash. They are found in most household detergents at concentrations of several per cent which is consistent with the estimate of 188,000 t/year for EU annual consumption (in 2000) provided in the HERA draft risk assessment[19] (HERA, 2005a).

Although considered corrosive to eyes and skin, sodium silicates have a low toxicity and their use in detergents is not considered to present significant risks to human health or to the environment. However, it should be noted that waste water treatment only removes 10% of the silicates present (HERA, 2005a).

3.5.3 Biodegradation

Sodium silicates are inorganic chemicals and biodegradation is of no relevance.

3.6 Dyes

3.6.1 Identified Chemicals

Table 3.9 lists those dyes identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.9: Dyes

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
30	???	Unspecified	???	y	

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[19] The HERA assessment covers five specified soluble silicates including entries 27 and 28 from Table 3.8 but, curiously, no mention is made of CAS 13870-28-5 (entry 29 from Table 3.8) which is specifically identified in numerous leading detergent brands produced by one of the main manufacturers.

3.6.2 Commentary

Dyes are sometimes used in detergents in very low concentrations (typically <0.1%). Of note is that there is no requirement to identify dyes under the Detergents Regulation unless present in concentrations of greater than 0.2%.

It is understood that the detergent industry uses a diverse range of some 150 to 200 dyes although detailed information on specific dyes is not generally published[20].

3.6.3 Biodegradation

Although it has been suggested that dyes are generally not readily biodegradable and have low toxicity (Smulders, 2002), it has not been possible to confirm the extent to which this applies to the range of dyes in use.

3.7 Dye Transfer Inhibitors

3.7.1 Identified Chemicals

Table 3.10 lists those dye transfer inhibitors identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.10: Dye Transfer Inhibitors

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
31	Polyvinyl polymers	Polyvinylpyrrolidone (PVP)	9003-39-8	y	

3.7.2 Commentary

Dye transfer inhibitors prevent loss of dye from washed garments and PVP is used in ‘colour-safe’ laundry detergent powders and liquids - albeit at low concentrations. The presence of PVP also inhibits soil redeposition (other anti-redeposition agents are discussed in Section 3.12).

The total EU consumption of PVP (and related substance PVPP - polyvinylpoly pyrrolidone) is estimated to be 3,500 t/year of which about 3,200 t/year are accounted for by pharmaceuticals, beer/wine clarification and food supplements (SCF, 2002). These figures suggest that use of PVP in detergents will be very low - perhaps of the order of 100 t/year.

PVP is sold in various grades (depending on molecular weight) ranging from K-15 (MW of around 10,000) to K-120 (MW of around 3.5 million). In detergents, the predominant form appears to be K-30 (MW of around 50,000).

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[20] Information provided by the industry trade association, AISE.

PVP is soluble, is unlikely to bioaccumulate (due to its high MW) and is approved for use in foods (JECFA, 1980). Although the environmental toxicity is low, there appear to be limited data available on the behaviour and fate of PVP in the environment.

3.7.3 Biodegradation

PVP does not appear to readily biodegrade but only one specific measurement has been identified.

3.8 Enzymes

3.8.1 Identified Chemicals

Table 3.11 lists those enzymes identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.11: Enzymes

No.	**Substance Group**	**Substance**	**CAS No.**	**Identified in Specification**	**Identified in Major Brands**
32	Protease	Unspecified		y	
33	Amylase/Cellulase/ Lipase	Unspecified		y	

3.8.2 Commentary

Since the 1960s, enzymes have been added in low concentrations to ‘biological’ detergents. The enzymes catalyse reactions which break down proteins (as found, for example, in food stains). Concerns over enzymes have focused on allergenic reactions in workers and consumers. As a consequence, the industry has moved from so-called ‘dusty’ non-encapsulated enzymes to double encapsulation (SDA, 2005).

Protease, with particular reference to subtilisin (CAS 9014-01-1[21]), is the most widely used enzyme in detergents with an estimated consumption of 900-950 t/year. HERA (2005b) reports that although there remains the potential for respiratory allergies and skin/eye irritation, the use of protease in detergents does not present a significant risk to consumers. In relation to the environment, although protease is moderately toxic to the aquatic environment (especially *Daphnia magna*), HERA estimate the associated risks to be low.

Other enzymes used in detergents include α-amylase (CAS 9000-90-2) and, more recently, cellulase (β-(1,4)-Glucanase) (CAS 9012-54-8) and lipase (CAS 9001-62-1). These have also been assessed by HERA (2005c) and estimated consumption figures in detergents are estimated as150, 15 and 8 t/year respectively. Available data suggest that these enzymes are less toxic and less irritating than protease.

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[21] HERA (2005b) reports that although this is the most commonly used CAS number, other CAS numbers include: 1395-21-7, 9073-77-2, 9001-92-7, 79986-26-8, 95979-76-3 and 689-17-1.

3.8.3 Biodegradation

Enzymes have been found to be readily biodegradable.

3.9 Fluorescent Whitening Agents

3.9.1 Identified Chemicals

Table 3.12 lists those fluorescent whitening agents (FWAs) identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.12: Fluorescent Whitening Agents

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
34	FWA-5	Benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis-,disodium salt	27344-41-8	y	
35	FWA-1	Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-(4-morpholinyl)-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt	16090-02-1	y	y

3.9.2 Commentary

Fluorescent whitening agents (optical brighteners) have been added to many detergents in low concentrations since the 1940s. By the early 1990s, there were seven main FWAs in use worldwide named FWA-1 to FWA-7 (Kramer, 1992) with FWA-8 introduced during the 1990s (van de Plassche, 1999). In Europe, FWA-1 and FWA-5 are the most common FWAs used in detergents with the usages of FWA-1 and FWA-5 estimated to be about 2,100 and 600 t/year respectively (HERA, 2003; HERA, 2004a).

FWAs are characterised by low mammalian and aquatic toxicities with very low bioaccumulation potentials.

3.9.3 Biodegradation

Although FWA-1 is considered to be readily biodegradable, FWA-5 is not. However, FWA-5 undergoes rapid photo-degradation in surface waters to produce readily biodegradable metabolites (Smulders, 2002; HERA, 2003). For this reason, the associated environmental risks have been estimated to be very low.

3.10 Foam Regulators

3.10.1 Identified Chemicals

Table 3.13 lists those foam regulators identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.13: Foam Regulators

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
36	Paraffins	Unspecified		y	
37	Polydimethyl siloxane	Polydimethyl siloxane (PDMS)	9016-00-6	y	

3.10.2 Commentary

Foam regulators limit the amount of foam generated during washing (primarily in machine washing) and are present in low concentrations (typically, 0.1-0.4%).

Reference is made to the use of paraffin oil (Smulders, 2002) and it is believed that these comprise *n*-paraffins (straight-chain *n*-alkanes), typically in the range C_{10} (*n*-decane) to C_{16} (*n*-hexadecane) - although data on specific paraffins in use have not been identified. Although mammalian toxicity is low, these *n*-paraffins may bio-accumulate and may be highly toxic in the aquatic environment. By way of example, EC50s of <0.1 mg/L are reported (in IUCLID data sheets) for the effects of *n*-decane on *Daphnia magna* and for the effects of *n*-tetradecane (C_{14}) on algae. The annual consumption of paraffins in detergents is probably of the order of 5,000 t/year (based on German data presented in Smulders, 2002).

PDMS is the most widely used silicon-based (inorganic) polymer with numerous applications utilising different polymer lengths with molecular weights ranging from less than 200 to more than 500,000 (Gelest, 2004). The molecular weights of PDMS polymers used in detergents are typically of the order of 30,000 (Stevens, 2006). Household consumption of PDMS within the EU is probably of the order of 20,000 t/year (based on estimates provided in Lukasiak *et al*, 2003) with an estimated 7,200 t/year used in detergents (Stevens, 2006).

PDMS is insoluble and although generally considered to be inert and non-toxic, available data on its properties are limited. However, there are extensive data[22] on the low molecular weight PDMS compounds and their effects on mammalian health (partly in response to concerns over the use of PDMS polymers in breast implants).

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[22] For example, numerous reports are available from the US Siloxane Research Programme (www.sehsc.com).

3.10.3 Biodegradation

Although *n*-paraffins are readily biodegradable, PDMS is not and would be classified as very persistent (vP). However, as discussed further in Section 4.9, PDMS may undergo hydrolysis when present in the soil.

3.11 Formulation Aids

3.11.1 Identified Chemicals

Table 3.14 lists those formulation aids identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.14: Formulation Aids

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
38	Toluene/cumene sulphonates	Unspecified		y	
39	Polyethylene glycols	PEG	25322-68-3	y	

3.11.2 Commentary

Toluene/cumene sulphonates are used to enhance detergent performance. The most common toluene sulphonate in use appears to be sodium toluene-4-sulphonate (CAS 657-84-1) while the most common cumene sulphonate appears to be sodium cumene sulphonate (CAS 28438-53-0). Various toluene, cumene and xylene sulphonates have been the subject of a HERA risk assessment (HERA, 2005d). These compounds are collectively referred to as hydrotropes[23] which are used (primarily) to assist the dissolving of water insoluble ingredients within cleaning products. The total EU consumption of these compounds in detergents is estimated (HERA, 2005d) to be 17,000 t/year (i.e. about 0.4% of the total detergent consumption).

The HERA assessment considers one sodium and two potassium toluene sulphonates - although the sodium compound considered is CAS 12068-03-0 (an isomer of CAS 657-84-1). The assessment also considers four xylene sulphonates and three cumene sulphonates (including the sodium salt referred to above).

Considered as a group, the sulphonates are soluble and are of low toxicity to both mammals and to the environment with limited bioaccumulation potential. As a result, the HERA report concludes that the use of these compounds in detergents presents insignificant health and environmental risks

Polyethylene glycols (PEGs) may be used in detergents but no detailed information on their use has been identified. PEGs are polymers with molecular weights ranging from

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[23] The HERA assessment relies on data being collated under the OECD/ICCA HPV programme for hydrotropes and the same data have also been presented by the US Soap and Detergent Association in developing a screening method for consumer product ingredients (SDA, 2005a).

200 to 10,000 and PEG products are generally identified by their typical molecular weights - hence PEG200, PEG1000, etc. PEGs are soluble and have a low toxicity (to both mammals and to the environment).

3.11.3 Biodegradation

The salts of toluene, cumene (and xylene) sulphonates all degrade rapidly under aerobic conditions as do the lower molecular weight PEGs. However the rate of biodegradation decreases with increasing molecular weights so that PEGs with molecular weights of a few thousand are inherently biodegradable.

3.12 Soil Repellents/Anti-Redeposition Agents

3.12.1 Identified Chemicals

Table 3.15 lists those soil repellents/anti-redeposition agents identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.15: Soil Repellents/Anti-Redeposition Agents

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
40	Carboxymethyl cellulose	Carboxymethyl cellulose	9000-11-7	y	
41	Anionic derivatives of polymers of terephthalic acid and polyethylene glycol	Unspecified		y	

3.12.2 Commentary

Carboxymethyl cellulose (CMC) is used in some detergents at low concentrations (typically 0.5-1%) to prevent dirt being re-deposited on garments during the wash cycle with an estimated EU consumption of, perhaps, 20,000 t/year. Limited data suggest that CMC is soluble and of low toxicity with a low bioaccumulation potential. It is worth noting that CMC is an approved food additive (E466).

Other anti-redeposition agents are reported to include anionic derivatives of polymers of terephthalic acid and polyethylene glycol (Smulders, 2002). Although terephthalic acid and polyethylene glycol may be used to produce PET (polyethylene terephthalate) - as found in most plastic drink bottles, specific data on the use of such polymers (and their anionic derivatives) in detergents have not been located thus preventing further analysis.

It would appear that the use of these polymers[24] is a key area of competition amongst manufacturers and, as a consequence, precise details on their composition are not publicised.

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[24] It is understood, for example, that use is also made of polymers based on ethoxylated amines.

3.12.3 Biodegradation

CMC is only poorly biodegradable.

3.13 Solvents

3.13.1 Identified Chemicals

Table 3.16 lists those solvents identified in detergents and summaries of their properties are presented in Annex 3.

Table 3.16: Solvents

No.	Substance Group	Substance	CAS No.	Identified in Specification	Identified in Major Brands
42	Alcohols	Ethanol	64-17-5	y	y
43	Alcohols	Isopropanol	67-63-0	y	
44	Alcohols	2-butoxy ethanol (butyl glycol)	111-76-2	y	
45	Alcohols	1-decanol	112-30-1	y	
46	Alcohols	Butoxydiglycol	112-34-5	y	y
47	Alcohols	Propylene glycol	57-55-6	y	
48	Alcohols	Glycerol	56-81-5	y	
49	Alcohols	2-amino ethanol	141-43-5	y	
50	Amines	Triethanolamine	102-71-6		y

3.13.2 Commentary

Solvents are used, primarily, in liquid detergents at concentrations of, typically, a few percent.

The solvents listed in Table 3.16 may all be characterised as being HPV chemicals, miscible with water and of low mammalian toxicity. In relation to environmental toxicity, the solvents are of generally low toxicity with limited potential for bioaccumulation (although data are limited). The exception is 1-decanol which has been found to be reasonably highly toxic to fish (LC50 of 0.6 mg/L) and to *Daphnia* (EC50 of 3 mg/L). The degree to which 1-decanol is used in EU detergents is not known.

3.13.3 Biodegradation

The solvents listed in Table 3.16 are all readily biodegradable (according to standard tests) with the possible exception of triethanolamine (TEA) which is generally regarded as readily biodegradable but some test results indicate a slower rate of biodegradation. The main use of TEA appears to be in fire fighting foams and its use in detergents is probably limited.

3.14 Screening of Ingredients

The properties of each of the 50 representative detergent ingredients were considered. In broad terms, those substances which are readily biodegradable with no other properties of potential concern (such as high aquatic toxicity) are unlikely to present significant risks to people or to the environment. On this basis, it was considered that further analysis of these substances was not merited. There are, however, a number of ingredients (and groups of ingredients) which are not readily biodegradable or have other properties of potential concern and these are subject to further analysis in Section 4.

This screening process is summarised in Table 3.17, with those ingredients requiring further analysis highlighted in bold.

Table 3.17: Screening of Non-surfactant Substances for Further Analysis

No.	Substance Group	Substance	CAS No.	Readily Biodegradable	Comment	Further Analysis
Acids and bases						
1	Acid	Acetic acid	64-19-7	y		n
2	Acid	Citric acid	77-92-9	y		n
3	Acid	Adipic acid	124-04-9	y		n
4	Base	Sodium hydroxide	1310-73-2	n/a	Inorganic	n
Bleaching agents, activators and stabilisers						
5	Active substances	Sodium perborate	11138-47-9	n/a	Inorganic but potential CMR due to proposed classification as a Repr.Cat.2	n
6	Active substances	Sodium metaborate	7775-19-1	n/a		n
7	Active substances	Sodium perborate monohydrate	10332-33-9	n/a		n
8	Active substances	Sodium perborate tetrahydrate	10486-00-7	n/a		n
9	Activators	TAED	10543-57-4	y		n
10	Active substances	Sodium percarbonate	15630-89-4	n/a	Inorganic	n
Builders, complexing agents, ion exchangers						
11	**Phosphonates**	**HEDP**	**2809-21-4**	**n**		**y**
12	**Phosphonates**	**HEDP-4Na**	**3794-83-0**	**n**		**y**
13	**Phosphonates**	**ATMP**	**6419-19-8**	**n**		**y**
14	**Phosphonates**	**DTPMP-xNa**	**22042-96-2**	**n**		**y**
15	**Polycarboxylates**	**Sodium polyacrylate**	**9003-04-7**	**n**		**y**
16	**Polycarboxylates**	**Polyacrylic acid**	**9003-01-4**	**n**		**y**
17	**Polycarboxylates**	**2-propenoic acid, polymer with 2,5 furandion, sodium salt**	**52255-49-9**	**n**		**y**
18	**Polycarboxylates**	**2-butenedioic acid (Z), polymer with 2-propenoic acid**	**29132-58-9**	**n**		**y**
19	Polycarboxylates	MW 3000-4000 (Unspecified)		n	Represented by entries 15 & 16	n
20	Polycarboxylates	MW 1000-70000 (Unspecified)		n	Represented by entries 17 & 18	n
21	Citrates	Disodium citrate	144-33-2	y		n
22	Citrates	Trisodium citrate	68-04-2	y		n

Table 3.17: Screening of Non-surfactant Substances for Further Analysis

No.	Substance Group	Substance	CAS No.	Readily Biodegradable	Comment	Further Analysis
23	**EDTA & Salts**	**EDTA**	**60-00-4**	**n**		**y**
24	**EDTA & Salts**	**EDTA tetrasodium salt**	**64-02-8**	**n**		**y**
25	**NTA**	**Trisodiumnitrilo triacetate**	**139-13-9**	**y**	**Carcinogen?**	**y**
26	Carbonates	Sodium carbonate	497-19-8	n/a	Inorganic	n
Corrosion inhibitors						
27	Silicates	Sodium metasilicate, anhydrous	6834-92-0	n/a	Inorganic	n
28	Silicates	Sodium silicate	1344-09-8	n/a	Inorganic	n
29	Silicates	Disodium disilicate	13870-28-5	n/a	Inorganic	n
Dyes						
30	**???**	**Unspecified**	**???**	**no data**		**y**
Dye transfer inhibitors						
31	**Polyvinyl polymers**	**Poly (N-vinyl pyrrolidone) PVP**	**9003-39-8**	**n**		**y**
Enzymes						
32	Protease	Subtilisin	9014-01-1	y		n
33	Amylase/Cellulase/ Lipase	Unspecified			See 33.1-33.3	n
33.1		Amylase	9000-90-2	y		n
33.2		Celleulase	9012-54-8	y		n
33.3		Lipase	9001-62-1	y		n
Fluorescent Whitening Agents						
34	**FWA-5**	**FWA-5 (DSBP)**	**27344-41-8**	**n**		**y**
35	FWA-1	FWA-1	16090-02-1	y		n
Foam regulators						
36	**Paraffins**	**Unspecified**		**y**	**Assumed to be C10-16 *n*-paraffins with high BCFs and high aquatic toxicities**	**y**
37	**Polydimethyl siloxane**	**Polydimethyl siloxane (PDMS)**	**9016-00-6**	**n**		**y**
Formulation aids						
38	Toluene/cumene sulphonates	Unspecified			See 38.1 & 38.2	n
38.1		Sodium toluene sulphonate	657-84-1	y		n
38.2		Sodium cumene sulphonate	28348-53-0	y		n
39	**Polyethylene glycols**	**PEG**	**25322-68-3**	**n**	**Higher MWs only**	**y**
Soil repellents/anti-redeposition agents						
40	**Carboxy methylcellulose**	**Carboxymethylcellulose**	**9000-11-7**	**n**		**y**

Table 3.17: Screening of Non-surfactant Substances for Further Analysis

No.	Substance Group	Substance	CAS No.	Readily Biodegradable	Comment	Further Analysis
41	**Anionic derivatives of polymers of terephthalic acid and polyethylene glycol**	**Unspecified**		**no data**		**y**
Solvents						
42	Alcohols	Ethanol	64-17-5	y		n
43	Alcohols	Isopropanol	67-63-0	y		n
44	Alcohols	2-butoxy ethanol (butyl glycol)	111-76-2	y		n
45	**Alcohols**	**1-decanol**	**112-30-1**	**y**	**High aquatic toxicity**	**y**
46	Alcohols	Butoxydiglycol	112-34-5	y		n
47	Alcohols	Propylene glycol	57-55-6	y		n
48	Alcohols	Glycerol	56-81-5	y		n
49	Alcohols	2-amino ethanol	141-43-5	y		n
50	**Amines**	**Triethanolamine**	**102-71-6**	**n?**		**y**

4. FURTHER ANALYSIS OF INGREDIENTS OF POTENTIAL CONCERN

4.1 Introduction

4.1.1 Substances Selected for Further Analysis

The screening exercise (as summarised in Table 3.17) resulted in the following specific substances and substance groups being selected for further analysis:

- phosphonates;
- polycarboxylates;
- EDTA and EDTA tetrasodium salt;
- nitrilotriacetic acid (NTA and salts);
- detergent dyes;
- dye transfer inhibitors with particular reference to polyvinylpyrrolidone (PVP);
- fluorescent whitening agent FWA-5;
- foam regulators with particular reference to paraffins (assumed to be C10-C16 *n*-paraffins) and polydimethyl siloxane (PDMS);
- formulation aids with particular reference to the use of polyetheylene glycols (PEG) with higher molecular weights (greater than, say, 2000);
- anti-redeposition agents with particular reference to the use of carboxymethyl-cellulose (CMC) and other polymers; and
- solvents with particular reference to the use of 1-decanol and triethanolamine.

4.1.2 Scope of Analysis

Overview

For each group of ingredients of potential concern, the further analysis involved:

- a review of (published) risk assessments;
- a review of European monitoring data (with particular emphasis on waste water treatment and surface waters);
- further discussion on degradation pathways; and
- determining whether further work was required.

Degradation

At this stage, it is important to emphasise that, for the vast majority of substances being considered, the key issue is not the uncertainty associated with degradation. In other words, for each substances, it is fairly apparent whether it biodegrades rapidly or not and/or whether it degrades in some other manner. This suggests that requirements for further biodegradation testing (in a similar manner as prescribed for surfactants under the

Detergents Regulation) of those ingredients identified in this report may not necessarily be the 'best' way forward.

It is, of course, accepted that degradation can take many routes. A key route is aerobic biodegradation in which organic compounds are broken down by micro-organisms when oxygen is present. It is this process which is encouraged during secondary treatment (using an activated sludge system) at waste water treatment plants (and a brief overview of waste water treatment processes is provided in Annex 4)

Since most organic ingredients present in detergents will end up in waste water treatment plants, the degree to which they undergo aerobic degradation is of interest. However, in some cases, other forms of environmental degradation are also important. By way of example, for materials which end up in sewage sludge, anaerobic biodegradation (in which organic compounds are broken down by micro-organisms when oxygen is not present) may also be important. Once released into the environment some compounds may degrade under sunlight (photo-degradation) or undergo chemical reactions with (or catalysed by) other materials present in the environment.

For each type of degradation, it is possible to measure the rate of degradation using one or more approved test methods. An overview of such methods is provided in Annex 5 with a particular emphasis on those for testing ready biodegradability.

4.2 Phosphonates

4.2.1 Chemicals Identified

Entries 11-14 of Table 3.17 (and Annex 3) comprise four phosphonates of potential concern due to their biodegradation properties (CAS Nos. 2809-21-4 (HEDP), 3794-83-0 (HEDP-4Na), 6419-19-8 (ATMP) and 22042-96-2 (DTPMP-xNa)).

4.2.2 Summary of Risk Assessments

An early review of the use of phosphonates in the Europe and USA (Gledhill & Feijtel, 1992) concluded that the environmental risks (in the aquatic compartment) were insignificant due to the low PECs (predicted environmental concentrations), low toxicity and low bioaccumulation potential. During the 1990s, a comprehensive environmental risk assessment of phosphonates (including HEDP, ATMP and DTPMP) with a focus on the Netherlands was undertaken (Jaworska *et al*, 2002). The conclusion was that the risks were not significant - although the *Daphnia* chronic test results for HEDP (as discussed further below) were put to one side. It is reported (HERA, 2004) that a further study was undertaken in the 1990s in Sweden but this has not been reviewed.

Under the OECD/ICCA HPV programme, the hazards associated with phosphonates were critically reviewed and the conclusions are summarised in Table 4.1 (overleaf). In summary, concern was focused on the environmental risks associated with HEDP (the most widely used group of phosphonates as shown in Table 3.7).

Table 4.1: Recommendations from SIDS Initial Assessment Profiles (April, 2004)

End Point	Conclusion	HEDP & salts	ATMP & salts	DTPMP & salts
Environment	The chemicals in this category are candidates for further work.	✓		
	The substances in this category possess properties indicating a hazard for the environment ... these hazards do not warrant further work as they are related to acute toxicity, pH effects and metal chelation, which may become evident only at very high exposure level.	✓	✓	✓
	They should nevertheless be noted by chemical safety professionals and users		✓	
	However, there are 2 unverifiable tests available for chronic *Daphnia* toxicity, of which one raises concern. A further, modern study will be conducted to clarify this. If the test indicates significant chronic toxicity to aquatic invertebrates, an exposure assessment should be conducted followed by a risk assessment	✓		
Human health	The chemicals in this category are currently of low priority for further work	✓		
	The chemicals in this category possess properties indicating a hazard for human health. Although these hazards do not warrant further work as they are related to pH effects and chelation properties, they should nevertheless be noted by chemical safety professionals and users		✓	✓

Sources: ICCA, 2004/2004a/2004b

A full risk assessment was published by HERA (2004) which came to the same conclusion. Specifically, the only concern was HEDP where the PECs exceeded the PNEC - where this was based on the chronic *Daphnia* test[25] referred to in Table 4.1 which generated a NOEC value of 0.1 mg/L. Given this concern, further studies have been planned (HERA, 2004) which, it is understood, will be completed by the end of 2006.

4.2.3 Summary of Monitoring Data

Waste Water Treatment

Phosphonates are substantially removed (typically, 50-90%) in waste water treatment plants (WWTPs) due to adsorption to the sludge.

Monitoring data are available for the year 1996 for seven Swiss WWTPs (Nowack, 1998). For ATMP, the measured concentrations in WWTP influent ranged from below the detection limit (14 µg/L) up to 239 µg/L; in effluent, all values were below the detection limit. For DTPMP (the parent substance for DTPMP-xNa), the concentration in WWTP influent ranged between below 29 µg/L (detection limit) up to 1,146 µg/L. The effluent concentration ranged between below detection limit up to 80 µg/L with most values (in six out of seven WWTPs) being below the detection limit.

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[25] In the absence of this test result, the NOEC for the aquatic environment would be determined by toxicity to algae. Although EC50 values in the range 1 - 10 mg/L may be derived under standard test conditions, these results are associated with nutrient removal (as occurs with other chelating agents - see Section 3.4.5) rather than with direct ecotoxicological effects (HERA, 2004).

More recent studies by Nowack (as reported in HERA, 2004) into ATMP at a German WWTP and DTPMP at a Danish WWTP gave similar results.

Environmental Monitoring

As of 1992, there were no available environmental monitoring results (Gledhill & Feijtel, 1992). Although there has been some limited monitoring of ATMP and DTPMP at WWTPs in recent years (as outlined above), there would appear to have been no further environmental monitoring (Danish EPA, 2001; HERA, 2004).

Modelling that has been done for Western European countries based on a detergent use of 6,000 kt/year has predicted a maximum raw sewage levels of phosphonates of 170 to 290 µg/L. Removal primarily via partitioning would result in average effluent levels ranging from 90 to 235 µg/L. and these levels would decrease by an order of magnitude upon dilution in receiving waters. Therefore, maximum phosphonate environmental levels would be expected to be below 30 µg/L (Gledhill & Feijtel, 1992). Other estimates on the concentration of phosphonates in water include:

- Jaworska *et al* (2002) calculated in the Netherlands a surface water Predicted Environmental Concentration of 4.9 µg/L and 1.15 µg/L for HEDP and ATMP respectively; and
- HERA (2004) estimate PECs of up to 26 µg/L (for 'local' HEDP surface water concentrations).

4.2.4 Aerobic Biodegradation

There is a consensus that phosphonates are not readily biodegradable and show only a low degree of ultimate biodegradation under standard test conditions (as summarised in HERA, 2004).

4.2.5 Other forms of Degradation

A wide range of experiments (as reported in HERA, 2004) suggest that there are a number of other routes by which phosphonates may degrade as summarised in Table 4.2.

Table 4.2: Summary of Other Degradation Routes for Phosphonates

Degradation Route	**Comment**
Anaerobic biodegradation	Limited data suggest not significant
Hydrolysis	Phosphonates are considered stable in water - but presence of metal ions, light and warmth can lead to hydrolysis
Photolysis	Some experimental results indicate limited degradation under sunlight which is catalysed by presence of metal ions (resulting in nearly 80% degradation in 17 days for HEDP)
Degradation in soil	Limited degradation with predicted half-lives of 45, 373 and 789 days for DTPMP, HEDP and ATMP respectively
Degradation in sediment	Limited degradation with predicted half-lives of 137.5, 471 and 376 days for DTPMP, HEDP and ATMP respectively
Degradation in river water	Limited data suggest that some degradation does occur (due to a combination of biodegradation, hydrolysis and photolysis) with an indicative half-life of 395 days

Source: HERA (2004)

4.2.6 Conclusion

There is a broad consensus that phosphonates degrade slowly and may present a risk to the environment with concern being focused on the potential aquatic chronic toxicity of HEDP (and its salts) to *Daphnia*. It is of note that there appears to be no monitoring data on HEDP (and/or its salts).

Although most of the phosphonates (used in household detergents) will end up in sewage sludge of which some is applied to agricultural land, available data indicate that the terrestrial toxicity of phosphonates is very low. On this basis, the presence of phosphonates in sewage sludge does not present a significant risk.

4.3 Polycarboxylates

4.3.1 Chemicals Identified

Entries 15-18 of Table 3.17 (and Annex 3) comprise four representative polycarboxylates of potential concern due to their biodegradation properties (CAS Nos. 9003-04-7, 9003-01-4, 52255-49-9 and 29132-58-92).

4.3.2 Summary of Risk Assessments

Polycarboxylates were introduced into detergents in the 1980s and an early review of their use with a focus on Germany (Opgenorth, 1992) suggested that environmental concentrations resulting from their use in detergents would be low due, largely, to their removal in waste water treatment. Furthermore, given their low toxicity and ecotoxicity, a further study with a European focus (ECETOC, 1993) concluded that the use of polycarboxylates presented no hazard to man and to the environment.

4.3.3 Summary of Monitoring Data

Waste Water Treatment

As for phosphonates, polycarboxylates are substantially removed in waste water treatment due to adsorption to the sludge. Removal rates increase with molecular weight from around 20% to 95% or more for activated sludge treatment with higher removal rates for tertiary treatment (using ferric chloride precipitation) (ECETOC, 1993).

No monitoring data on the presence of polycarboxylates in waste water treatment influent or effluent have been located. However, some calculations have been made in the past and relevant data are presented in Table 4.3.

Table 4.3: Calculated Waste Water Concentrations of Polycarboxylates

Medium	Calculated concentration (µg/L)	Reference
Raw waste water	2,900 – 3,800	Zini, 1995; Schwuger, 1997
Primary effluent	3,100	Zini, 1995
Secondary effluent	260 – 300	Zini, 1995; Schwuger, 1997

Of note is that field measurements from a US study (Guiney *et al*, 1998) on two polycarboxylates (which although not used in detergents had comparable molecular weights and properties[26]) showed similar influent concentrations (1,820 and 3,100 µg/L) and secondary effluent concentrations (<300 µg/L) to those presented in Table 4.3. However, due to the strong adsorption, high sludge concentrations were measured (1,079 and 1,218 mg/kg dw).

Environmental Monitoring

As of the early 1990s, there were no available environmental monitoring results (Opgenorth, 1992; ECETOC, 1993) although surface water concentrations were predicted to be below 0.5 mg/L (ECETOC, 1993). More recent calculations estimate the concentration of polycarboxylates in rivers receiving secondary effluent from WWTPs at 30 µg/L (Zini, 1995) and the concentration in drinking water at 5 µg/L (Schwuger, 1997).

4.3.4 Aerobic Biodegradation

There is a consensus that polycarboxylates are not readily biodegradable.

4.3.5 Other forms of Degradation

There is no evidence of significant anaerobic biodegradation (amongst higher MWs) (ECETOC, 1993). For soils, Guiney *et al* (1998) suggest a degradation rate of 10% per year which, with repeated sludge applications, leads to a steady state concentration of 110 mg/kg dw (for one of the polycarboxylates studied).

4.3.6 Conclusion

Although polycarboxylates do not readily biodegrade, it is unlikely that their use in detergents would lead to significant risks to consumers or to the environment due to their low toxicity and ecotoxicity. However, there are no available monitoring data and concentrations in sludge-treated soils may be significant.

4.4 EDTA and Salts

4.4.1 Chemicals Identified

Entries 23 and 24 of Table 3.17 (and Annex 3) comprise edetic acid (EDTA, CAS No. 60-00-4) and EDTA tetrasodium salt (CAS No. 64-02-8). In the discussion which follows, these two compounds are considered collectively as EDTA (unless otherwise specified).

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[26] The study examined a polymer emulsion (used in floor finishes) with a molecular weight of 50,000 to 60,000 (comparable to that of around 65,000 assumed for the P(AA-MA) copolymers used in detergents) and a resin polymer (used in inks) with a molecular weight of 4,500 to 9,000 (comparable to that of around 4,500 assumed for the P(AA) homopolymers used in detergents).

4.4.2 Summary of Risk Assessments

EDTA has been widely used for many years due its ability to remove metals. An early review of its use with a European focus (Wolf & Gilbert, 1992) suggested that surface water concentrations would be orders of magnitude below those at which adverse effects would occur.

EDTA and its tetrasodium salt have been the subjects of ESR risk assessments (ECB, 2004; ECB, 2004a).

These have been reviewed by CSTEE which endorsed (CSTEE, 2003b) the findings of the risk assessments that EDTA and its salts were not readily degradable and, for some uses including some large facilities using industrial detergents, that there is a need for limiting the risks (referred to as a Conclusion (iii)). However, CSTEE (2003b) noted that the predicted surface water concentrations were probably overestimated and expressed this reservation:

> *"It is the opinion of the CSTEE that conclusion iii) for some use emissions in the aquatic environment should be accepted as preliminary and more information should be provided for a better assessment of exposure"*

4.4.3 Summary of Monitoring Data

Waste Water Treatment

Available data suggest that EDTA and its salts are not generally removed during waste water treatment[27]. As a consequence, it has been estimated that waste water effluent would typically have EDTA levels of 140-310 µg/L (Wolf & Gilbert, 1992). This estimate appears to be borne out by various data from European WWTPs as indicated in Table 4.4.

Table 4.4: Reported Waste Water Concentrations of EDTA

Medium	Concentration (µg/L)	Year	Location (notes)	Reference
WWTP influent WWTP effluent	30 – 150 30 – 150	1987	Zurich-Glatt (CH)	Alder *et al*, 1990
WWTP effluent	1,000	1990	Munich (DE)	IUCLID
WWTP effluent	20 – 353 (Jun) 219 – 5,524 (Mar) 11.7 – 23 (Dec)	1991	Niederglatt WWTP (CH)	Kari & Giger, 1996
WWTP effluent	0.74 – 2.2	1995	3 Swiss WWTPs	Nowack *et al*, 1996
WWTP effluent	1.5 – 409	1996	10 Swiss WWTPs	Nirel *et al*, 1998
WWTP influent WWTP effluent	28,000 5,800	1998	Finnish WWTP	Kaluza *et al*, 1998

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[27] However, research has shown that increasing the pH within treatment plants can result in a removal rate of 80% (see, for example, van Ginkel *et al*, 1997). Although of limited relevance to general municipal treatment plants, large industrial users with their own on-site treatment plants could significantly reduce EDTA concentrations in effluents by increasing the pH of the treatment process.

Environmental Monitoring

Assuming a dilution factor of 10 for waste water treatment effluents, it might be expected that river EDTA levels would be less than 30 µg/L. This is consistent with river monitoring data from the early/mid 1980s (as reported in Wolf & Gilbert, 1992) from Germany (0-50 µg/L), UK (<15-60 µg/L), Switzerland (<10-54 µg/L) and Austria (17-43 µg/L).

More recent data (largely from Germany and Switzerland) suggest a progressive reduction in EDTA river water levels during the late 1980s and early 1990s (as shown in Table 4.5 overleaf). Groundwater and drinking water levels have also been shown to be generally less than 30 µg/L with levels in lakes generally an order of magnitude lower (although significantly higher concentrations have been measured in Lake Greifensee, Switzerland).

4.4.4 Aerobic Biodegradation

EDTA and its salts are only poorly biodegradable using standard tests although, as noted above, aerobic biodegradation is enhanced under alkaline conditions.

4.4.5 Other forms of Degradation

The environmental behaviour and fate of EDTA and its salts has been the subject of considerable research interest. There is a general consensus that metal-EDTA complexes are particularly stable in the aquatic environment[28] with the notable exception of the Fe(III)-EDTA complex which undergoes rapid photodegradation (Nowack, 1996; Kari & Giger, 1996; Sykora, 2001; Satroutdinov *et al*, 2003). It is of note that the Fe(III)-EDTA complex may account for 30% of EDTA in surface waters and that its photodegradation products are readily biodegradable (Nowack, 2002).

4.4.6 Conclusion

Available data indicate that EDTA and its salts may be of concern to the environment with regard to their use in industrial and institutional (I&I) cleaning - but not for household detergents (where their use is limited). Apart from the direct risk, there is the potential for the (soluble) EDTA to mobilise metals from sediments and soils leading to contamination of surface and ground waters. However, as previously noted (see Section 3.4.5), the EDTA RAR notes that the associated risk is not expected to be significant (ECB, 2004).

Although there remains considerable scope for further research into the precise behaviour of EDTA in the environment (CSTEE, 2003b), it should be noted that closely related compounds (such as EDDA and EDDS) which may deliver similar detergent performance are readily biodegradable (Sykora, 2001; Satroutdinov *et al*, 2003; Dixon, 2003). However, these substances also readily form metal complexes which may not be so readily biodegradable (see, for example, Vandevivere, 2001).

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[28] However, it should be noted that after prolonged research, Sadroutdinov *et al* (2003) were able to demonstrate microbial degradation of calcium, magnesium and manganese EDTA complexes by a specific bacterial strain under laboratory conditions.

Table 4.5: Reported Environmental Concentrations of EDTA (from mid-1980s)

Medium	Concentration (µg/L)	Year	Location (notes)	Reference
River water	4 – 90	1987	German rivers	IUCLID
	11 – 31	1988	German rivers	IUCLID
	24 – 47	1989/90	River Neckar (DE)	Schwuger, 1997
	29	1985	River Ruhr (DE)	IUCLID
	33.5	1986		
	27	1987		
	22.5	1988		
	18	1989		
	23	1990		
	18.5	1991		
	13	1992		
	10.5	1993		
	3 – 20	1990	River Rhine (DE)	Schwuger, 1997
	2.9 – 29	1991	Switzerland	Giger *et al*, 1991
	11.7 – 23.4 (3 locations)	1991	River Glatt (CH)	Xue *et al*, 1995
	2.9 – 55.5 (3 locations))	1992		
	5.84 – 26.3 (2 locations)	1993		
	6.25 – 35.3	1993	German rivers	IUCLID
	12.8	1995	River Glatt (CH)	Nowack *et al*, 1996
	25	2000	River Itter (DE) 1km from WWTP	Wind, 2004
	means: 1.9 - 11 (8 locations)	2000	River Elbe (DE)	TZW (2003)
	means: 0.7 - 6.6 (12 locations)	2001	River Rhine (CH/DE/NL)	
	means: 3.5 - 11 (9 locations)	2001	River Ruhr (DE)	
	means: <0.5 - 11.6 (26 locations)	2001	13 German Rivers	
Lake water	3	1987	Lake Constance	Schwuger, 1997
	1	1987	Lake Geneva	
	1 – 4	1990s	Swiss lakes	Houriet, 1996
	60 – 1,170	1996	Lake Greifensee (CH)	Nowack *et al*, 1996
Groundwater	5 – 25	1984	Switzerland	Giger, 1986
	3.7 – 43	1986	Glatt (CH)	ACPL, 1986 in Wolf & Gilbert, 1992
	2.4 – 10	1986	Rhein basin (CH)	
	5 - 20	1995	Switzerland	Nowack *et al*, 1996
	0.1 – 15	1996	Switzerland	Houriet, 1996
Drinking water	25 (mean)	1984-1986	River Ruhr (DE)	IUCLID
	25 (median)	1987	River Ruhr (DE)	Dietz, 1987
	<10 – 15	1987	Germany	IUCLID
Lake sediment	0.08–0.31 mg/kg	1997	Lake Saimaa (FI)	Sillanpäa *et al*, 1997

4.5 Nitrilotriacetic Acid (NTA)

4.5.1 Chemicals Identified

Entry 25 of Table 3.17 (and Annex 3) is nitrilotriacetic acid (NTA, CAS No. 139-13-9). As already indicated, NTA is used directly or as a trisodium salt in detergents (and are often collectively referred to as NTA).

4.5.2 Summary of Risk Assessments

NTA was introduced into detergents in the 1960s as an alternative builder to phosphate. Although NTA is not genotoxic, it has long been recognised that NTA is a possible human carcinogen (NCI, 1977), a view endorsed by IARC (1990 & 1999). The current IARC Group 2B classification is based on the formation of tumours in the urinary tracts of rodents. The associated threshold concentration (below which tumours do not appear) is well above those concentrations found in the environment.

In March 2006, the Commission's Working Group on the Classification and Labelling of Dangerous Substances decided to classify NTA, trisodium salt as a Category 3 Carcinogen with an R40 label (*limited evidence of a carcinogenic effect*) with a specific concentration limit of 5%[29].

The German authorities are responsible for the preparing the human health ESR RAR (for NTA, trisodium salt) and this will be discussed (for the first time) at a forthcoming meeting of the appropriate committee.

Trisodium nitrilotriacetate (NTA, trisodium salt) is the subject of an environmental ESR RAR also prepared by the German authorities (ECB, 2005) which was published following endorsement of an earlier draft (dated December 2003) by SCHER (2004). Due to the low environmental toxicity of NTA and its rapid biodegradation, NTA (and its salts) are not considered to present a significant risk to the environment (referred to as a Conclusion (ii)).

4.5.3 Summary of Monitoring Data

In Switzerland, levels of NTA (and EDTA) were extensively monitored 'before' and 'after' the cessation of the use of phosphate detergents in 1986. Similarly, levels of NTA (and EDTA) have been extensively monitored in Germany.

Waste Water Treatment

Available data suggest that NTA (and its salts) are substantially removed during waste water treatment resulting in effluent concentrations of, generally, less than 50 µg/L as illustrated in Table 4.6.

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[29] As such, products and preparations with an NTA, trisodium salt content below 5% are not covered by these classification and labelling requirements.

Table 4.6: Reported Waste Water Concentrations of NTA

Medium	Concentration (µg/L)	Year	Location (notes)	Reference
WWTP influent WWTP effluent	60 – 450 3 – 30	1984	Zurich-Glatt WWTP (CH)	Giger *et al*, 1987
WWTP influent WWTP effluent	330 – 1,490 5 – 50	1987		Schwuger, 1997
WWTP influent WWTP effluent	100 – 300 <2 – 23	1987	Hesse WWTPs (DE)	Schwuger, 1997
WWTP influent WWTP effluent	64 – 68 8 - 16	1988	Biefeld-Heppen WWTP (CH)	Schwuger, 1997
WWTP effluent	17.2 – 195 (Jun) 5.7 – 15.3 (Mar) 15.3 – 34.4 (Dec)	1991	Niederglatt WWTP (CH)	Kari & Giger, 1996
WWTP effluent	<2 - 740	1992	UK (10 plants)	FWR, 1992 in ECB, 2005

Environmental Monitoring

Assuming a dilution factor of 10 for waste water treatment effluents, it might be expected that river NTA levels would be less than 5 µg/L. Although this may be generally true, there are locations where higher concentrations can be found (as shown in Table 4.7). This is perhaps surprising given the rapid biodegradation of NTA.

Table 4.7: Reported Environmental Concentrations of NTA

Medium	Concentration (µg/L)	Year	Location (notes)	Reference
River water	0.8 - 10 (annual means)	1990	Switzerland (10 locations)	Verschueren, 2001
	~1 - 36.3	1991	Swiss rivers	Xue *et al*, 1995 Schwuger, 1997
	1.48 - 28.7	1992	Swiss rivers	Schwuger, 1997 Xue *et al*, 1995
	<0.5 - 3.5	1991-92	German rivers	Schwuger, 1997
	<2 - 43 (all) mean 16 (poor rivers) mean <2 (good rivers)	1992	UK rivers (25 locations)	FWR, 1992 in ECB, 2005
	Niederglatt: 3.8 – 9.6 Rheinsfelden: 3.8	1993	River Glatt (CH)	Xue *et al*, 1995
	<2 (N = 78) <10 (N = 84)	1995(?)	Austria (85 locations)	FEA, 1996 in ECB, 2005
	90% < 10 (N = 67) 90% < 100 (N = 84)	1997-98 (monthly)	German rivers (84 locations)	LAWA, 2000 in ECB 2005
	3	2000	River Itter (DE) 1km from WWTP	Wind, 2004
	means: 0.3 - 6.3 (8 locations)	2000	River Elbe (DE)	TZW, 2003
	means: <0.5 - 1.3 (12 locations)	2001	River Rhine (CH/DE/NL)	
	means: <1 - 3.9 (9 locations)	2001	River Ruhr (DE)	
	means: <0.5 - 5.1 (26 locations)	2001	13 German Rivers	

Table 4.7: Reported Environmental Concentrations of NTA

Medium	Concentration (μg/L)	Year	Location (notes)	Reference
Lake water	0.1	1990	Lake Constance	Schwuger, 1997
	<0.5	1993	5 Swiss lakes	IAWR, 1993 in ECB, 2005
	<10	1990s	Swiss lakes	Houriet, 1996
Groundwater/ drinking water	1 - 5	1980s-1990s	Various locations	Bucheli-Witschel & Egli, 2001
Drinking water	<0.5 – 1.4	1993	Germany	Schwuger, 1997

4.5.4 Aerobic Biodegradation

As detailed in the ESR (ECB, 2005), there is consensus that NTA is readily biodegradable using a range of standard tests - although, in some cases, the formation of metal-NTA complexes may slow the rate of degradation. It is likely that it is this factor which explains the higher than expected measurements reported in Table 4.7.

4.5.5 Other forms of Degradation

As for EDTA, it has been noted that Fe(III)-NTA undergoes rapid photodegradation (ECB, 2005).

4.5.6 Conclusion

Although NTA appears not to be of concern to the environment, its presence in a detergent (as for EDTA) excludes the award of an eco-label due to its potential carcinogenicity. NTA, trisodium salt has recently been classified as a Category 3 Carcinogen with an R40 label. Further discussions (at EU level) on the results of the (as yet unpublished) human health risk assessment are imminent.

4.6 Detergent Dyes

4.6.1 Chemicals Identified

Entry 30 of Table 3.17 (and Annex 3) comprises detergent dyes. As discussed in S3.6, it is understood that these comprise a diverse range of 150 to 200 specific chemicals.

4.6.2 Summary of Risk Assessments

No risk assessments relating to detergents dyes have been identified.

4.6.3 Summary of Monitoring Data

No relevant data have been identified.

4.6.4 Aerobic Biodegradation

Although it would be expected that dyes are resistant to degradation, no specific data have been identified.

4.6.5 Other forms of Degradation

Although it would be expected that dyes are resistant to degradation, no specific data have been identified.

4.6.6 Conclusion

At this stage, it is not possible to conclude that dyes do not present any human or environmental risks. However, on the other hand, no evidence has been identified to suggest that dyes present a potential problem.

Since the dyes are present in very low concentrations (typically, <0.1%), it is unlikely that they will be required to be identified by the Detergents Regulation which only requires information to be provided on dyes present in concentrations of greater than 0.2%.

4.7 Polyvinylpyrrolidone (PVP)

4.7.1 Chemicals Identified

Entry 31 of Table 3.17 (and Annex 3) is polyvinylpyrrolidone (PVP, CAS No. 9003-39-8) which may be of potential concern due to its biodegradation properties.

4.7.2 Summary of Risk Assessments

PVP was patented in 1939 and used, initially, in blood plasma during the second world war before being used more widely in the pharmaceutical industry (Schmidt, 1999). It has been used in personal care products since the 1950s and for many years has been used as a food additive.

The safety of the use of PVP as a food additive was assessed in 1966, 1973 and 1980 by an WHO/FAO committee which established an ADI (Allowable Daily Intake) of up to 50 mg/kg bodyweight in 1987 (JECFA, 1980; SCF, 2002). In 1995, PVP was approved for use as a (European) food additive (E1201) (BASF, 2004). In summary, PVP has been used in consumer products for over 50 years and there is a general consensus that it is of no concern from a human/mammalian toxicology point of view.

In relation to the environment, no specific assessments have been identified. However, 1-vinyl-2-pyrrolodine has been the subject of an ESR RAR[30]. Although of limited relevance to the environmental risks of PVP, the CSTEE (2001) indicates that the EU consumption of PVP is about 20,000 t/year. It is of note that this is substantially greater than the figure of 3,500 t/year estimated by the SCF (2002) as discussed in S3.7. However, in any event, it appears that the use in detergents is a very minor use of PVP.

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[30] The draft environmental RAR was published in 1999, reviewed by CSTEE in 2001, and the full RAR was published in 2003.

There appears to be a general consensus that PVP is of limited environmental concern due to its solubility, low toxicity and low bioaccumulation potential. As a consequence, PVP is permitted in eco-labelled detergents.

4.7.3 Summary of Monitoring Data

No data identified.

4.7.4 Aerobic Biodegradation

Available data suggest that PVP is inherently but not readily biodegradable.

4.7.5 Other forms of Degradation

No data available.

4.7.6 Conclusion

PVP is 'safe' for human use and there appears to be a general consensus that PVP is of limited environmental concern. Nevertheless, further data would be desirable to demonstrate that PVP presents no significant environmental risks.

4.8 Fluorescent Whitening Agent FWA-5

4.8.1 Chemicals Identified

Entry 34 of Table 3.17 (and Annex 3) is the fluorescent whitening agent FWA-5 (CAS No. 27344-41-8) which may be of potential concern due to its degradation properties.

4.8.2 Summary of Risk Assessments

According to Kramer (1992), much of the research into FWAs was undertaken during the early 1970s. In summary, although limited bioaccumulation has been observed, the ecotoxicity of FWAs (in general) is low. Furthermore, although degradation is limited, FWAs are substantially removed by waste water treatment, due to strong adsorption to sludge, resulting in very low emissions to surface waters.

A further risk assessment into FWAs was undertaken in 1999 with a focus on the Netherlands (van de Plassche, 1999). This assessment concluded that the risks associated with the use of FWA-5 in detergents were unlikely to be of concern - although, the environmental risks associated with (the more widely used) FWA-1 in detergents may be of concern (depending on the degree of degradation assumed).

More recently, FWA-5 has been the subject of a comprehensive HERA assessment (HERA, 2003). This notes that more than 90% of FWA-5 is used in household detergents[31] with the highest market share being in Spain and Switzerland while FWAs

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[31] As noted in Section 3.9.2, the estimated consumption of FWA-5 in household detergents is estimated ot be 600 t/year while that of FWA-1 is 2,100 t/year.

are not used in Nordic countries. Due to its relatively low toxicity and low bioaccumulation potential[32], the HERA assessment concludes that the use of FWA-5 in detergents would not be expected to result in adverse effects to humans or to the environment.

4.8.3 Summary of Monitoring Data

As for EDTA and NTA, levels of FWAs have been extensively monitored in Germany and Switzerland.

Waste Water Treatment

Monitoring data from WWTPs in Germany and Switzerland, mainly in the 1990s, show (Table 4.8) a maximum concentration of FWA-5 in influent of 21.3 µg/L. In WWTP effluent, the maximum concentration is 8.9 µg/L. It is of note that the effluent concentrations at Swiss WWTPs tend to be higher than those in German installations.

Table 4.8: Reported Waste Water Concentrations of FWA-5

Medium	Concentration (µg/L)	Year	Location	Reference
Waste water effluent	3.3 – 8.9	1986	Four Swiss WWTPs	Schuessler, 1986
Waste water influent Waste water effluent	4.0 – 4.5 0.4 – 1.2	1993	River Isar (DE)	Ciba Geigy in van de Plassche, 1999
Waste water effluent	1.5	1994	Chemnitz (DE)	
Waste water influent Waste water effluent	5.1 – 7.0 0.6 – 2.5	Mid-1990s	German WWTP	
Waste water influent Waste water effluent	6.9 – 21.3 3.3 – 8.9	Mid-1990s	Swiss WWTPs	Unspecified in van de Plassche, 1999
W'water primary effluent W'water secondary effluent	10.6 ± 4.1 6.4 ± 0.7	Mid-1990s	Zurich, Glatt WWTP (CH)	Poiger *et al*, 1998
Waste water effluent	2.1 – 8.4	1995-96	Swiss WWTPs	Stoll, 1997 in van de Plassche, 1999

Environmental Monitoring

Kramer (1992) reports that a 1975 European (seven countries) monitoring programme of FWAs in rivers failed to detect any FWAs apart from in one Swedish river[33] with levels of up to 8 ppb (8 µg/L).

More recent data are available for German and Swiss rivers in the 1990s. These show (Table 4.9) that the maximum concentration of FWA-5 in river water was about 1 µg/L. As for the waste water effluent concentrations discussed above, the concentrations

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[32] Although some studies from the 1970s appear to show limited bioaccumulation in fish (as reported in Kramer, 1992), these are not considered further in subsequent assessments (i.e. van de Plassche, 1999 and HERA, 2003).

[33] Whether or not this had any influence on the current position that FWAs are not used in Nordic detergents is not known.

monitored in Switzerland are higher than those in Germany. For lake water, data for two Swiss lakes from the mid-1990s show a maximum concentration of about 1.5 µg/L.

The recent 2003 HERA report on the substance also contains the results of modelling of FWA-5 concentrations in rivers in several parts of Europe. The modelling took into account the photolysis rates for FWA-5 at winter time. The range of predicted concentrations range from about 0.2 µg/L (in Germany) to over 0.8 µg/L (in Norway).

Table 4.9: Reported Environmental Concentrations of FWA-5

Medium	Concentration (µg/L)	Year	Location	Reference
River water	<0.002 – 0.258	1993	German rivers (Isar, Teltow Canal, Wupper, Leine, Chemnitz)	Ciba Geigy in van de Plassche, 1999; Hochberg *et al*, 1997 in HERA, 2003
	0.041 – 0.574	1994	Five Swiss rivers	Jakob *et al*, 1994 in van de Plassche, 1999
	0.014 – 0.36	1994	River Chemnitz (DE)	Ciba Geigy in van de Plassche, 1999
	0.011 – 1.091 (Mean values: 0.024 – 0.634)	1995-96	Swiss rivers (Rhine, Saane, Aare, Rhone, Thur, Glatt)	Stoll, 1997 in HERA, 2003
River water (predicted concentrations adjusted for photolysis)	0.634 0.228 0.233 0.759 0.706 0.546 0.848	2003	Glatt (CH) Chemnitz (DE) Naples (IT) Madrid (ES) Stockholm (SE) Helsinki (FI) Oslo (NO)	HERA, 2003
Lake water	0.010 – 1.476	1995-96	Swiss lakes (Greinfesee, Aabach)	Stoll, 1997 in van de Plassche, 1999; Stoll *et al*, 1998
Lake sediment	0.1 – 1.632 µg/kg (mean: 0.67)	1993-94	Lake Greifensee (CH)	Stoll, 1997 in HERA, 2003

4.8.4 Aerobic Biodegradation

There is a general consensus that FWA-5 does not biodegrade.

4.8.5 Other forms of Degradation

Once released to surface waters, FWA-5 undergoes rapid isomerisation and photodegradation to produce benzaldeyhyde-2-sulphonic acid salt (the sodium salt is CAS No. 1008-72-6) and 4,4'-biphenyldicarboxaldehyde (CAS No. 66-98-8) - both of which are readily biodegradable (HERA, 2003). Furthermore, the 4,4'-biphenyldicarboxaldehyde also oxides to 4,4'-biphenyldicarboxylic acid (CAS No. 787-70-2).

Clearly, this photodegradation process relies on light and would not be significant in sediments or sludges (although this process could occur when sewage sludge is placed on agricultural land). However, perhaps of more interest from an environmental risk perspective is that there appears to be no readily available data on the ecotoxicity of the FWA-5 degradation products.

4.8.6 Conclusion

The reported concentrations of FWA-5 in the environment are more than an order of magnitude below the PNEC. On this basis, FWA-5 is unlikely to present a significant risk to people or to the environment. However, there remains the possibility that the degradation products are of potential concern.

4.9 Foam Regulators

4.9.1 Chemicals Identified

Entries 36 and 37 of Table 3.17 (and Annex 3) comprise foam regulators with particular reference to paraffins (assumed to be C10-C16 *n*-paraffins) and polydimethyl siloxane (PDMS, CAS No. 9016-00-6). Paraffins may be of concern due to their ecotoxicity while PDMS is not readily biodegradable.

4.9.2 Summary of Risk Assessments

n-Paraffins

Although data exist on properties of paraffins (and other oil products), there do not appear to be any specific risk assessments. Indeed, the oil industry's association, CONCAWE, only commenced risk assessment work on oil products in 2003[34] (in response to the forthcoming implementation of REACH).

However, since the mid-1990s, the industry has been actively involved in developing environmental classification and labelling[35]. Of note is a report by the solvents industry (HSPA, 2000), which recommends that commercial paraffins (C10-C18) merit no environmental classification and labelling on the grounds that paraffins have: low aquatic toxicity; rapid biodegradability; and bioconcentration factors (BCFs) of less than 100. Although it is accepted that the solubility of paraffins is much lower than toxic levels for fish, this does not extend to consideration of algae where toxic effects may be observed at comparable levels. Perhaps of more concern is that there is a clear inconsistency between the BCF factors of less than 100 (for individual paraffins) quoted in the HSPA report and that, for example, of over 42,000 presented in the IUCLID data sheet for tetradecane.

In any event, it would be expected that *n*-paraffins (whether or not dissolved) would be readily removed in waste water treatment plants.

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[34] See www.concawe.be

[35] Annex I of the Dangerous Substances Directive (67/548/EEC of 23 June 1967) contains a list of harmonised classifications and labelling for substances or groups of substances, which are legally binding within the EU. The list is regularly updated through Adaptations to Technical Progress (ATP). The 18th ATP (May 1993) introduced the requirement to account for environmental effects which led to the oil and related industries having to develop a consistent approach across various products.

PDMS

The commercial production of silicones (of which PDMS is the most common) dates back to the 1940s and current global production is around 850 kt/year (Colas, 2005) of which about one third is used in Europe.

In 1994, a comprehensive review of PDMS was published (ECETOC, 1994). This review concluded that the PDMS had a low toxicity and was not of concern. Such findings were confirmed in a recent general review of siloxanes by the Danish EPA (2005) although there were concerns over potential reproductive effects of low molecular weight cyclic-siloxanes and over the high bioconcentration factors of phenyl siloxanes - neither of which are used in detergents. Further risk assessment work has recently been completed by the European Silicone Industry Association. Due to its insolubility, the focus of the report (Stevens, 2006) is on the behaviour and effects in soils and sediments. The report concludes that PDMS possesses no ecotoxicological properties of concern.

4.9.3 Summary of Monitoring Data

No specific data on *n*-paraffins have been located.

Some data on PDMS have been located. There are various studies dating back to the 1970s on the fate of PDMS in waste water treatment plants suggesting that it is effectively removed (>95%) during treatment. However, more recent limited UK data (as quoted in Stevens, 2006) suggest that, in practice, the removal rate may be significantly lower (70-80%) due to adsorption of PDMS to suspended solids in the final effluent. In any event, Watts (1995) concludes that PDMS has no adverse effects on the waste water treatment process.

Table 4.10 summarises the available data as presented in Stevens (2006).

Table 4.10: Reported Concentrations of PDMS

Medium	Concentration (mg/kg dw)	Year	Location	Reference
Waste water influent	72 - 84 µg/L 108 - 119 µg/L	2001?	Stretford WWTP (UK) Crewe WWTP (UK)	Webb *et al*, 2002 in Stevens, 2006
Waste water effluent	20.5 - 29.5 µg/L 19.4 - 25.6 µg/L	2001?	Stretford WWTP (UK) Crewe WWTP (UK)	Webb *et al*, 2002 in Stevens, 2006
Sewage sludge	mean 340	1980s	11 German WWTPs	Siebert, 1988 in Stevens, 2006
Sewage sludge (UK industrial areas)	1200 & 1700	1997?	Nottingham WWTP	CES, 1998 in Stevens, 2006
	840 - 930	1997?	Stockport WWTP	
	515 1335	2001?	Stretford WWTP Crewe WWTP	Webb *et al*, 2002 in Stevens, 2006
Surface water	No European data but world data suggest below detection limit of 5µg/L			
River sediment (industrial)	mean <5 peak <80	1980s	River Rhine	Siebert, 1988 in Stevens, 2006
	mean 3.3 (42 samples)	2000?	River Rhine	CES, 2000 in Stevens, 2006
River sediment (remote)	0.04 & 0.07	2000?	River Wilde Weisseritz (German/Czech border)	

Table 4.10: Reported Concentrations of PDMS

Medium	Concentration (mg/kg dw)	Year	Location	Reference
Sludge amended soils	<detection limit 0.33 - 0.63	1980s	4 German locations 3 German locations	Siebert, 1988 in Stevens, 2006
Sludge & sandy soil	9.3 (90%)	1997?	Near Stockport WWTP	CES, 1998 in Stevens, 2006
Sludge & clay soil	33 (90%)			

As has already been indicated, the PDMS polymers used in detergents have the generic formula CH_3 $\{(CH_3)_2$ Si $O\}_N$ $(CH_3)_2$ Si CH_3. For a molecular weight of the order of 30,000 the value of N will be the order of 400. In relation to siloxanes more generally, concern has tended to focus on the first four siloxanes in the series[36] and on low molecular weight cyclic-siloxanes (with particular reference to octamethylcyclotetra-siloxane (D4) and decamethylcyclopentasiloxane (D5)). In the Nordic countries, there has been an extensive monitoring programme of these compounds during 2003-05 (Nordic Council of Ministers, 2005). In broad terms, the concentrations of the cyclic-siloxanes were found to be two orders of magnitude greater than for the linear PDMSs. In respect of the linear PDMSs, the findings were consistent with those presented in Table 4.10 in that the compounds were substantially removed by waste water treatment, were not detectable in surface waters but were detected in sewage sludge and in sediments.

4.9.4 Aerobic Biodegradation

There is consensus that *n*-paraffins undergo rapid biodegradation whilst PDMS does not. Extensive research indicates that PDMS (and other silicones) can be degraded by microbial action of particular bacteria (albeit slowly) (Lukasiak *et al*, 2003).

4.9.5 Other forms of Degradation

For paraffins, no relevant data have been identified.

Since most of the PDMS used in detergents will end up in sewage sludge which may be added to agricultural land, there is an interest in its behaviour in soil. Work from mid/late 1990s indicates that PDMS degrades faster in 'dry' soils than in 'wet' soils. In particular, clay minerals catalyse the 'de-polymerisation' of PDMS[37] to form dimethylsilanol ($(CH_3)_2$ Si $(OH)_2$) which undergoes further degradation (Colas, 2005). However, under other soil conditions, PDMS may remain in the soil for 20 years or more (Lukasiak *et al*, 2003).

It is worth noting that in laboratory trials (Tolle *et al*, 1994) and field trials (Traina *et al*, 2002), the addition of PDMS containing sewage sludge to soil has shown no significant effects on the growth of crops.

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[36] N = 1 (hexamethyl disiloxane); N = 2 (octamethyl trisiloxane); N = 3 (decamethyl tetrasiloxane); and N = 4 (dodecamethyl pentasiloxane).

[37] Thus it would be expected that PDMS concentrations would be lower in clay than in sandy soils - as indeed illustrated by the (limited) results presented in Table 4.10.

4.9.6 Conclusion

In relation to *n*-paraffins, it is unlikely that significant amounts will reach the environment due to a combination of rapid biodegradation and waste water treatment. Nevertheless, available data on properties such as aquatic toxicity and bioaccumulation are highly uncertain which make it difficult to conclude with confidence that the risks to the environment are of no concern.

The use of PDMS in detergents contributes to its presence in soils and sediments. Although considered persistent, PDMS degrades in the environment - particularly in dry, clay soils. Furthermore, there are few concerns over the risks associated with the higher molecular weight PDMS compounds as used in detergents. More generally, there is evidence to suggest that low molecular weight siloxanes (with particular regard to cyclic-siloxanes - although these are not present in PDMS used in detergents) represent a common pollutant, albeit at concentrations below the threshold for concern.

4.10 Formulation Aids

4.10.1 Chemicals Identified

Entry 39 of Table 3.17 (and Annex 3) is polyetheylene glycols (PEG, CAS No. 25322-68-3) of which those with higher molecular weights (say, 2,000) may be of potential concern due to their degradation properties.

4.10.2 Summary of Risk Assessments

Studies on the human/mammalian toxicity of PEG have been available since the 1940s with the conclusion that PEG has a very low toxicity (JEFCA, 1980a).

No environmental risk assessment studies have been identified.

4.10.3 Summary of Monitoring Data

No data have been identified.

4.10.4 Aerobic Biodegradation

As has already been indicated, the biodegradability diminishes with increasing molecular weight. However, extensive research over the past 40 years has identified various micro-organisms which can be used to biodegrade particular PEG compounds (Kawai, 2003).

4.10.5 Other forms of Degradation

There are also a number of studies (particularly from the early 1980s) demonstrating that PEG compounds can undergo anaerobic biodegradation (Kawai, 2003).

4.10.6 Conclusion

Due to its high solubility, low bioaccumulation potential and low toxicity, there is little to suggest that PEG presents any significant risk to the environment - even allowing for the fact that higher molecular weight PEGs are not readily biodegradable.

4.11 Anti-Redeposition Agents

4.11.1 Chemicals Identified

Entries 40 and 41 of Table 3.17 (and Annex 3) comprise anti-redeposition agents with particular reference to the use of carboxymethylcellulose (CMC, CAS No. 9000-11-7) and polymers based on terephthalic acid and PEG, both of which may be of concern due to their biodegradability.

4.11.2 Summary of Risk Assessments

CMC

CMC has been used in detergents since the late 1940s and, as of 1988, this use accounted for over 15% of the global production. In a review of its use in detergents, Batelaan *et al* (1992) conclude that CMC is a harmless substance due to its degradation and low toxicity. A view endorsed a decade later by Smulders (2002).

Other Polymers

No risk assessment work has been identified.

4.11.3 Summary of Monitoring Data

No specific data have been identified.

4.11.4 Aerobic Biodegradation

Aerobic biodegradation of CMC is slow, being measured in weeks (Batelaan *et al*, 2002)

4.11.5 Other forms of Degradation

Batelaan *et al* (1992) describes how CMC may be degraded by enzymatic hydrolysis (with particular regard to the action of cellulases - which may also be found in detergents as discussed in Section 3.8) and by anaerobic biodegradation.

4.11.6 Conclusion

It is unlikely that the use of CMC in detergents presents significant risks to people or to the environment due, primarily, to its low toxicity. However, further data on levels found in the environment would provide further substantiation of this view.

4.12 Solvents

4.12.1 Chemicals Identified

Entries 45 and 50 of Table 3.17 (and Annex 3) comprise solvents with particular reference to 1-decanol (CAS No. 112-30-1) and triethanolamine (CAS No. 102-71-7). 1-Decanol may be of concern due to its ecotoxicity while triethanolamine is not readily biodegradable (under strict test conditions).

4.12.2 Summary of Risk Assessments

In a brief summary, the Danish EPA (2001) noted the high aquatic toxicity and potential for bioaccumulation of 1-decanol.

A German industry assessment (BUA, 1994) concluded that triethanolamine did not present a significant risk to humans. However, despite its relatively low ecotoxicity and low bioaccumulation potential, there was some uncertainty as to the risk to the environment (with particular regard to the risk to algae). Under the HPV programme, the SIDS profile concluded that the risks to people and the environment were low but further data on exposures would be desirable (OECD, 1997).

Although triethanolamine was, until recently, not considered to be carcinogenic, a recent US report concluded that triethanolamine was found to cause tumours in mice following a two-year dermal study (NTP, 2004).

4.12.3 Summary of Monitoring Data

No specific monitoring data have been identified.

4.12.4 Aerobic Biodegradation

1-decanol undergoes rapid biodegradation. Although triethanolamine (TEA) is generally regarded as being readily biodegradable, there are numerous test results presented in the IUCLID data sheet which suggest a slower rate of biodegradation as discussed further in Annex 5. In summary, although TEA does not pass the ready biodegradation tests, it shows substantial biodegradation in ‘inherent’ and ‘simulation’ tests. In other words, the tests indicate that TEA is likely to rapidly biodegrade under environmental conditions.

4.12.5 Other forms of Degradation

No specific data have been identified.

4.12.6 Conclusion

It is unlikely that the use of 1-decanol in detergents presents significant risks to people or to the environment due, primarily, to its rapid biodegradation.

Further data are required to reach a firm conclusion on whether triethanolamine is likely to be of concern.

4.13 Summary

Eleven organic non-surfactant ingredients of detergents have been reviewed. The overall conclusions are summarised in Table 4.11 with further detail provided in Table 4.12 (overleaf).

Table 4.11: Summary of Analysis

Level of Concern	**Ingredient and Reason for Concern**
Ingredients of concern:	EDTA and EDTA tetrasodium salt - concern to the environment with regard to their use in industrial/institutional cleaners
Ingredients which may be of concern but uncertainties remain:	Phosphonates (HEDP) - concerns over potential toxicity to *Daphnia*
	Nitrilotriacetic acid (NTA) - not of concern to the environment but some concerns over potential carcinogenicity (but rarely used in household detergents)
	Fluorescent whitening agent FWA-5 - lack of data on degradation products
Ingredients on which there is insufficient data to reach a conclusion:	Detergent dyes - very few data available (a situation which may persist)
	Solvents (triethanolamine) - lack of monitoring data and concerns over potential carcinogenicity
Ingredients which are unlikely to be of concern but uncertainties remain:	Polycarboxylates - lack of monitoring data (with particular regard to sludge-treated soil concentrations)
	Phosphonates (ATMP and DTPMP) - lack of monitoring data
	Dye transfer inhibitors: polyvinylpyrrolidone (PVP) - lack of environmental data
	Foam regulators (paraffins) - lack of environmental effects data
	Foam regulators (PDMS) - although the associated risks are low, PDMS may persist in some soils
	Anti-redeposition agents (CMC) - lack of monitoring data
	Solvents (1-decanol) - general lack of data
Ingredients of no concern:	Detergent formulation aids (polyetheylene glycols)

Table 4.12: Summary of Further Analysis of Ingredients of Potential Concern

Ingredient	**Conclusion from Analysis**
Phosphonates	There is a broad consensus that phosphonates degrade slowly and may present a risk to the environment with concern being focused on the potential aquatic chronic toxicity of HEDP (and its salts) to *Daphnia*. It is of note that there appears to be no monitoring data on HEDP (and/or its salts). Although most of the phosphonates (used in household detergents) will end up in sewage sludge of which some is applied to agricultural land, available data indicate that the terrestrial toxicity of phosphonates is very low. On this basis, the presence of phosphonates in sewage sludge does not present a significant risk.
Polycarboxylates	Although polycarboxylates do not readily biodegrade, it is unlikely that their use in detergents would lead to significant risks to consumers or to the environment due to their low toxicity and ecotoxicity. However, there are no available monitoring data and concentrations in sludge-treated soils may be significant.
EDTA and EDTA tetrasodium salt	Available data indicate that EDTA and its salts may be of concern to the environment with regard to their use in industrial and institutional (I&I) cleaning - but not for household detergents (where their use is limited). Apart from the direct risk, there is the potential for the (soluble) EDTA to mobilise metals from sediments and soils leading to contamination of surface and ground waters. However, the EDTA RAR notes that the associated risk is not expected to be significant.
Nitrilotriacetic acid (NTA)	Although NTA appears not to be of concern to the environment, its presence in a detergent (as for EDTA) excludes the award of an eco-label due to its potential carcinogenicity. NTA, trisodium salt has recently been classified as a Category 3 Carcinogen with an R40 label. Further discussions (at EU level) on the results of the (as yet unpublished) human health risk assessment are imminent.
Detergent dyes	At this stage, it is not possible to conclude that dyes do not present any human or environmental risks. However, on the other hand, no evidence has been identified to suggest that dyes present a potential problem.
Dye transfer inhibitors: polyvinyl-pyrrolidone (PVP)	PVP is ‘safe’ for human use and there appears to be a general consensus that PVP is of limited environmental concern. Nevertheless, further data would be desirable to demonstrate that PVP presents no significant environmental risks.
Fluorescent whitening agent FWA-5	The reported concentrations of FWA-5 in the environment are more than an order of magnitude below the PNEC. On this basis, FWA-5 is unlikely to present a significant risk to people or to the environment. However, there remains the possibility that the degradation products are of potential concern.
Foam regulators: paraffins (assumed to be C10-C16 *n*-paraffins) and polydimethyl siloxane (PDMS)	In relation to *n*-paraffins, it is unlikely that significant amounts will reach the environment due to a combination of rapid biodegradation and waste water treatment. Nevertheless, available data on properties such as aquatic toxicity and bioaccumulation are highly uncertain which make it difficult to conclude with confidence that the risks to the environment are of no concern. The use of PDMS in detergents contributes to its presence in soils and sediments. Although considered persistent, PDMS degrades in the environment - particularly in dry, clay soils. Furthermore, there are few concerns over the risks associated with the higher molecular weight PDMS compounds as used in detergents.
Detergent formulation aids:- polyetheylene glycols (PEG)	Due to its high solubility, low bioaccumulation potential and low toxicity, there is little to suggest that PEG presents any significant risk to the environment - even allowing for the fact that higher molecular weight PEGs are not readily biodegradable.
Anti-redeposition agents: carboxy-methylcellulose (CMC)	It is unlikely that the use of CMC in detergents presents significant risks to people or to the environment due, primarily, to its low toxicity. However, further data on levels found in the environment would provide further substantiation of this view.
Solvents: 1-decanol and triethanolamine	It is unlikely that the use of 1-decanol in detergents presents significant risks to people or to the environment due, primarily, to its rapid biodegradation. Further data are required to reach a conclusion on whether triethanolamine is likely to be of concern.

5. IMPLICATIONS OF INCREASED USE OF ZEOLITES

5.1 Introduction

The underlying objective of this report is to consider the implications of substituting detergents which are phosphate based to those that are zeolite based. As already outlined, there was a substantial movement from the use of STPP in laundry detergents to that of zeolites from the mid-1980s to the mid-1990s. This section briefly reviews the use and concerns over the use of phosphate and zeolites in detergents as well as providing a commentary on related issues with particular regard to eutrophication.

5.2 Phosphate Detergents

5.2.1 Introduction

STPP ($Na_5P_3O_{10}$) is manufactured from phosphate rock (most of which is used for phosphate fertilisers).

STPP is an efficient and proven builder in detergents. Its key properties are:

- sequestering of hardness salts (and keeping them in solution);
- removal and prevention of encrustation on fibres;
- enhancement of washing processes; and
- carrier for other powder constituents.

5.2.2 Health & Environmental Concerns

There are no concerns over adverse health effects associated with the use of STPP in detergents. The prime concern over use of phosphate detergents is that it increases the phosphorus load on the environment which, in turn, can lead to problems of eutrophication. Untreated (or partially treated) effluent will lead to additional phosphorus in surface water.

Where the phosphorus is removed by (tertiary) sewage treatment, the resulting sludge[38] may be:

- applied directly to agricultural land;
- disposed of to landfill; or
- incinerated.

Application of the sludge (or, conceivably, of the incinerator ash) to land will also lead to additional phosphorus being introduced to the environment. Clearly, treatment processes do not destroy elemental phosphorus. As of 2000, about half of the sewage

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[38] Of note is that in Spain, it is claimed that significant amounts of sewage sludge are also disposed of to surface waters (CEC, 2004).

sludge from all types of treatment plants in the EU-15 was re-used on agricultural land (CEC, 2004).

5.2.3 Co-builders and Other Ingredients

As discussed in Section 2, both phosphate and zeolite based detergents employ co-builders and contain many other ingredients - which have been reviewed in the previous two sections. As already indicated, it appears that many of the chemicals are used in both types of detergent thus limiting the potential for comparison of the risks associated with each type of detergent.

5.3 Zeolite Detergents

5.3.1 Introduction

As discussed further in Annex 2, a zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions. More than 150 zeolites have been synthesised but the more common ones of commercial importance are zeolite types A, X, Y and ZSM-5.

Zeolites used in detergent formulations exhibit the following properties:

- high binding capacity for multivalent metal ions, particularly calcium ions;
- enhancement of the action of synthetic surfactants;
- alkaline reaction;
- anti-deposition properties (soil suspension power), particularly by adsorption of molecularly dispersed substances and heterocoagulation with pigments;
- support for the action of anti-foaming agents; and
- assistance with the crystallisation of sparingly soluble compounds such as, for example, calcium carbonate.

5.3.2 Health & Environmental Concerns

As discussed in Annex 2, Zeolite A is the dominant zeolite used in detergents and this has been the subject of a comprehensive risk assessment (HERA, 2004b) which concludes that zeolites do not present significant risks to people or to the environment. However, it should be noted that there is insufficient information to determine whether the environmental behaviour of newer zeolites (with particular reference to Zeolites P and X) is similar to that of Zeolite A.

5.3.3 The Need for Co-builders

An effective detergent builder needs to be able to remove both calcium and magnesium during the wash cycle. In phosphate detergents, STPP (the main builder) forms strong complexes with calcium and magnesium ions in solution preventing their precipitation with the detergent surfactant or as carbonates (reducing deposition of solids onto clothing and avoiding loss of detergent surfactant).

Although zeolites remove calcium and magnesium from solution, they require the assistance of a second (soluble) builder, or 'co-builder' to remove calcium/magnesium deposits from the surface if textiles. Whilst Zeolite A had first been combined with sodium triphosphate, the addition of polycarboxylate subsequently proved to be significantly more effective.

The polycarboxylates are able to delay the formation and precipitation of poorly soluble calcium carbonate, by inhibiting crystal growth even when applied at low concentrations in the sub-stoichiometric range (threshold effect) and through their dispersive action. This finding led to what has been, since 1983, the dominant builder system for phosphate-free detergents and which is comprised of Zeolite A, polycarboxylate and sodium carbonate (ZeoDet, 2000).

These co-builders and other ingredients have been reviewed in the previous sections and, as already noted, many ingredients are used in both phosphate and zeolite based detergents.

5.4 Eutrophication

5.4.1 Overview

Eutrophication may be defined (as in the Urban Waste Water Directive[39]) as:

> *the enrichment of water by nutrients especially compounds of nitrogen and phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and the quality of the water concerned.*

As such, the presence of phosphates in the environment can create problems of eutrophication. There is a general consensus that the four main sources of phosphates in the environment are detergents, other human sources, use of phosphate fertilisers and livestock. Domestic sewage includes phosphates from detergents and human excretia. The relative importance of each varies from country to country and from catchment to catchment.

As indicated in Section 2.3.1, the current use of phosphate fertilisers in the EU-25 is about 1.5 million t (as P)/year. This is less than half of that used from the early 1970s to the late 1980s and is forecast to decrease further in the coming decade (EFMA, 2005). By contrast, the current consumption of phosphate-based detergents is estimated (see Table 2.9) to be about 1.8 million t/year which is equivalent to about 110,000 t (as P)/year.

Whilst the use of phosphate-based detergents is not the main contributor to phosphorus loads, it is significant. By way of example, a major study (ERWG, 1996) into the Danube Basin and the north-western shelf reported that the potential reduction in

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[39] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment (OJ L135, 30/5/1991, p40)

phosphorus (associated with STPP use in detergents) could amount to 15,000 tP/year. Reducing this nutrient load was identified as a key priority for tackling eutrophication in the region. Further studies of the Danube basin have shown that a substantial reduction in phosphorous loads have been achieved through an increased use of phosphate-free detergents and improved waste water treatment (BUA, 2003).

As detailed in WRc (2002), such studies resulted in a significant reduction in the use of STPP detergents through a combination of regulatory bans and voluntary actions (including AISE's 'wash-right' campaign (AISE, 2001)). However, in its Opinion on the WRc report, CSTEE (2003) considers that the degree to which reductions in the use of STPP detergents contribute to water quality improvements has yet to be fully evaluated. At the request of DG Enterprise, CSTEE carried out further examination on this issue and subsequently reported (CSTEE, 2003a) that, in some areas, removal of STPP from detergents would significantly reduce problems of eutrophication and, furthermore, the use of zeolite-based detergents should not present undue problems. It is worth noting that industry is sponsoring research (at the Spanish National Research Institute INIA) to fully evaluate the role of phosphate detergents in eutrophication (CEEP, 2006).

5.4.2 Eutrophication in the EU

A detailed account of which rivers, lakes and coastal areas have been designated as 'sensitive areas' due to eutrophication within the EU-15 countries is provided in CEC (2004). More generally, the European Environment Agency has provided a comprehensive overview of the levels in phosphates in EU waters and how these have changed in recent years - and this is used as the prime reference for the summary below.

Rivers

EEA (2003) reports that, in general, phosphate levels declined in rivers from 1990 to 2000. For Western Europe, mean values declined from 150 µgP/l in 1990 to 80 µgP/l in 2000 with similar figures for the Accession Countries with a decline from 110 µgP/l in 1992 to 80 µgP/l in 2000. The levels in Northern Europe were much lower but remained unchanged at 10 µgP/l.

Lakes and Reservoirs

For lakes and reservoirs, there has been a progressive reduction in phosphorus levels (and eutrophication). EEA (2003) reports that the percentage of lakes with summer concentrations in excess of 25 µgP/l has decreased from around 30% in 1981-1986 to a little over 20% in 1996-2001. Much of this reduction is attributed to implementation of the Urban Waste Water Directive. However, there remain many lakes, particularly in Western Europe and the Accession Countries, where excessive levels of phosphorus remain an issue. Although reductions in phosphorus use (essentially through use of zeolite based detergents) and improvements in waste water treatment will reduce the phosphorus load on surface waters, such reductions may be offset by the use of phosphate fertilisers. By way of example, while phosphorus levels have steadily declined in Lake Constance and Ijsselmeer, they have steadily increased in Loughs Neagh and Erne (in Northern Ireland).

Seas and Coastal Zones

EEA (2003) reports that, as would be expected, discharges of phosphorus from rivers are, by far, the most significant sources of phosphorus found in the marine environment. As indicated above, these originate mainly from waste-water treatment plants and agriculture and have been substantially reduced in recent years. As detailed in an earlier report (EEA, 2001), there are particular concerns over the Baltic, the North Sea and some coastal areas of the Irish and Mediterranean Seas.

5.5 Waste Water Treatment

Most of the chemicals used in detergents find their way into waste water (sewage) treatment plants. As discussed further in Annex 4, the degree to which these chemicals and other contaminants are removed from the effluent discharged to river or sea depends on the level of treatment.

Material that is not discharged from WWTP is retained in the sludge which may be disposed of to landfill, incineration or directly to agricultural land. Data on sludge re-use (i.e. application to land) that most countries re-use about half of the sludge.

Although there has been debate over the implications for sewage sludge of moving from phosphate to zeolite detergents, there is an emerging consensus that the use of zeolites in detergents should not increase the volume of sewage sludge produced - particularly when one considers the additional sludge volumes associated with phosphate removal in tertiary treatment.

5.6 Potential Benefits of Moving to Zeolite Detergents

5.6.1 Overview

As already indicated, the key benefit associated with moving from phosphate to zeolite detergents is reducing the phosphorus load to the environment which, in turn, will reduce problems of eutrophication. Although it may be possible to link reduced levels of eutrophication to monetary values, it may be difficult to assign this value as a ‘benefit’ to changing detergents as the same result may be achieved by improved provision of tertiary treatment and/or improved management of phosphate fertiliser applications.

In qualitative terms, the greatest benefits would accrue in those countries with a high phosphate detergent use, a low provision of tertiary treatment (resulting in significant phosphorus loads being discharged directly to rivers/lakes/seas) and existing severe problems of eutrophication. At the other extreme, countries with very low phosphate detergent use would obtain few benefits from a future requirement to move to zeolite (or other phosphate-free) detergents.

5.6.2 Phosphate Detergent Use

As discussed in Section 2, phosphate-based detergents are used for both laundry and dishwashers. Although seven countries (Germany, Austria, Italy, Ireland, Netherlands, Belgium and Luxembourg) are 'phosphate-free', this relates only to laundry detergents.

Estimates of per capita consumption of phosphate-based detergents (used in both laundry and dishwashers) was presented in Table 2.8 and these have been grouped as shown in Table 5.1.

Table 5.1: Annual Phosphate Detergent Use Per Capita

Score	Description	Applicable Countries
1	Very Low (<2 kg/person)	Slovenia, Luxembourg, Italy, Austria, Ireland, Belgium, Germany, Netherlands
2	Low (2-4 kg/person)	Lithuania, Slovakia, Estonia, Latvia, Hungary, Denmark, Sweden, Finland
3	Medium (4-6 kg/person)	France, Greece, UK, Malta, Czech Republic
4	High (>6 kg/person)	Cyprus, Portugal, Poland, Spain

Source: Based on Table 2.8.

5.6.3 Tertiary Treatment

Data on the percentages of national populations connected to tertiary treatment are presented in Annex 4. These can be re-presented as shown in Table 5.2.

Table 5.2: Percentage of Population Provided with Tertiary Treatment

Score	Description	Applicable Countries
1	High (>75%)	Denmark, Germany, Finland, Sweden, Netherlands
2	Medium (20-75%)	Austria, Estonia, Cyprus, UK, Italy, Poland, France (?)
3	Low (<20%)	Luxembourg, Belgium, Greece, Hungary, Spain, Portugal, Ireland, Slovenia, Malta, Czech Republic, Lithuania, Latvia, Slovakia

Source: Based on data in Annex 4

5.6.4 Extent of Eutrophication

Each country within the EU-25 has designated 'sensitive areas' as defined by the Urban Waste Water Directive. This provides an indication of the extent of (or, in a few countries, concern over) eutrophication within each country as illustrated in Table 5.3.

Table 5.3: Extent of (Concern over) Eutrophication

Score	Description	EU-15	New Member States
0	No sensitive areas		Malta
1	Some sensitive areas	France, Greece, Ireland, Italy, Portugal, Spain, UK	Hungary, Slovenia, Cyprus
2	Entire territory (effectively) designated as 'sensitive area'	Austria, Belgium, Denmark, Sweden, Luxembourg, Finland, Netherlands, Germany	Estonia, Latvia, Lithuania, Poland, Slovakia, Czech Republic

Source: Based on Hosner (2004) and CEC (2004).

5.6.5 Degree of Benefits

As an indicator of which countries would have the greatest potential benefits if they were to become 'phosphate-free', the product of the three factors presented in Tables 5.1 to 5.3 was derived and the results are summarised in Table 5.4 (with the full results presented in Table 5.5).

Table 5.4: Benefits of Moving to Phosphate-Free Detergents

Score	Description	Countries
>10	Maximum Benefits	Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal, Slovakia
5-10	Some Benefits	Greece, Cyprus, Estonia, UK, Luxembourg, Hungary, Belgium, France
1-5	Few Benefits	Denmark, Finland, Austria, Sweden, Ireland, Slovenia, Italy, Netherlands, Germany
0	No Benefits	Malta

Table 5.5: Derivation of 'Benefits' Score

Country	Scores for:			Product
	Phosphate Detergent Use	Tertiary Treatment	Eutrophication	
Belgium	1	3	2	6
Czech Republic	3	3	2	18
Denmark	2	1	2	4
Germany	1	1	2	2
Estonia	2	2	2	8
Greece	3	3	1	9
Spain	4	3	1	12
France	3	2	1	6
Ireland	1	3	1	3
Italy	1	2	1	2
Cyprus	4	2	1	8
Latvia	2	3	2	12
Lithuania	2	3	2	12
Luxembourg	1	3	2	6
Hungary	2	3	1	6
Malta	3	3	0	0
Netherlands	1	1	2	2
Austria	1	2	2	4
Poland	4	2	2	16
Portugal	4	3	1	12
Slovenia	1	3	1	3
Slovakia	2	3	2	12
Finland	2	1	2	4
Sweden	2	1	2	4
United Kingdom	3	2	1	6

Whilst it is acknowledged that the approach presented here is fairly simplistic, it does demonstrate that the (potential) benefits associated with moving to phosphate-free detergents vary significantly from country to country. As already indicated, in those countries which are already ‘phosphate-free’ or have no eutrophication issues (i.e. Malta), there are generally few benefits to be obtained. However, there could be significant benefits in some countries (notably Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal and Slovakia).

5.6.6 Commentary on Poland and the UK

Poland

Based on the information presented above, Poland has a high per capita phosphate consumption, a medium provision of tertiary treatment and extensive eutrophication. As a consequence, Poland is identified as one of the countries which would benefit most from a move away from phosphate-based laundry detergents.

Recognition of the relationship between increasing phosphorus inputs to surface waters and the subsequent increase in eutrophication of water bodies gave rise to public concern during the 1970s and 1980s. In 1991, a law was established that limited the maximum amount of phosphorus in laundry detergents from 9% to 6% (equivalent to 25% STPP). An environmental campaign was initiated in 1994 by the Institute for Ecology of Industrial Areas and carried out in stages over a period of nearly two years at a cost of around €60,000 (UNEP, 1998) as outlined in the box below.

Local Awareness Project “Washing may be cheaper” (Poland)

The objective of the campaign was to increase the awareness of the environmental impact of domestic laundry detergents and to reduce the discharge of phosphate to domestic wastewater. The campaign was addressed to the whole population of Poland with special attention focused on the region of a large water reservoir in Goczalkowice where algae blooms have been occurring since the late 1980s. The reservoir is situated in the upper course of Vistula River and constitutes the source of drinking and domestic water for several million people downstream. The campaign targeted users located both downstream and upstream. In Poland the use of septic tanks, which are not always leak-proof, and the disposal of waste waters directly to the nearest water body are still relatively common.

A multi-media approach was used and local press, radio, and television were engaged throughout the entire period of the campaign. The campaign message explained that laundry detergents used in households were one of the major sources of phosphates in surface waters and that changes in consumer behaviour could lead to a better use of water and improved selection and use of appropriate chemical products which, in turn, could significantly reduce causes of eutrophication of waters in lakes and reservoirs.

Consumers were informed that the quantity of laundry detergents depends on several factors including the hardness of water used for the laundry (the softer the water, the less laundry detergent should be used). Consumers were advised to use the laundry detergent in the quantity corresponding to the water hardness. They were also advised to: carefully choose suitable laundry detergents; make maximum use of washing machine capacity; and buy laundry detergents in large packages.

An information leaflet describing water hardness and principles of economic and ecologically “inexpensive” laundry was sent to the population using soft water. In the next phase, stickers, to be fixed to washing machines, were distributed. During the campaign many additional projects were accomplished, such as developing instructions for washing machines with information on water hardness, drawing up maps of water hardness, as well as conducting scientific and educational seminars.

The results of the campaign were monitored throughout the entire period. An opinion poll was conducted at the beginning and end of the campaign by a professional survey centre. The research indicated a several percent increase in the awareness of the general public with regard to the effect of laundry detergent on eutrophication and the understanding of the relationship between water hardness and the

Local Awareness Project "Washing may be cheaper" (Poland)
amount of laundry detergent used. Constant monitoring of inflows to the sewage treatment plant was also performed which showed a decrease in the phosphate content in the sewage. These findings confirmed that the objectives of the campaign were achieved. In spite of the formal termination of the campaign, the implementation of its objectives has continued through regional centres of environmental education. The role of the manufacturers of laundry detergent, who provided maps of water hardness and disseminated individual water hardness testers, was also important.
Source: UNEP, 1998

It has been estimated that more than half of the phosphates used in Polish detergents end up in the Baltic Sea (Dubik, 2000) and that Poland is a key contributor of phosphates to Baltic Sea (Schernewski & Neumann, 2002).

Although phosphate-free laundry detergents were introduced into Poland in early 2000 their use remains limited (Polish Ecological Club, nd).

United Kingdom

Under the Urban Waste Water Treatment Directive, and as of August 2004, 127 water bodies in the UK were designated as Sensitive Areas (Eutrophic) as shown in Table 5.6. The highest numbers of eutrophic sites are found in the Anglian and Midlands regions of England, with relatively few found in Wales, Scotland and Northern Ireland.

Table 5.6: Location of Sensitive Areas (Eutrophic) in the UK

UK Region	Number of Sensitive Areas
Anglian (East)	33
Midlands	26
North West	14
South West	11
Southern	11
Thames	10
North East	7
England (Total)	***112***
Northern Ireland	5
Scotland	5
Wales	5
UK (Total)	**127**

Source: Defra, www.defra.gov.uk

The most comprehensive data[40] available cover regional concentrations of orthophosphates, which show a large peak in annual average concentrations around 1989-90, and a smaller peak in 1996-97.

Since 1997, concentrations of orthophosphates have generally declined in the UK. The regions with the highest concentrations are Thames, Midlands, North West and Anglian (all in England) and these are shown in Figure 5.1.

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[40] Available from: www.defra.gov.uk/environment/statistics/inlwater/iwnutrient.htm

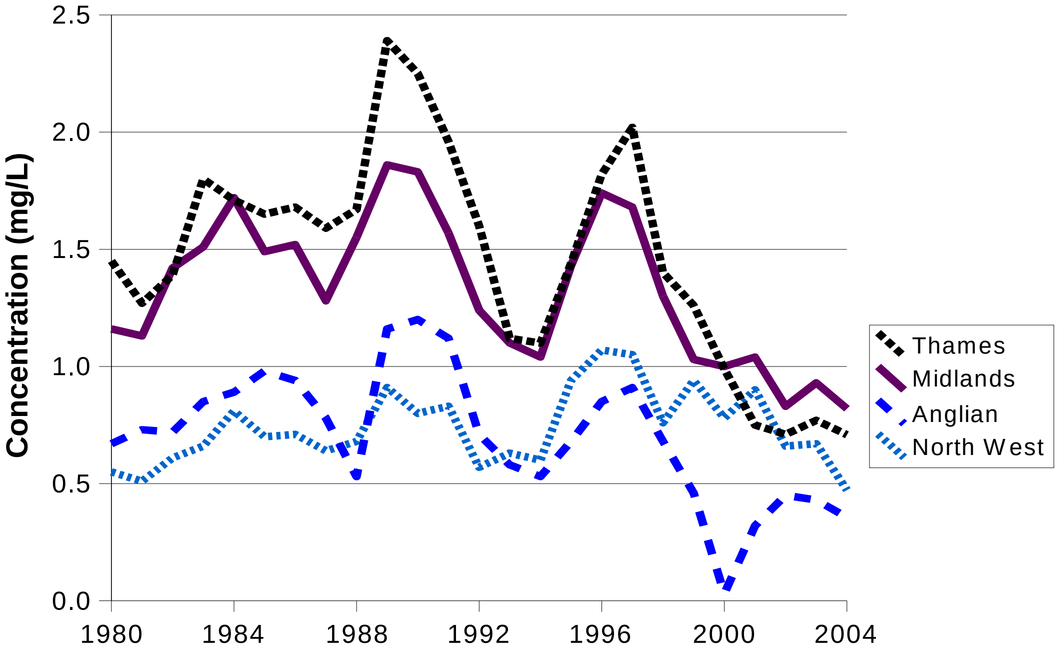

Figure 5.1: Variation in Orthophosphate Concentrations in the UK Regions with the Highest Concentrations (1980-2004)

However, high concentrations of (ortho)phosphate are considered to be those greater than 0.1 mg/L. In 2004, 53% of UK rivers had high concentrations, compared to 50% in 1995, leading Defra to conclude that despite recent improvements in sewage treatment, the proportion of English rivers with high phosphorous concentrations has remained relatively constant over the last ten years.

It has been estimated that detergent products contribute around one quarter of the amount of phosphorus to sewage as human wastes (Water UK, 2002). Furthermore, it has been suggested that reduced phosphorus inputs to surface water from waste water treatment plants during the 1990s were mainly attributable to the reduced use of phosphate in detergents (Environment Agency, 2000). However, such reductions in the phosphate content of household laundry detergents have been partially offset by increases from the use of domestic dishwasher detergents (British Sulphur Publishing, 1998).

To address the risks and impacts of eutrophication, the Environment Agency published a national eutrophication strategy in 2000 (Environment Agency, 2000). This aims to reduce nutrient inputs to water, especially from sewage treatment works and agriculture. The water companies' investment programme for 2000 to 2005 included phosphate removal schemes at over 180 sewage-treatment works, mainly in Thames, Anglian and Midlands regions. However, it is recognised that further steps may be needed where the receiving river is at risk from eutrophication, including the need to address diffuse pollution from agriculture.

5.6.7 Reduction in Tertiary Treatment Costs

Under the Urban Waste Water Directive, tertiary treatment (which removes phosphates) is required at waste water treatment works serving populations of 10,000 or more and which discharge into 'sensitive' areas (i.e. at risk of eutrophication). However, under the Water Framework Directive[41], many more actions will be required for surface and coastal waters to reach 'good ecological status' and the reduction of phosphorous is likely to be a key requirement.

To provide an indication of the potential costs, the UK provides an illustrative example. The UK uses about 300,000 t/year of phosphate detergents (i.e. 75,000 t/year of STPP) but only 27% of the population are connected to tertiary treatment. Furthermore, most UK rivers and lakes do not have good ecological status in relation to phosphorous levels (Arup/Oxera, 2005; UKTAG, 2006). A detailed review of four English catchments indicated that WWTP effluents account for 50% of the phosphorous load on average although the individual catchment figures ranged from 20% to 80%. The cost of providing a tertiary treatment plant is understood to be in the region €2m and using such figures, the estimated cost (incorporating discounting) of phosphorous removal is about €30 per kg (Arup/Oxera, 2005) although the figure varies with nature and size of works, expected effluent standard, etc.

Phosphate detergents account for about 45% of the UK market. If this situation remained, it would be necessary to remove the order 75,000 t/year of STPP (equivalent to 19,000 t/year of phosphorous) from waste water. At present, about 27% of this is removed in existing tertiary treatment plants.

The annual cost of this P-removal can then be estimated to be €416m (= 73% x 19,000 x 1,000 x 30). On this basis, it could be argued that these large costs could be avoided (thus providing a benefit) if the UK was to complete its move to phosphate-free detergents. Clearly, this is an estimate which is open to debate on several grounds. By way of example, under the UWW Directive, tertiary plants will be required for larger population centres so that associated (capital) costs cannot be avoided. Similarly, reduction in phosphate loads (through moving to zeolite detergents) may not remove the need to provide additional tertiary treatment under the Water Framework Directive (or indeed, under the Habitats Directive) due to the phosphate load from human excretia. It would therefore appear that the value of €416m derived above is likely to represent the upper bound of the potential benefits of moving to phosphate-free detergents through avoiding costs associated with removing phosphorous from waste water.

Since the UK consumes about 20% of EU phosphate detergents, this suggests an upper value estimate for the EU-25 of €2bn.

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[41] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy (Water Framework Directive (WFD)) (OJ L327, 22/12/2000, p1)

5.7 Potential Costs of Moving to Zeolite Detergents

5.7.1 Overview

There are a number of potential costs (or disbenefits) associated with moving from phosphate to zeolite detergents, including:

- disruption of the phosphate supply chain;
- need for detergent formulators to reformulate/rebrand detergents;
- potential increase in risks to the people and/or the environment; and
- costs of additional testing.

Although it has not been possible to develop a comprehensive analysis, these are briefly discussed in turn below.

5.7.2 Disruption of Phosphate Supply Chain

WRc (2002) reports that there are six EU manufacturers of STPP with plants in France, Belgium, Spain, Netherlands and Germany (two) which clearly would be affected in the event of a further move towards zeolite detergents. However, such losses would be offset, to a greater or lesser extent, by an expansion of activities within the EU-based zeolite producers. WRc (2002) reports that there are nine main EU zeolite manufacturers with plants in Hungary, Italy, UK, Spain (two), Germany, Belgium, Slovenia and Netherlands.

5.7.3 Reformulation & Rebranding

Across the EU-25, there are numerous detergents (and other products) which have been developed to cater for a wide range of cleaning requirements, water and wash conditions, national legislative requirements, consumer preferences (including such matters as choice of name, colour and fragrance), etc.

Although it might be expected that some of the larger formulators would find it relatively easy to substitute one phosphate detergent with a comparable zeolite detergent currently marketed in another country with similar conditions and consumers, there would still be some costs associated with re-branding. However, the situation becomes more complex where there are smaller formulators (which are likely to include SMEs) serving only the domestic market with phosphate detergents. A change in formulation may well place such formulators at a disadvantage leading to a loss of their market share to the large international companies - particularly in those countries with limited experience of zeolite detergent formulation (such as Poland). Membership statistics for the detergents trade association (AISE) suggest that there could be few hundred SME formulators across the EU-25, each producing several formulations. The costs of reformulation (with particular regard to costs associated with performance testing) could vary from, say, €5k to €100k per formulation. Taking a figure of €20k as an average, this could lead to reformulation costs of €20m for 1,000 formulations.

It is worth noting that the current co-existence of phosphate and zeolite detergents in many countries suggests that there would be a limited impact on the costs of detergent products to consumers. In other words, there is not a significant price differential between phosphate and zeolite detergents.

5.7.4 Increase in Risks to People and the Environment

Table 4.11 listed various detergent ingredients which may be of concern due to their associated risks. One of the drivers for this study has been the view that a move from phosphate to zeolite detergents would lead to the presence of additional co-builders and other ingredients which would, potentially, present hazards to people and the environment (CSTEE, 2003b; CEEP, 2005).

The various co-builders and other ingredients have been reviewed and the results were summarised in Table 4.11. Those of potential concern are listed below in Table 5.7, together with a comment on their likely use.

Table 5.7: Ingredients of Potential Concern by Detergent Type

Ingredient	**Of Concern?**	**Comment**
EDTA (and salts)	Yes	Limited use in household detergents but concern over industrial/institutional use
Phosphonates (HEDP)	Maybe but uncertainties remain	Used in zeolite-based detergents and, to a lesser extent, in phosphate detergents
Nitrilotriacetic acid (NTA)		Limited use in household detergents but concerns over carcinogenicity and use in cleaning formulations
FWA-5		Probably used in zeolite and phosphate detergents
Detergent dyes	Maybe but insufficient data to reach a conclusion	Probably used in zeolite and phosphate detergents
Solvents (triethanolamine)		Probably used in zeolite and phosphate detergents (in limited quantities)

Source: Table 4.11

5.7.5 Additional Costs for Testing

As set out in the Specifications, it was originally envisaged that this study would need to focus on issues associated with biodegradation testing - about which there has been an extensive and protracted debate in relation to surfactants culminating in the testing requirements set out in the Detergents Regulation.

The full suite of ready biodegradation and other standardised tests are described in Annex 5. As discussed in Annex 5, the properties (solubility, adsorption, etc.) of the chemical to be tested dictate, to some extent, the most appropriate test(s) to use. However, it is important to note that the costs of the selected biodegradation test[42] are dependent on the nature of the test rather than on the nature of the chemical being tested. For a simple ‘screening’ ready biodegradation test (using, for example, a single measurement from an ISO 10708 test), the cost may be as little as €500. Whilst this may

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[42] This discussion on testing and costs is based on information kindly supplied by SafePharm Laboratories and Brixham Environmental Laboratory. As these are UK companies, it may well be the case that laboratories in some other Member States would be less expensive.

provide sufficient information for the manufacturer/supplier as to whether a particular chemical is likely to be classified as readily biodegradable or not, a comprehensive test under GLP (Good Laboratory Practice) with a full report for submission to regulators will cost several thousand euros. Although multiple tests are likely to attract a discount, individual ready biodegradation tests are likely to range in cost from around € 3.000 (for OECD 301D and equivalent tests) to around € 6.000 (for the CO_2 evolutions tests OECD 301B and OECD 310 and equivalent tests). Although the cost of a Zahn-Wellens test (OECD 302B and equivalent tests) would be comparable to the more expensive ready biodegradation tests, the costs of other inherent and simulation biodegradation tests could be a factor of two, or more, higher.

More generally, however, the analysis presented in this report suggests that the issue of biodegradation testing is unlikely to be a key issue since most of the ingredients studied have been shown to be either clearly persistent or readily biodegradable. It is accepted that, in some cases, further testing will be required under REACH irrespective of whether the ingredient is destined for zeolite and/or phosphate detergents. It is important to stress that, under the current proposals, the requirements of REACH do not extend to polymers and, of course, vary with different tonnage bands.

Even where extensive data on properties exist, it is likely that there will be a need for further assessments of the risks in some cases. Clearly, this process has progressed significantly in recent years through the industry-led HERA project assessments and the ESR assessments being undertaken by the Competent Authorities.

5.8 Summary

The use of phosphates in detergents contributes to the phosphorous load on the environment which, in turn, contributes to the problems of eutrophication in rivers, lakes and seas. Moves to zeolite-based (or ‘phosphate-free’) laundry detergents have reduced the relative contribution of detergents to the problems of eutrophication. However, such benefits have been offset by the continuing rise in ownership and use of dishwashing machines which generally use phosphate-based detergents.

Further moves to phosphate-free (laundry) detergents will provide the most benefits to those countries with a high phosphate-based detergent consumption, a low provision of tertiary treatment and extensive problems of eutrophication. Such conditions may be applied (to a greater or lesser extent) to seven EU Member States: Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal and Slovakia.

Although there will be associated costs to detergent formulators - primarily as a result of performance testing for new formulations, these are likely to be more than offset by reducing the extent of phosphorous removal required at waste water treatment plants. Perhaps of more concern will be the transfer of market share from SMEs producing and/or formulating phosphate-based detergents in new Member States to international companies which are already supplying phosphate-free products to other European markets.

In relation to non-surfactant organic ingredients used in detergents, analysis of the composition of modern detergents suggests that many substances are used in both phosphate and zeolite-based (laundry) detergents (albeit in different concentrations). As a consequence, concerns over a particular ingredient cannot be readily associated with, say, zeolite-based detergents. Nevertheless, detailed analysis of available data suggests that there remain uncertainties and potential concerns over a number of the ingredients found in detergents.

Although, in due course, further testing will be required under REACH, it is important to stress that such requirements do not apply to polymers. It could therefore be argued, that in the absence of REACH testing requirements, some testing of the polymers found in detergents (including polycarboxylates, polyvinylpyrrolidone, polydimethylsiloxane, poylethyleneglycol and carboxymethylcellulose) would be desirable.

6. OVERALL FINDINGS

6.1 Detergents

The overall consumption of detergents in the EU-25 is probably of the order of six million tonnes per year. Most detergents are used in the household (especially for laundry and dish washing).

Modern detergents may contain 30 or more ingredients. The main ingredients are surfactants which perform the cleaning process through surface chemical reactions. The environmental behaviour and fate of surfactants has been the subject of extensive research which has led, most recently, to the Detergents Regulation[43], which regulates the nature of surfactants used in detergents with particular regard to their biodegradability.

Builders are another important group of ingredients which assist the cleaning process by removing calcium and magnesium ions. Historically, many detergents contained sodium tripolyphosphate (STPP) but this was considered to be contributing to the problems of eutrophication. As a consequence, there was a move towards non-phosphate (or 'phosphate-free') laundry detergents. This resulted in a large increase in the use of zeolite based detergents (together with the associated necessary co-builders) from the mid-1980s to the mid-1990s. However, it is important to note that detergents used in dishwashers are still generally phosphate-based.

The focus of this study is on the current use of organic co-builders and other organic non-surfactant ingredients and associated implications in terms of risks to people and to the environment. It was the intention that this would build on earlier research undertaken for the Commission (WRc, 2002) and take into account of the views of the Scientific Committee on Toxicity, Ecotoxicity and the Environment[44] (CSTEE, 2003 & 2003a). Furthermore, it was hoped that the analysis would facilitate comparison of the costs and benefits of moving from phosphate to zeolite based detergents.

6.2 Identifying Ingredients of Potential Concern

For this study, a list of 50 non-surfactant ingredients (both organic and inorganic) was derived with a focus on those used in household laundry and dish washing detergents. This list was based on those ingredients identified in the Specification with additional ingredients identified in detergent products. It is, of course, accepted that, in recent months, companies have taken further steps to provide comprehensive listings of ingredients in their products as well as associated data sheets (as required by the Detergents Regulation). Furthermore, it is accepted that some of the ingredients (including fragrances) which are now listed (in the public domain) as being present in detergents are not considered in this report.

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[43] Regulation (EC) No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents (OJ L104, 8/4/2004, p1) which came into effect on 8th October 2005.

[44] Now the Scientific Committee on Health and Environmental Risks (SCHER).

For each of these ingredients, a one-page summary of key properties (physico-chemical, toxicological and environmental) was prepared. These summaries provided a basis for determining whether or not a particular ingredient was likely to be of potential concern.

Particular attention was given to those organic ingredients which were not readily biodegradable or had other properties of particular concern. In relation to inorganic ingredients, the only one of concern was sodium perborate which is widely used (in various forms) in detergents as a bleaching agent. The issue is over the potential classification of sodium perborate as Toxic to Reproduction Category 2. Such a classification would lead sodium perborate to be a designated CMR substance which, in turn, could mean that it would no longer be used in detergents[45]. Although this issue has yet to be resolved, the main focus of this report is on organic rather than inorganic compounds.

Based on a review of the ingredient properties, eleven groups of detergent ingredients were identified as being of potential concern comprising:

- phosphonates;
- polycarboxylates;
- EDTA and EDTA tetrasodium salt;
- nitrilotriacetic acid (NTA);
- detergent dyes;
- dye transfer inhibitors with particular reference to polyvinylpyrrolidone (PVP);
- fluorescent whitening agent FWA-5;
- foam regulators with particular reference to paraffins (assumed to be C_{10}-C_{16} *n*-paraffins) and polydimethyl siloxane (PDMS);
- formulation aids with particular reference to the use of polyetheylene glycols (PEG) with higher molecular weights (greater than, say, 2000);
- anti-redeposition agents with particular reference to the use of carboxymethyl-cellulose (CMC) and other polymers; and
- solvents with particular reference to the use of 1-decanol and triethanolamine.

6.3 Further Analysis of the Ingredients of Potential Concern

For each group of ingredients of potential concern, further analysis involved:

- a review of (published) risk assessments;
- a review of monitoring data (with particular emphasis on waste water treatment and surface waters);
- further discussion on degradation pathways; and
- determining whether further work was required.

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[45] Under the latest (29th) Amendment to the Marketing and Use Directive (Directive 2005/90/EC), CMR substances (Categories 1 and 2) and preparations containing them should no longer be placed on the market.

It is important to stress that comprehensive data on the identified groups are not available - with particular reference to monitoring data. Nevertheless, for some ingredients, such as EDTA, there are detailed risk assessments and extensive monitoring data from a few countries. For other ingredients, notably dyes, there is a lack of published information on which to comment. A summary of the analysis is presented in Table 6.1. Entries highlighted in bold are those where there is potential concern (including those for which there are considerable data uncertainties).

Table 6.1: Summary of Further Analysis of Ingredients of Potential Concern

Ingredient	**Conclusion from Analysis**
Phosphonates	**There is a broad consensus that phosphonates degrade slowly and may present a risk to the environment with concern being focused on the potential aquatic chronic toxicity of HEDP (and its salts) to *Daphnia*. It is of note that there appears to be no monitoring data on HEDP (and/or its salts). Although most of the phosphonates (used in household detergents) will end up in sewage sludge of which some is applied to agricultural land, available data indicate that the terrestrial toxicity of phosphonates is very low. On this basis, the presence of phosphonates in sewage sludge does not present a significant risk.**
Polycarboxylates	Although polycarboxylates do not readily biodegrade, it is unlikely that their use in detergents would lead to significant risks to consumers or to the environment due to their low toxicity and ecotoxicity. However, there are no available monitoring data and concentrations in sludge-treated soils may be significant.
EDTA and EDTA tetrasodium salt	**Available data indicate that EDTA and its salts may be of concern to the environment with regard to their use in industrial and institutional (I&I) cleaning - but not for household detergents (where their use is limited). Apart from the direct risk, there is the potential for the (soluble) EDTA to mobilise metals from sediments and soils leading to contamination of surface and ground waters. However, the EDTA RAR notes that the associated risk is not expected to be significant.**
Nitrilotriacetic acid (NTA)	**Although NTA appears not to be of concern to the environment, its presence in a detergent (as for EDTA) excludes the award of an eco-label due to its potential carcinogenicity. NTA, trisodium salt has recently been classified as a Category 3 Carcinogen with an R40 label. Further discussions (at EU level) on the results of the (as yet unpublished) human health risk assessment are imminent.**
Detergent dyes	**At this stage, it is not possible to conclude that dyes do not present any human or environmental risks. However, on the other hand, no evidence has been identified to suggest that dyes present a potential problem.**
Dye transfer inhibitors: polyvinyl-pyrrolidone (PVP)	PVP is 'safe' for human use and there appears to be a general consensus that PVP is of limited environmental concern. Nevertheless, further data would be desirable to demonstrate that PVP presents no significant environmental risks.
Fluorescent whitening agent FWA-5	**The reported concentrations of FWA-5 in the environment are more than an order of magnitude below the PNEC. On this basis, FWA-5 is unlikely to present a significant risk to people or to the environment. However, there remains the possibility that the degradation products are of potential concern.**
Foam regulators: paraffins (assumed to be C10-C16 *n*-paraffins)	In relation to *n*-paraffins, it is unlikely that significant amounts will reach the environment due to a combination of rapid biodegradation and waste water treatment. Nevertheless, available data on properties such as aquatic toxicity and bioaccumulation are highly uncertain which make it difficult to conclude with confidence that the risks to the environment are of no concern.
and	
polydimethyl siloxane (PDMS)	The use of PDMS in detergents contributes to its presence in soils and sediments. Although considered persistent, PDMS degrades in the environment - particularly in dry, clay soils. Furthermore, there are few concerns over the risks associated with the higher molecular weight PDMS compounds as used in detergents.

Table 6.1: Summary of Further Analysis of Ingredients of Potential Concern	
Ingredient	**Conclusion from Analysis**
Detergent formulation aids:- polyetheylene glycols (PEG)	Due to its high solubility, low bioaccumulation potential and low toxicity, there is little to suggest that PEG presents any significant risk to the environment - even allowing for the fact that higher molecular weight PEGs are not readily biodegradable.
Anti-redeposition agents: carboxy-methylcellulose (CMC)	It is unlikely that the use of CMC in detergents presents significant risks to people or to the environment due, primarily, to its low toxicity. However, further data on levels found in the environment would provide further substantiation of this view.
Solvents: 1-decanol	It is unlikely that the use of 1-decanol in detergents presents significant risks to people or to the environment due, primarily, to its rapid biodegradation.
and **triethanolamine**	**Further data are required to reach a conclusion on whether triethanolamine is likely to be of concern.**

With reference to Table 6.1, there are three key observations:

- many detergents contain ingredients which may be of concern in relation to the associated risks, primarily, to the environment;
- for many of the ingredients, there remains considerable uncertainty as to their environmental fate (based on available published information); and
- although the rate of biodegradation is a significant factor, there is little doubt as to whether a particular ingredient readily biodegrades or not.

6.4 Costs and Benefits of Moving to Zeolite-based Detergents

6.4.1 Use of Ingredients in Detergents

At the outset of this study, it was envisaged that the moving from phosphate to zeolite based detergents would involve replacing the phosphate with zeolites together with a number of other necessary ingredients (termed co-builders). In practice, it has been found that many of these co-builders, such as phosphonates and polycarboxylates, are used in both types of detergents. In other cases, notably EDTA and NTA, their use in household detergents is limited and the overall consumption has not changed significantly with the move (in some countries) to phosphate-free detergents.

With reference to those ingredients over which there is potential concern (as highlighted in Table 6.1), Table 6.2 (overleaf) provides an overview of their use in detergents. As can be seen, this table suggests that moving from phosphate to zeolite based detergents would only lead to an increase in the use of phosphonates. This, in turn, suggests that, overall, changes in the (environmental) risks will be associated with those of phosphonates.

Table 6.2: Ingredients of Potential Concern by Detergent Type

Ingredient	Of Concern?	Comment
EDTA (and salts)	Yes	Limited use in household detergents but concern over industrial/institutional use
Phosphonates (HEDP)	Maybe but uncertainties remain	Used in zeolite-based detergents and, to a lesser extent, in phosphate detergents
Nitrilotriacetic acid (NTA)		Limited use in household detergents but concerns over carcinogenicity and use in cleaning formulations
FWA-5		Probably used in zeolite and phosphate detergents
Detergent dyes	Maybe but insufficient data to reach a conclusion	Probably used in zeolite and phosphate detergents
Solvents (triethanolamine)		Probably used in zeolite and phosphate detergents (in limited quantities)

6.4.2 Benefits of Moving to Zeolite Detergents

The key benefit associated with moving from phosphate to zeolite detergents is reducing the phosphorus load to the environment which, in turn, will reduce problems of eutrophication. In qualitative terms, the greatest benefits would accrue in those countries with a high phosphate detergent use, a low provision of tertiary treatment (resulting in significant phosphorus loads being discharged directly to rivers/lakes/seas) and existing severe problems of eutrophication. On the other hand, countries with limited phosphate detergent use would obtain few benefits from any future requirement to move to zeolite (or other phosphate-free) detergents.

These three parameters (phosphate detergent use, provision of tertiary treatment, problems of eutrophication) were assessed for each of the EU-25 countries using a simple scoring system (as described in Section 5.6) and the results are summarised in Table 6.3.

Table 6.3: Benefits of Moving to Phosphate-Free Detergents

Score	Description	Countries
>10	Maximum Benefits	Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal, Slovakia
5-10	Some Benefits	Greece, Cyprus, Estonia, UK, Luxembourg, Hungary, Belgium, France
1-5	Few Benefits	Denmark, Finland, Austria, Sweden, Ireland, Slovenia, Italy, Netherlands, Germany
0	No Benefits	Malta

Whilst it is acknowledged that the approach is fairly simplistic, it does demonstrate that the (potential) benefits associated with moving to phosphate-free detergents vary significantly from country to country. As already indicated, in those countries which are already ‘phosphate-free’ or have no eutrophication issues (i.e. Malta), there are generally few benefits to be obtained. However, there could be significant benefits in some countries (notably Czech Republic, Poland, Spain, Latvia, Lithuania, Portugal and Slovakia).

Although determining economic values for such benefits is complex, there is another benefit of reducing the costs of phosphorous removal. Based on consideration of the UK (as discussed in Section 5.6), an upper bound estimate (for the EU-25) of €2bn was derived. Clearly, this is an estimate which is open to debate on several grounds. By way of example, under the Urban Waste Water Directive[46], tertiary plants will be required for larger population centres so that associated (capital) costs cannot be avoided. Similarly, reduction in phosphate loads (through moving to zeolite detergents) may not remove the need to provide additional tertiary treatment under the Water Framework Directive[47] (or indeed, under the Habitats Directive[48]) due to the phosphate load from human excretia.

6.4.3 Costs of Moving to Zeolite Detergents

Overview

There are a number of potential costs (or disbenefits) associated with moving from phosphate to zeolite detergents, including:

- disruption of the phosphate supply chain;
- need for detergent formulators to reformulate/rebrand detergents;
- potential increase in risks to the people and/or the environment; and
- costs of additional testing.

Disruption of Phosphate Supply Chain

It is reported that there are six EU manufacturers of STPP (WRc, 2002) which clearly would be affected in the event of a further move towards zeolite detergents. However, such losses would be offset, to a greater or lesser extent, by an expansion of activities within the EU-based zeolite producers.

Reformulation and Rebranding

Although it might be expected that some of the larger formulators would find it relatively easy to substitute one phosphate detergent with a comparable zeolite detergent currently marketed elsewhere, the situation becomes more complex where there are smaller formulators (which are likely to include SMEs) serving only the domestic market with phosphate detergents. A change in formulation may well place such formulators at a disadvantage leading to a loss of their market share to the large international companies - particularly in those countries with limited experience of zeolite detergent formulation (such as Poland). The average costs of reformulation (with particular regard to costs associated with performance testing) have been assumed to be €20k per formulation. For 1,000 formulations, this could lead to reformulations costs of €20m or more

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[46] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment (OJ L135, 30/5/1991, p40).

[47] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy (Water Framework Directive (WFD)) (OJ L327, 22/12/2000, p1).

[48] Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora (OJ L206, 22/7/1992, p7) (as amended).

It is worth noting that the current co-existence of phosphate and zeolite detergents in many countries suggests that there would a limited impact on the costs of detergent products to consumers. In other words, there is not a significant price differential between phosphate and zeolite detergents.

Increase in Risks to People and the Environment

Based on the discussion presented above, it is unlikely that a move from phosphate to zeolite based detergents would lead to a significant increase in risks to people and the environment. However, further confirmatory evidence of this would be desirable.

Additional Costs for Testing

Biodegradation testing is relatively inexpensive. An indicative screening test may cost as little as €500 although a comprehensive test with a full report for submission to regulators will cost several thousand euros (or more depending on the test selected).

More generally, however, the analysis presented in this report suggests that the issue of biodegradation testing is unlikely to be a key issue since most of the ingredients studied have been shown to be either clearly persistent or readily biodegradable. It is accepted that, in some cases, further testing will be required under REACH irrespective of whether the ingredient is destined for zeolite and/or phosphate detergents. It is important to stress that, under the current proposals, the requirements of REACH do not extend to polymers and, of course, vary with different tonnage bands.

Even where extensive data on properties exist, it is likely that there will be a need for further assessments of the risks in some cases. Clearly, this process has progressed significantly in recent years through the industry-led HERA project assessments and the ESR assessments being undertaken by the Competent Authorities.

6.4.4 Summary

Based on the analysis presented above, it would appear that there would be significant benefits in moving from phosphate to zeolite based detergents. The benefits would be greatest amongst some of the new Member States (Czech Republic, Poland, Latvia, Lithuania and Slovakia) as well as Spain and Portugal.

However, the necessity for reformulation of detergents would also impact most upon smaller companies (SMEs) producing detergents for the domestic market in these countries. There may also be costs in terms of increased risks to people and to the environment associated with the increased use of those ingredients used in zeolite based detergents. Although there appear to be few such concerns in those countries which are now phosphate-free, uncertainties remain as highlighted above.

6.5 Discussion of the Way Forward and Recommendations

Detergents are used extensively throughout the European Union. From a chemical risk management perspective, they may be characterised as having a wide dispersive use and as being used in high volumes. It is therefore desirable to ensure that detergent ingredients do not present risks to human health or to the environment.

The use of sodium tripolyphosphate (STPP) as the main builder in detergents contributes to the phosphorous load in the environment which, in turn, contributes to problems of eutrophication. Although moves to phosphate-free laundry detergents have reduced this load, it is important to note that most detergents for dishwashing machines are phosphate-based.

Recommendation 1): the detergents industry should be encouraged to develop phosphate-free detergents for dishwashing machines.

Although the development of phosphate-free detergents involves the development of new products or reformulation of existing phosphate-based products, this study has found that many of the 50 ingredients found in leading household detergents may be used in both phosphate and phosphate-free detergents. It is important to note that the overall number of ingredients used in detergents (including cleaning products more generally) within the EU-25 will be significantly greater than these 50 identified ingredients. The Detergents Regulation now requires information on these ingredients to be made more widely available.

Although no evidence has been found to suggest that ingredients used in detergents (whether or not phosphate-based) are, in practice, particularly harmful to people or to the environment, there a number of ingredients over which there remain uncertainties on their properties, environmental fate and associated risks.

It is recognised that, for some of these substances, the requirements of REACH will ensure that more comprehensive data on basic properties and associated health and environmental effects are collated and published. However, REACH does not currently extend to polymers.

Recommendation 2): discussions should be held with the detergents industry to agree a data set (on properties, health and environmental effects) which could be collated and published for the various polymers used in detergents.

It is recognised that whether or not a particular ingredient may be classified as 'readily biodegradable' provides a useful screening tool. However, the analysis presented in this report suggests that, even for persistent ingredients, there may be no associated risks (i.e. the PEC/PNEC ratio is less than one) due to environmental degradation and/or low environmental toxicity. Given the range of current detergent ingredients which are not readily biodegradable, it is not considered practicable to impose a ready biodegradation criterion (in a similar manner as for surfactants under the Detergents Regulation). However, there is a need for an analysis of the associated risks which takes account of the life-cycle of the ingredient. By way of example, such an assessment would consider not only the degradation of the ingredient but also the rate of degradation of the metabolites and their associated risks. Similarly, if a particular ingredient was found to be removed in waste water treatment by adsorption to the sludge, further information on the potential effects of adding such sludge to agricultural soil should be obtained. It is of course accepted that such studies have been undertaken for many of the ingredients considered in this report by Competent Authorities (under the ESR programme), the industry-led HERA programme and other industry groups (such as the CEEP study on PDMS).

It may be the case that where detergent ingredients have been studied and that the associated risk assessments demonstrate that there are no risks, then these ingredients could be declared ‘no risk’. This, in turn, creates the possibility of formulating detergents with ‘no risk’ ingredients.

Although further moves to phosphate-free detergents would reduce the phosphorous load on the environment, the relative importance of the various sources of phosphorous and their associated contributions to eutrophication at a regional level have yet to be fully established. As such, there remains a degree of uncertainty over the benefits of moving to phosphate-free detergents, as well as the over the risks, depending on the ingredients used.

Recommendation 3): the use of phosphate-free detergents should not be encouraged unless all the ingredients can be demonstrated to present no risks to people or to the environment.

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Annex 1

Specifications

WORKING DOCUMENT

TECHNICAL ANNEX

1. OBJECTIVES OF THE STUDY

The study will consist of two independent parts:

I/ PART I

In the context of the European Community policies on sustainable development, the Commission is awarding a study aimed at evaluating the possible health/environmental risk related to the use of non-surfactant organic chemicals in detergent formulations, including detergents used in industrial and institutional applications. Among other parameters, the contractor will determine and analyse the effects on the environment of the incomplete biodegradation (primary / ultimate) of non-surfactant organic compounds. The study will cover the 25 states of the European Union. This study will provide a comprehensive compilation and critical analysis of available environmental data and included in a risk assessment analysis. All these data will pave the way for the subsequent Commission decision to introduce, or not, EU legislation for a biodegradability criterion for non-surfactant organic chemicals in detergents. In this context, the contractor will gather relevant information in order to:

1/ Analyse and compile an exhaustive set of available data on the function, use condition (taking into account regional diversity, habits of the population, etc), and volumes (production, consumption within the EU of the most representative and relevant non-surfactants organic detergent ingredients based respectively on their market share by volume placed on the EU market, as well as on their potential environmental impact. A set of representative substances has been listed under the twelve main categories of non-surfactant organic compounds (Annex 1) used in detergents and cleaning products, including industrial and institutional applications. The first task of the contractor will be to assess the adequacy of the selection of substances listed in the Annex 1 on the basis, in particular, on their biodegradability features and volume consumption. If necessary, the contractor will modify this list if he, or the Commission, judges it necessary. The study will also gather data and information with regard to the concentrations of these representative chemicals, where it is relevant, in the different environmental compartments (water, soil, and sediment) and in living organisms.

2/ Evaluate the intrinsic properties of the representative chemicals mentioned above through a critical analysis of their physical and chemical properties, toxicological and eco-toxicological characteristics available from the international literature. The contractor will include the latest EU classification for those non-surfactant organic chemicals. On the basis of these data, the contractor will identify, where it is relevant, those non-surfactant organic chemicals in detergents that require further hazard evaluation.

3/ Review the available test methods that have been used at International, European or National level to determine the primary/ultimate biodegradability characteristics of the main representative and relevant non-surfactant organic detergent chemicals. The contractor will analyse the results obtained using these methods (heterogeneity of the results, lack of data...).

4/ Summarize available health and environmental risk assessments and risk management practices applicable to the main non-surfactant organic chemicals in detergent and cleaning products. In addition, the report will evaluate the environmental impact due to a poor aerobic biodegradation, during the last 30 years, of the main representative and relevant non-surfactant organic compounds used in detergent formulations (see paragraph 1 above). On the basis of these data, the contractor will identify, where it is relevant, those non-surfactant organic chemicals in detergents that require further risk assessment.

5/ Having identified which test methods would be suitable for the main representative non-surfactant organic chemicals used in detergent formulations, the contractor will draw up a preliminary impact assessment in order to evaluate the repercussions for the industry concerned if such methods should become mandatory, paying particular attention to the impact on SME's.

6/ Evaluate the usefulness of primary/ultimate biodegradability assessment (aerobic conditions) as an instrument for regulating the environmental effects of these main representative and relevant non-surfactant organic chemicals. The contractor will list, where relevant, additional/alternative test methods that might be applied to regulate environmental impact (photochemical biodegradability for example...).

7/ The contractor will identify how prevalent the problem to be addressed is, the gravity and nature of the consequences. The contractor will provide, where this is relevant, a set of costeffective measures to reduce the risk to the environment.

2. DESCRIPTION OF THE WORK.

In the context of (l):

The contractor will begin this literature review by compiling and analysing the available information on the common characteristics of the main groups of non-surfactant organic chemicals and their most important representatives used in the detergent formulations in the 25 EU Member States: functions (molecular structure, chemical and physical intrinsic properties ...), use conditions, production and consumption (over the last decade), provisions that must be fulfilled by the Member States to comply with the first pillar of EU legislation (e.g. Dir 67/548/EEC, Dir 1999/45/EC, Regulation N 93/793/EC, Dir 91/414/EC, Dir 98/8/EC, Dir 76/769/EEC, Dir 96/82/EC, Dir 76/768/EC, Dir 91/689/EEC ...).

The contractor will also compile and analyse the available data on the concentrations of these chemicals in the different environmental compartments (river and lake sediments, freshwater, influents and effluent of wastewater treatment plants (WWTP), sewage sludge, landfills, soil, marine compartments, aerosol) and in food and compare these results with those of other organic compounds commonly found in the environment.

In the context of (2):

The contractor will evaluate the existing data on the toxicological and ecological properties of the representative and relevant non-surfactant organic detergent chemicals included in the twelve categories mentioned in Annex 1 on the different environmental compartments.

This evaluation will review existing data dealing with hazard assessment, paying attention to the intrinsic ecological profile of the substances concerned (e.g. Eco-toxicity, bioaccumulation, persistence, biodegradation ...). In particular, effects on soil are to be considered when sewage sludge has been spread on agricultural land. Effects on river and marine sediments are also to be considered. The hazard properties of biodegradation products (toxic metabolites) should also be addressed.

In addition, the toxicological profile of these chemical must be assessed taking the potential bio-accumulation of those chemicals in the food chain and the subsequent associated human health risks into account.

The contractor will then compile and analyze all available data with regard to the degree of aerobic primary / ultimate biodegradable of the main representative and relevant non-surfactant organic detergent chemicals.

In the context of (3):
The contractor will review the biodegradability tests methods that have been used to determine the biodegradation characteristics of non-surfactant organic compounds. The report will take into account ongoing ISO and OECD activities in this area.

In the context of (4):
Using the compilation and analysis of data and the risk assessments from the last three decades, the contractor will carry out a critical analysis of the impact on health and environment by non-surfactant organic detergent chemicals poorly biodegradable in aerobic conditions. Variations in the EU of parameters such as use patterns and environmental conditions should be taken into account.

The contractor will evaluate the effect of WWTP processes, when correctly applied, on the removal of these chemicals and the subsequent impact on the environmental exposure of non-surfactant chemicals..

The contractor will identify and evaluate the strengths and weaknesses of the available test methods. In particular, the contractor will examine which methodologies are the most appropriate to determine aerobic biological degradation characteristics of non-surfactant organic chemicals relevant for the conditions encountered in WWTP.

In addition the contractor will evaluate whether and under which conditions some chemicals might pose an environmental risk due to their poorly biodegradable properties. The contractor will report on chemicals for which data are associated with doubtful outcomes (some complexing agents, for example listed in Annex 2).

Lastly, the contractor will (i) identify, where it is appropriate, those chemicals for which no suitable biodegradation testing methods are available and/or data are missing and ii) analyse if and which alternative removal mechanisms relevant for WWTPs exist in the case of poorly biodegradable non-surfactant organic detergent ingredients.

In the context of (5):
With regard to the biodegradability test methods that are considered technically suitable, the contractor will take into account the different costs involved making distinction between large, medium and small companies, and the need to implement management procedures, i.e. good laboratory practice and/or ISO accreditation standards. The cost will be considered on the basis of the current capacities of laboratories and on feasibility. Cost is to be evaluated for the different substances individually, and on a global basis for families of products and for individual companies. Cost will take into consideration parameters such as requirements to carry out tests but also requirements to replace substances that might fail the tests. The contractor will give an overall estimation of the percentage of chemicals by number and by volume that might fail the primary/ultimate biodegradability tests and the inherent implications of a ban that should apply with such a scenario, taking into account the availability of substitutes.

In addition, the contractor will indicate, for each of the substances that fail the tests, the detergent sectors and type of industry that are mainly concerned (industrial & institutional applications, dishwashing / laundry detergent areas, SME sectors, etc).

In the context of (6):
The contractor will evaluate the role that primary/ultimate biodegradation criteria, or other test methods (such as photochemical degradation test, for example) could play as key parameters within the risk assessment procedure for the purpose of regulating the environmental effects of non-surfactant organic chemicals used in detergents.

In the context of (7):
The contractor will identify how prevalent the problem to be addressed is, the gravity and nature of the consequences. The contractor will then assess the potential economic and social impacts of various possible measures, highlighting in particular the cost and benefits and advantages/disadvantages of each particular approach.

PART II/

An opinion was issued on 12-13 November 2003 by the Scientific Committee on Toxicity, Eco-toxicity and the Environment (CSTEE) entitled “the environmental impact (reduction in eutrophication'[2]) that would result from banning sodium tripolyhosphate (STPP in household detergents”. In this opinion, the Scientific Committee had recommended to assess the environmental and health risk of zeolite-based detergent, including the co-builders (polycarboxylates, phosphonate, NTA, citrate...) often used in combination with zeolites.

The contractor will conduct an environmental and health risk assessment for the main relevant phosphate substitute co-builders that are used in combination with zeolites in household detergents. The contractor will evaluate the environmental cost/benefit which would result from a substitution of STPP by zeolite and co-builders taking into account, in particular, the regional distribution parameter.

The contractor will also investigate possible additional effects on the aquatic environment, in particular due to the increase of suspended Zeolite-based solids and of sedimentation in natural aquatic ecosystem.

In addition the contractor will consider whether the increase in sludge volume due to Zeolite will be significant, and whether problems may arise from the disposal of any excess sludge.

Meetings: The contractor should be prepared to attend a kick-off meeting at the Commission's premises in Brussels and several other meetings in Brussels at regular intervals (of about 3 month) to discuss the progress of the work. This may include presentations of the study results to a group of experts in Brussels.

The task specified above shall be executed on the contractor’s premises, with the exception of the meetings which will be held in Brussels.

Each conclusion drawn up for parts I and II of the report must be supported by reliable data, be well-argued, and be developed in a coherent comprehensive manner.

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[2] the CSTEE issued its opinion on the basis, in particular, of the report (June 2002) " phosphates and alternative detergent builders" carried out by the WRc and awarded by the European Commission.

ANNEX 1

Main non-surfactant organic chemicals
Non-exhaustive list

The following groups of detergent ingredients should be addressed :

- Acid and bases

ACIDS AND BASES	
Acids	**Acetic acid** (CAS No. 64-19-7)
	Citric acid (CAS No. 77-92-9)

- Bleaches: Bleach-active compounds / Bleach activators /Bleach catalysts / Bleach stabilisers

BLEACHING AGENTS	
	Bleach-active: Na-perborate **Bleach Activator:** Tetraacetyl ethylenediamine. (CAS No. 10543-57-4) **Bleach Stabiliser:** Phosphonate/s

- Builders; Complexing agents / Ion exchangers /

COMPLEXING AGENTS	
Phosphonates -–C-PO3-H2 groups	HEDP= 1-Hydroxy ethane diphosphonic acid (HEDP - CAS No. 2809-21-4) ATMP= Amino tris methylenephosphonic acid (ATMP - CAS No. 6419-19-8)
Polycarboxylates	Sodium polyacrylate (CAS No. 9003-04-7) Polyacrylic acid (CAS No. 9003-01-4) Acrylic acid polymers with maleic anhydride, sodium salt (CAS No. 52255-49-9) Polycarboxylates with a molecular weight of 3,000-4,000 Polycarboxylates with a molecular weight of 1,000-70,000
Sodium citrate	Sodium citrates – Disodium citrate (CAS No. 144-33-2) Trisodium citrate (CAS No. 68-04-2)

EDTA and EDTA Tetra sodium salt	Ethylenediamine tetra acetate, EDTA, (CAS No. 60-00-4) EDTA tetra sodium salt (CAS No. 64-02-8
Trisodiumnitrilotriacetate (NTA)	Nitrilotriacetate, NTA, (CAS No. 139-13-9)

- Corrosion inhibitors

CORROSION INHIBITORS	
	Na-silicate (not organic)

- Dyes

[to be completed]

- Dye transfer inhibitors

DYE TRANSFER INHIBITORS	
	PVP: Poly(N-vinyl pyrollidone)

- Enzymes

Enzymes	
	Proteases Amylase/Cellulase/Lipase

- Fluorescent Whitening agents

Fluorescent Whitening Agents	
	FWA-5 FWA-1

- Foam regulators

Foam Regulators	
	Paraffins Polydimethyl siloxane (PDMS)

- Formulation aids

Formulation Aids	
	Toluene/cumene sulphonates Polyethylene glycols

- Soil repellant/antideposition agens

Antiredisposition Agents	
	Carboxymethylcellulose Polymers of terephthalic acid and polyethylene glycol

- Solvents

SOLVENTS	
Alcohols or alkyl alcohol	**Ethanol** (CAS No. 64-17-5)
	Isopropanol (propan-2-ol) (CAS No. 67-63-0)
	2-Butoxy ethanol (butyl glycol) (CAS No. 111-76-2)
	1-Decanol (CAS No. 112-30-1)
	Butoxy diglycol (CAS No. 112-34-5)
	Propylene glycol (CAS No. 57-55-6)
	Glycerol (CAS No. 56-81-5)
	2-Amino ethanol (CAS No. 141-43-5)

ANNEX 2

Non exhaustive list of non surfactant organic chemicals in detergents that need to be tackled with

A/ INCOMPLETE OR HETEROGENEITY IN THE BIODEGRADABILITY TEST RESULTS

- **Complexing agents**: Phosphonates -–C-PO3-H2 groups; Sodium Polyacrylate, Polyacrylic acid, Acrylic acid polymers with Maleic anhydride; Disodium citrate and Trisodium citrate, Trisodiumnitrilotriacetate (NTA).

- **Solvents**: Etanol and dipropylene glycol

Annex 3

Biodegradability testing under aerobic conditions (Preliminary results)

Organic Substance	Biodegradability		Threshold	Standard Biodegradation Test	References Sources
	Ultimate	Primary	% Aerobic		
1. Complexing Agents					
Phosphonates $-C-PO_3-H_2$ groups	Little	Little		301 E: Ready biodegradability. Modified OECD Screening	CETOX[3] (2001)
				Biological Oxygen Demand Test BOD$_{20}$ Test	
				OECD 301D: Ready Biodegradability Closed Bottle Test	
				Sapromat Test	
HEDP 1-Hydroxy ethane diphosphonic acid CAS No. 2809-21-4	Little	Little	23-33% DOC removals (Dissolved Organic Carbon) ULTIMATE BIODEGRADABILITY	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test[4]	Gledhill[5] and Feijtel 1992
ATMP Amino tris Methylenephosphonic Acid CAS No. 6419-19-8	Little	Little	23-33% DOC removals ULTIMATE BIODEGRADABILITY	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test	Gledhill and Feijtel 1992
Polycarboxylates	Not rapidly			Biological Oxygen Demand Test BOD$_5$ Test	ECETOC 1993[6]
Sodium Polyacrylate CAS No 9003-04-7				Biological Oxygen Demand Test BOD$_{10}$ Test	

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[3] CETOX. Environmental and Health Assessment of Substances in Household. Detergents and Cosmetic Detergent Products. Environmental Project No. 615 2001. http://www.mst.dk/udgiv/publications/2001/87-7944-596-9/html/default_eng.htm Updated 2001.

4 In this method, the measure of the concentration of dissolved organic carbon or the chemical oxygen demand is used to assess the ultimate biodegradability of the test substance.

[5] GLEDHILL, W.E. AND T.C.J. FEIJTEL. Environmental properties and safety assessment of organic phosphonates used for detergent and water treatment applications, p. 261-285. In N.T. de Oude (ed.), Detergents, The Handbook of Environmental Chemistry, Volume 3. Part F. Anthropogenic Compounds. Springer-Verlag, Berlin Heidelberg, Germany (review). 1992.

[6] ECETOC. Polycarboxylate polymers as used in detergents. Joint Assessment of Commodity Chemicals. No.23. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium. 1993.

Organic Substance	Biodegradability		Threshold	Standard Biodegradation Test	References Sources
	Ultimate	Primary	% Aerobic		
Polyacrylic acid CAS No 9003-01-4				302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test	
Acrylic acid polymers with Maleic anhydride, sodium salt CAS No 52255-49-9					
Polycarboxylates with a molecular weight of 3,000-4,000		No evidence			
Polycarboxylates with a molecular weight of 1,000-70,000	Slow	Slow	< 14% ULTIMATE BIODEGRADABILITY	301 E: Ready biodegradability. Modified OECD Screening	ECETOC 1993
			< 20% ULTIMATE BIODEGRADABILITY	Flask fitted with C02 absorbers.	
Sodium citrate	Rapidly		90% ThOD (Theoretical Oxygen Demand) ULTIMATE BIODEGRADABILITY	OECD 301D: Ready Biodegradability Closed Bottle Test During 30 days	IUCLID 2000[7]
Disodium citrate CAS No. 144-33-2	Rapidly				
Trisodium citrate CAS No. 68-04-2	Rapidly				
Ethylenediamine tetra acetate EDTA. CAS No. 60-00-4	Not readily But Inherently		10% Carbon dioxide evolution ULTIMATE BIODEGRADABILITY	Sturm test	CETOX 2001
			22% DOC removal (Dissolved Organic Carbon) ULTIMATE BIODEGRADABILITY		
			37% DOC removal (Dissolved Organic Carbon) ULTIMATE BIODEGRADABILITY	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test	Wolf and Gilbert 1992
Nitrilotriacetate NTA CAS No. 139-13-9			90% Biodegradation	Test with activated sludge 9 and 13 days	CETOX 2001
			20% Biodegradation ULTIMATE BIODEGRADABILITY	OECD 301 B: Ready Biodegradability CO2 Evolution (Modified Sturm Test) 28 days	CETOX 2001
			Not occur	Shake flask Method	Perry et al. 1984.[8]

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[7] IUCLID. CD-ROM. Public data on high volume chemicals. Year 2000 edition, Joint Research Centre, European Chemicals Bureau. Ispra, Italy. 2000.

[8] PERRY, R. Detergent builders and water-quality –a changing scene. Effl. Water Treat. J., 21, 446-449. 1981.

Organic Substance	Biodegradability		Threshold	Standard Biodegradation Test	References Sources
	Ultimate	Primary	% Aerobic		
			Not occur	Biological Oxygen Demand Test	
2. Bleaching Agents					
Tetraacetyl ethylenediamine CAS No. 10543-57-4	Readily		95% DOC removal (Dissolved Organic Carbon) (ULTIMATE BIODEGRADABILITY)	301 E: Ready biodegradability. Modified OECD Screening 28 days	IUCLID 2000
3. Acids and bases					
Acetic Acid CAS No. 64-19-7	Yes		95% Biodegradation (ULTIMATE BIODEGRADABILITY)	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test 5 days	CETOX 2001
Citric acid CAS No. 77-92-9	Readily		98% Biodegradation (ULTIMATE BIODEGRADABILITY)	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test 48 hours	CETOX 2001
4. Solvents					
Ethanol CAS No. 64-17-5	Rapidly		37 to 86% ThOD (Theoretical Oxygen Demand) (ULTIMATE BIODEGRADABILITY)	BOD$_5$	CETOX 2001
			74 and 84% DOC removal (Dissolved Organic Carbon) (ULTIMATE BIODEGRADABILITY)	BOD 5 and 20 days respectively	IUCLID 2000
Isopropanol (propan-2-ol) CAS No. 67-63-0	Rapidly		95% DOC removal (Dissolved Organic Carbon) (ULTIMATE BIODEGRADABILITY)	301 E: Ready biodegradability. Modified OECD Screening 21 days	CETOX 2001
			99.9% Biodegradation (ULTIMATE BIODEGRADABILITY)	303 A: OECD Activated Sludge Units 3 hours	
2-Butoxy ethanol (Butyl glycol) CAS No. 111-76-2	Rapidly		95% DOC removal (Dissolved Organic Carbon) (ULTIMATE BIODEGRADABILITY)	301 E: Ready biodegradability. Modified OECD Screening 28 days	IUCLID 2000
1-Decanol CAS No. 112-30-1			86% ThOD (Theoretical Oxygen Demand) (ULTIMATE BIODEGRADABILITY)	OECD 301D: Ready Biodegradability Closed Bottle Test 30 days	CETOX 2001

Butoxy diglycol CAS No. 112-34-5	Readily		60% ThOD (Theoretical Oxygen Demand) (ULTIMATE BIODEGRADABILITY)	OECD 301C: MITI (I) Test 28 days	IUCLID 2000
Propylene glycol CAS No. 57-55-6	Rapidly		100% Biodegradation	Aerobic biodegradability test with activated sludge 24 hours	CETOX 2001
Glycerol CAS No. 56-81-5	Readily		63% ThOD (Theoretical Oxygen Demand) (ULTIMATE BIODEGRADABILITY)	OECD 301C: MITI (I) Test 14 days	CETOX 2001
			93% ThOD (Theoretical Oxygen Demand) (ULTIMATE BIODEGRADABILITY)	OECD 301D: Ready Biodegradability Closed Bottle Test 30 days	
2-Amino ethanol CAS No. 141-43-5	Rapidly		> 95% DOC removal (Dissolved Organic Carbon) (ULTIMATE BIODEGRADABILITY)	OECD 301A: Ready Biodegradability DOC Die-Away 4 days	IUCLID 2000
			> 80 ThCO2 (Theoretical CO2 production) (ULTIMATE BIODEGRADABILITY)	OECD 301 B: Ready Biodegradability CO2 Evolution (Modified Sturm Test) 19 days	
Dipropylene glycol CAS No. 25265-71-8	Inherently		100% Biodegradation	302 B: Inherent Biodegradability OECD Zahn-Wellens /EVPA Test	CETOX 2001
			16% ThOD (Theoretical Oxygen Demand)	OECD 301D: Ready Biodegradability Closed Bottle Test 28 days	IUCLID 2000

Annex 2

Zeolites and their Properties

A2.1 Introduction

A zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions. As the pores preferably absorb molecules that fit snugly inside the pores and exclude molecules that are too large, they act as sieves on a molecular scale. Therefore, zeolites are a sub-set of molecular sieves.

Zeolites consist of robust, crystalline silica (SiO_2) frameworks. At some places in the framework, Al^{3+} has replaced Si^{4+} and the framework carries a negative charge. Loosely held cations that sit within the cavities preserve the electroneutrality of the zeolite. Some of those cations are amenable to cation exchange and are able to reversibly interact with polar molecules. These properties have significantly contributed to the commercial success of zeolites (Maesen & Marcus, 2001).

Chemically, zeolites are represented by the empirical formula:

$$\underset{\substack{\text{extra-framework}\\ \text{cations}}}{M_{2/x}O} \quad \bullet \quad \underset{\text{framework}}{Al_2O_3 \bullet ySiO_2} \quad \bullet \quad \underset{\text{sorbed phase}}{wH_2O}$$

where M is a metal ion (usually Na^+), x is the cation valence, y is 2 to 10, and w represents the water contained in the voids of the zeolite. However, in this analysis, the more simplified generic formula of $Na_x[(AlO_2)_x(SiO_2)_y]\ .zH_2O$ will be used.

Synthetic zeolites are manufactured from SiO_2^- and $Al_2O_3^-$ containing substances, for instance silicic acid sodium salts, aluminium hydroxides, or aluminates, at temperatures greater than 50 °C and with alkalihydroxides (NaOH) as catalysts. They occur as fine white powders or pastes as well as granulates.

A2.2 Zeolite Characteristics

Zeolites used in detergent formulations exhibit the following properties:

- high binding capacity for multivalent metal ions, particularly calcium ions;
- enhancement of the action of synthetic surfactants;
- alkaline reaction;
- anti-deposition properties (soil suspension power), particularly by adsorption of molecularly dispersed substances and heterocoagulation with pigments. This prevents the 'greying' of clothes and allows for the removal of dyes. In conjunction with the relatively low sodium concentration associated with zeolite as compared with soluble builders, this leads to a reduced risk of dyes discolouring other items. Zeolite is therefore the builder of choice for special products termed 'colour detergents';
- support for the action of anti-foaming agents; and
- assistance with the crystallisation of sparingly soluble compounds such as, for example, calcium carbonate (ZeoDet, 2000; MFG, 1996).

Studies have shown that, despite its insolubility, Zeolite A does not lead to excessive incrustation of fibres. This is due to its specific, optimised particle shape (rounded corners and edges) and particle size (mean value 3.5 µm).

A2.3 Types of Zeolites Used in Detergents

A2.3.1 Overview

More than 150 zeolites have been synthesised but the more common ones of commercial importance are zeolite types A, X, Y, and ZSM-5. The natural zeolites have not gained the commercial importance of the synthetic zeolites due to limitations in availability, large variations in the mineral composition, crystal size, porosity and pore diameter. In spite of a large global consumption of nearly 4 million t/y (2.5 million tonnes from China), they are used in a number of low-tech applications of limited market value. The application areas of natural zeolites can be broadly classified as building materials, agriculture, and others; the consumption in these sectors being in the ratio 6:2:1 (Technical Insights, 2001).

In 1974, Henkel introduced Zeolite A (Linde Type A or LTA) in detergents as a replacement for the environmentally undesired phosphates in Germany. In the USA, Procter and Gamble also started utilising zeolites. While the chemical composition and the basic performance properties of the individual detergent zeolites (Zeolite A, Zeolite P, Zeolite X) are almost identical, the individual types have different crystalline structures resulting for instance, in a firmer binding of calcium ions by Zeolite P and a higher magnesium binding capacity of Zeolite X compared to Zeolite A (HERA, 2004b).

A2.3.2 Zeolite A

The zeolites available for detergents today (Zeolite A, Zeolite P, Zeolite X) have significantly different crystalline structures. The basic unit of the zeolite used in detergents since the 1970s, Zeolite A ($Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\ .27H_2O$), often also referred to as Zeolite NaA or Zeolite 4A, comprises 8 cubo-octahedrons linked via 12 cuboids to a cavity which is referred to as the α-cage. The 'windows' (pores) of these cages have a diameter of 0.42 nm, and can therefore be permeated only by small molecules or ions. Whilst calcium ions diffuse relatively easily into the interstices, the smaller magnesium ions are impeded by a hydrate shell, and are, therefore, incorporated more slowly. Only at higher temperatures, when the hydrate shell of the magnesium ion is gradually removed, does the rate of ion exchange increase (ZeoDet, 2000).

A2.3.3 Zeolite P

Zeolites of the P type with a higher y value in the general structural formula have been known for quite some time, but were unsuitable for detergents due to their inadequate calcium binding. Recently a new type of Zeolite P was developed with a y value of nearly 1.0 and a high calcium exchange capacity. The new type, also referred to as Zeolite MAP (Maximum Aluminium P), possesses a flexible, layered crystal structure. As a result of the somewhat narrower pores of approximately 0.3 nm, and the more flexible, adaptable crystal structure, the calcium ions are bound more firmly than in the case of Zeolite A (ZeoDet, 2000).

Due to their higher selectivity for Ca^{2+} ions, especially at higher calcium loadings, and their faster kinetics, MAP-type zeolites are 10-30% more weight effective than Zeolite 4A as water softeners under practical washing conditions (Ineos, 2002).

The high liquid carrying capacity (LCC)[1] of zeolites and of MAP type zeolites in particular allows non-tower processing routes to be used, thus saving on capital investment and energy costs. In this way formulators gain the freedom to further optimise their formulations, minimize zeolite use, reduce fillers and maximize plant throughput (Ineos, 2002).

Zeolite P displays better compatibility with sodium percarbonate, which is increasingly replacing sodium perborate in detergents. Due to the improved builder properties of the new zeolites, the co-builder (e.g. polycarboxylates) content of detergents can be reduced considerably (ZeoDet, 2000).

A2.3.4 Zeolite X

Following the development of a more economic production process, Zeolite X was recently introduced into the detergent market. Like Zeolite P, the chemical composition of this zeolite is also virtually identical to that of Zeolite A. As with Zeolite A, the basic building blocks of Zeolite X are cubo-octahedrons, which are linked to a faujasite structure via hexagonal prisms. Due to its larger pore diameter of 0.74 nm, Zeolite X is capable of more readily including magnesium ions. The result is a significantly higher magnesium binding capacity compared to Zeolite A and Zeolite P (ZeoDet, 2000).

A2.3.5 Zeolite AX

A further new development on the market is a co-crystallite comprised of 80% Zeolite X and 20% Zeolite A. This grade, referred to as Zeolite AX, displays calcium and magnesium exchange properties which are superior to those of a blend of the pure zeolites (ZeoDet, 2000).

According to a zeolite producer, Zeolite AX is produced by special synthesis conditions that allow the co-crystallisation of Zeolite A together with Zeolite X (where the X content is about 80%). This should not be confused with the simple blend of Zeolite A and Zeolite X because its performance is claimed to be better than that of the blend.

The calcium exchange capacity of this AX type is in the range of a commercial Zeolite A or P for detergents. Moreover, it exhibits an increased exchange rate both towards calcium and magnesium ions. The calcium ions uptake after a short time is better than that of any other detergent zeolite, whether in the presence of excess sodium ions or not.

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[1] Detergent powders contain both solid and liquid components. In order to produce a free-flowing detergent powder, the solid components need to absorb the liquids. Detergent formulators are often forced to use excessive amounts of solid builder or filler to incorporate the required amount of actives in their formulations (Ineos, 2002)

The producer claims that this AX type is particularly suited for detergent manufacturing where all its characteristics lead to important advantages in comparison with a common detergent zeolite. These advantages are more evident at low (<40°C) and medium (40°C - 60°C) washing temperature. The very high liquids adsorption capacity makes this zeolite the ideal builder for ultra compact powder detergents.

A2.4 Current Use of Different Types of Zeolites

While the more recently developed zeolite types P and X may have improved performance properties, Zeolite A represents the most prominent type of zeolite used in detergents. Although the European consumption of zeolites rose significantly from the mid-1980s to the mid-1990s (due to the demand for phosphate-free detergents), the consumption has remained reasonably static at around 650 thousand t/yr in recent years (ZeoDet, 2000).

A2.5 The Need for Co-builders

STPP forms strong complexes with Ca^{2+} and Mg^{2+} ions in solution preventing their precipitation with the detergent surfactant or as carbonates (reducing deposition of solids onto clothing and avoiding loss of detergent surfactant). Zeolites, on the other hand, possessing selectivity for calcium and/or magnesium over sodium are suitable alternatives to STPP.

All detergent zeolites are characterised by high aluminium content. According to Löwenstein's rule, not more than half the Si atoms in the crystal lattice can be replaced by Al atoms. In the case of detergent zeolites, a Si/Al ratio of 1 or virtually 1 is achieved. This in turn results in a maximum content of Na^+ ions, which are necessary to neutralise the AlO^{2-} units. Since Na^+ ions are able to move in the zeolite pores, they can easily be exchanged for calcium ions, and sometimes other ions (ZeoDet, 2000).

The principal obstacles to ion exchange of Ca^{2+} and Mg^{2+} are the large hydration shells surrounding the ions. The hydrated cations are too large to enter the zeolite pores without shedding a number of their associated water molecules. Because of its higher charge density, the Mg^{2+} cation, bare radius 72 pm, has a larger and more tightly held hydration sphere than Ca^{2+}, bare radius 112 pm. In addition, the rate of dissociation of water molecules from the hydration shells is slower for Mg^{2+} than Ca^{2+}. Consequently, the removal of Mg^{2+} from solution by a zeolite is typically less efficient than that of Ca^{2+}.

Zeolite A has mainly been used as a detergent builder due to its high calcium selectivity and its kinetics while it has also been combined with Zeolite X which removes magnesium more effectively than Zeolite A. In the late 1990, a new type of zeolite, Zeolite P, possessing a Si:Al ratio of 1:1 was developed and introduced to detergent formulations (Townsend & Coker, 2001).

An effective detergent builder needs to be able to remove both calcium and magnesium in two ways. First, these cations need to be removed from solution. Zeolites can succeed in controlling calcium levels in that respect. With regard to the second aspect, it is important to note that calcium is bound with soil on the fabric itself and helps the soil to adhere to the surface of textiles. For the removal of such deposits, zeolites require the assistance of a second (soluble) builder, or 'co-builder' (Townsend & Coker, 2001).

Whilst Zeolite A had first been combined with sodium triphosphate, the addition of polycarboxylate subsequently proved to be significantly more effective.

The polycarboxylates are able to delay the formation and precipitation of poorly soluble calcium carbonate, by inhibiting crystal growth even when applied at low concentrations in the sub-stoichiometric range (threshold effect) and through their dispersive action. This finding led to what has been, since 1983, the dominant builder system for phosphate-free detergents and which comprises Zeolite A, polycarboxylate and sodium carbonate (ZeoDet, 2000).

Other substances that are used in conjunction with zeolites in order for zeolites to achieve detergency performance equivalent to that of STPP, include citrate and phosphonates. Optimisation of the surfactant system is also an option to allow zeolite-containing laundry detergents to get a performance which is very similar to that of phosphate-based detergents.

Annex 3

Summaries of Properties of Non-Surfactant Chemicals

General Information

Project Reference 0

(EINECS) Name	EINECS or common name of chemical				
EINECS No.	where available	**CAS No.**	where available		
Synonyms	more common synonyms (but, generally, not trade names)				
Formula	Simplified chemical formula	**Mol. Wt.**	as given		
Classification	see Note overleaf				
Ambient State		**Melting Point**		**Boiling Point**	
Relative Density		**Vapour Pressure Pa**			
Water Solubility mg per L		**Partition Coefficient log Kow**			

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Based on standard tests (required under REACH, Annex V (>1 t/yr), S6.1). In vivo tests required under Annex VI (>10 t/yr)
Eye Irritation	Based on standard tests (required under REACH, Annex V (>1 t/yr), S6.2). In vivo tests required under Annex VI (>10 t/yr)
Skin Sensitisation	Based on standard tests (required under REACH, Annex V (>1 t/yr), S6.3)
Mutagenicity	In vitro genotoxcity (Annex V (>1 t/yr), S6.4) with further testing (including in vivo) required under Annexes VI (>10 t/yr), VII (>100 t/yr) and VIII (>1000 t/yr)
Acute Toxicity	Based on standard tests (required under REACH, Annex VI (>10 t/yr), S6.5)
Repeated Dose Toxicity	Based on 28d test (required under REACH, Annex VI (>10 t/yr), S6.6) and chronic (90d) testing required under Annex VII (>100 t.yr)
Reproductive Toxicity	Required under REACH, Annex VI (>10 t/yr), S6.7) with additonal requirements under Annexes VII (>100 t/yr) and VIII (>1000 t/yr)

Environmental Toxicity

Aquatic Toxicity	Short-term results for Daphnia (Annex V (>1 t/yr), S7.1) and for fish (Annex VI (>10 t/yr)) with further acute/chronic tests under Annex VII (>100 t/yr)
Degradation	Should be considered under REACH, Annex VI (>10 t/yr), S7.2 with testing under Annexes VII (>100 t/yr) and VIII (>1000 t/yr)
Bioconcentration	Testing required under REACH, Annex VII (>100 t/yr), S7.3 with further testing under Annex VIII (>1000 t/yr)
Terrestrial Toxicity	If appropriate, tests required under REACH, Annex VII (>100 t/yr), S7.4 with consideration to long-term testing under Annex VIII (>1000 t/yr)

P?		**vP?**		**B?**		**vB?**		**T?**		**PBT?**		**vPvB?**	

Comments on above: *Main source often given as IUCLID - i.e the IUCLID data sheets dated 18/19 February 2000 as held on the ECB's ESIS database.*

Note on Classification & Labelling

Annex I of the Dangerous Substances Directive (67/548/EEC of 23 June 1967) contains a list of harmonised classifications and labellings for substances or groups of substances, which are legally binding within the EU. The list is regularly updated through Adaptations to Technical Progress (ATP). In the entries which follow, reference is made to the classification and risk phrases (as summarised below) from the latest list (April 2004) which incorporates ATP 29.

For those ingredients not listed in Annex I, reference may be made to classification and risk phrases from manufacturers and other sources. It is important to note that these often vary from source to source.

Classification and Risk Phrases used in Annex I, Directive 67/548/EEC

Classification	Hazard	Description of hazard
E	Explosive	Chemicals that explode.
O	Oxidising	Chemicals that react exothermically with other chemicals.
F+	Extremely Flammable	Chemicals that have an extremely low flash point and boiling point, and gases that catch fire in contact with air.
F	Highly Flammable	Chemicals that may catch fire in contact with air, only need brief contact with an ignition source, have a very low flash point or evolve highly flammable gases in contact with water.
T+	Very Toxic	Chemicals that at very low levels cause damage to health.
T	Toxic	Chemicals that at low levels cause damage to health.
Carc Cat 1	Category 1 Carcinogens	Chemicals that may cause cancer or increase its incidence.
Carc Cat 2	Category 2 Carcinogens	
Carc Cat 3	Category 3 Carcinogens	
Muta Cat 1	Category 1 Mutagens	Chemicals that induce heritable genetic defects or increase their incidence.
Muta Cat 2	Category 2 Mutagens	
Muta Cat 3	Category 3 Mutagens	
Repr Cat 1	Cat 1 Reproductive Toxins	Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or an impairment in reproductive functions or capacity.
Repr Cat 2	Cat 2 Reproductive Toxins	
Repr Cat 3	Cat 3 Reproductive Toxins	
Xn	Harmful	Chemicals that may cause damage to health.
C	Corrosive	Chemicals that may destroy living tissue on contact.
Xi	Irritant	Chemicals that may cause inflammation to the skin or other mucous membranes.
N	Dangerous for the Environment	Chemicals that may present an immediate or delayed danger to one or more components of the environment

Risk Phrases	
R1	Explosive when dry
R2	Risk of explosion by shock, friction, fire or other sources of ignition
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4	Forms very sensitive explosive metallic compounds
R5	Heating may cause an explosion
R6	Explosive with or without contact with air
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R12	Extremely flammable
R14	Reacts violently with water
R15	Contact with water liberates extremely flammable gases
R16	Explosive when mixed with oxidising substances
R17	Spontaneously flammable in air
R18	In use, may form flammable/explosive vapour-air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation
R21	Harmful in contact with skin

R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R27	Very toxic in contact with skin
R28	Very toxic if swallowed
R29	Contact with water liberates toxic gas
R30	Can become highly flammable in use
R31	Contact with acids liberates toxic gas
R32	Contact with acids liberates very toxic gas
R33	Danger of cumulative effects
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R39	Danger of very serious irreversible effects
R40	Limited evidence of a carcinogenic effect
R41	Risk of serious damage to eyes
R42	May cause sensitisation by inhalation
R43	May cause sensitisation by skin contact
R44	Risk of explosion if heated under confinement
R45	May cause cancer
R46	May cause heritable genetic damage
R48	Danger of serious damage to health by prolonged exposure
R49	May cause cancer by inhalation
R50	Very toxic to aquatic organisms
R51	Toxic to aquatic organisms
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R54	Toxic to flora
R55	Toxic to fauna
R56	Toxic to soil organisms
R57	Toxic to bees
R58	May cause long-term adverse effects in the environment
R59	Dangerous for the ozone layer
R60	May impair fertility
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child
R64	May cause harm to breast-fed babies
R65	Harmful: may cause lung damage if swallowed
R66	Repeated exposure may cause skin dryness or cracking
R67	Vapours may cause drowsiness and dizziness
R68	Possible risk of irreversible effects
Risk Phrases are often used in combination as illustrated below	
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R23/25	Toxic by inhalation and if swallowed
R36/37/38	Irritating to eyes, respiratory system and skin
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R68/22	Harmful: possible risk of irreversible effects if swallowed

General Information

Project Reference 1

(EINECS) Name	Acetic Acid		
EINECS No.	200-508-7	**CAS No.**	64-19-7
Synonyms	Ethanoic acid; ethylic acid; methanvecarboxylic acid; vinegar acid.		
Formula	C2 H4 O2	**Mol. Wt.**	60
Classification	R10; C, R35 (Annex I)		
Relative Density	1.05	**Vapour Pressure Pa**	1500 at 20 deg C
Water Solubility mg per L	Miscible	**Partition Coefficient log Kow**	about -0.35

Ambient State	Liquid	**Melting Point**	16.5 deg C	**Boiling Point**	118 deg C

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Corrosive/irritating (rabbit/guinea pig)
Eye Irritation	Highly irritating (rabbit)
Skin Sensitisation	May cause skin sensitisation (MSDS)
Mutagenicity	Negative results in vitro but positive in vivo
Acute Toxicity	Oral: LD50 600 mg/kg bw (rabbit). Higher results for dermal route.
Repeated Dose Toxicity	Various data
Reproductive Toxicity	Some data suggest reprotoxicity

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 75 mg/L (96hr to freshwater fish). Crustacea: EC50 32 mg/L (24hrs). Algae: NOEC <10 mg/L (5 minutes) *No chronic data*
Degradation	4. Readily Biodegradable (results suggest 65-95% after 5 days) in activated sludge
Bioconcentration	Less than 100 (MSDS)
Terrestrial Toxicity	EC0 1 microL/L (generination effects on *Lolium perenne*)

P?	No	**vP?**	No	**B?**	Maybe	**vB?**	Maybe	**T?**	Maybe	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000 with further information from manufacturers' MSDSs.*

General Information

Project Reference 2

(EINECS) Name	Citric Acid				
EINECS No.	201-069-1			**CAS No.**	77-92-9
Synonyms	2-hydroxy-1,2,3-propanetricarboxylic acid; 2-hydroxy-1,2,3-propanetricarbonic acid.				
Formula	$C_6 H_8 O_7$			**Mol. Wt.**	192
Classification	Xi, R36/38 (typical example)				
Ambient State	Solid	**Melting Point**	Decomposes	**Boiling Point**	No data
Relative Density	1.67			**Vapour Pressure Pa**	No data
Water Solubility mg per L	576-1630 at 20 deg C			**Partition Coefficient log Kow**	-1.72 at 20 deg C

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Slighly irritating (rabbit)
Eye Irritation	Highly irritating (rabbit)
Skin Sensitisation	No data
Mutagenicity	Negative
Acute Toxicity	Oral LD50: 3000 mg/kg bw (rat)
Repeated Dose Toxicity	No data
Reproductive Toxicity	No effects detetected

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 c500 mg/L (96hrs freshwater); Daphnia: EC50 c120 mg/L (72hrs); Algae: EC3 640 mg/L (7 days). *No chronic data.*
Degradation	4. Readily biodegradable (98% after 48hrs in deomestic sewage)
Bioconcentration	No data - but unlikely to be significant
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main sources: IUCLID data sheet dated 19 February 2000 and HERA (2005) with further information from manufacturers' MSDSs.*

General Information

Project Reference 3

(EINECS) Name Adipic Acid

EINECS No. 204-673-3 **CAS No.** 124-04-9

Synonyms 1,4-Butanedicarboxylic acid; 1,6-Hexanedioic acid.

Formula C6 H10 O4 **Mol. Wt.** 146

Classification Xi, R36 (Annex 1)

Ambient State Solid **Melting Point** 152 deg C **Boiling Point** >200 deg C

Relative Density 0.65 **Vapour Pressure Pa** Very low

Water Solubility mg per L c15 g/L at 20 deg C **Partition Coefficient log Kow** -0.104 to +0.093

Human/Mammalian Toxicity

Skin Irritation/Corrosion Slightly irritating (rabbit)

Eye Irritation Moderately irritating (rabbit)

Skin Sensitisation Negative (guinea pig) but provokes asthmatic response in humans

Mutagenicity Negative in vitro and in vivo

Acute Toxicity Oral LD50 940 mg/kg bw (rat);

Repeated Dose Toxicity Effects observed amongst rats at feed rates of >500 mg/day

Reproductive Toxicity No effects observed

Environmental Toxicity

Aquatic Toxicity Fish: LC50 c100 mg/L (96hrs freshwater); Daphnia: EC50 85.7 mg/L (24hrs); Algae: EC50 c30 mg/L (72-96hrs). *No chronic data*

Degradation 4. Readily biodegradable (>90% after 5 days in activated sludge)

Bioconcentration Negligible (MSDS)

Terrestrial Toxicity No data

P? No **vP?** No **B?** Maybe **vB?** Maybe **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 19 February 2000 with further information from manufacturers' MSDSs.*

General Information

Project Reference 4

(EINECS) Name	Sodium Hydroxide		
EINECS No.	215-185-5	**CAS No.**	1310-73-2
Synonyms	Caustic soda; Lye; Sodium hydrate;		
Formula	NaOH	**Mol. Wt.**	40
Classification	C, R35 (Annex I)		

Ambient State	Liquid	**Melting Point**	10 to 320 deg C	**Boiling Point**	105 to 1390 deg

Relative Density	1.5 (approx)	**Vapour Pressure Pa**	120 at 20 deg C
Water Solubility mg per L	400 to 1000 at 20 deg C	**Partition Coefficient log Kow**	Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Corrosive (rabbit); Irritating (human)
Eye Irritation	Corrosive (rabbit)
Skin Sensitisation	Not considered to be a skin sensitiser
Mutagenicity	Mostly negative in vitro but positive in Chinese hamsters and in in vivo tests with grasshoppers
Acute Toxicity	Oral LDLo 500 mg/kg bw (rabbit). Dermal LD50 1350 mg/kg bw (rabbit)
Repeated Dose Toxicity	Effects observed in cattle
Reproductive Toxicity	No reprotox data but developmental effects observed in mice

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 45mg/L (96hrs freshwater). Crustacea : EC50 30 mg/L (48hrs shrimp). *No chronic data*
Degradation	5. Not applicable
Bioconcentration	Not applicable
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000 and OECD SIDS (as presented to SIAM 14, March 2002).*

General Information

Project Reference 5

(EINECS) Name Perboric acid, sodium salt

EINECS No. 234-390-0

CAS No. 11138-47-9

Synonyms Metaborate peroxyhydrate; Sodium perborate monohydrate; Sodium perborate tetrahydrate; Sodium peroxoborate. *Note that this compound is essentially a mixture of sodium perborate monohydrate (see Entry 7) and tetrahydrate (see Entry 8)*

Formula See Entries 7 & 8

Mol. Wt. 100-150

Classification See Entries 7 & 8

Ambient State Solid

Melting Point 60 deg C

Boiling Point Not applicable

Relative Density 0.4 to 0.9

Vapour Pressure Pa Negligible

Water Solubility mg per L c20 g/L at 20 deg C

Partition Coefficient log Kow Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion Irritating (rabbit)

Eye Irritation Highly irritating (rabbit)

Skin Sensitisation Not sensitising (guinea pig)

Mutagenicity Positive results in vitro

Acute Toxicity Oral: LD50 1060 mg/kg bw (mouse); LOEL 50 mg/kg bw (dog). Dermal >2000 mg/kg bw. IV: LD50 78 mg/kg bw (dog).

Repeated Dose Toxicity Tests suggest NOAEL of 200 mg/kg bw but one test suggested changes in growth rates induced at 50 mg/kg bw (rabbit)

Reproductive Toxicity Tests (with tetrahydrate) on rats found developmental effects suggesting a NOAEL of 100 mg/kg bw for both maternal and developmental toxicity (draft RAR)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 51 mg/L (96hrs fresh water). Daphnia: EC50 11 mg/L (48hrs). Algae: EC50 18 mg/L (96hrs) . *No chronic data.*

Degradation 5. Not applicable

Bioconcentration Not applicable

Terrestrial Toxicity No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	Yes	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: IUCLID (dated 18 February 2000); draft ESR RAR (Umweltbundesamt, 2003).*

General Information

Project Reference 6

(EINECS) Name	Sodium metaborate, anhydrous				
EINECS No.	231-891-6			**CAS No.**	7775-19-1
Synonyms	Sodium metaborate; Sodium monoborate; Boric acid, monosodium salt				
Formula	B O2 . Na			**Mol. Wt.**	65.8
Classification	Likely to be similar to Entries 7 & 8				
Ambient State	Solid	**Melting Point**	966 deg C	**Boiling Point**	1434 deg C
Relative Density	2.464			**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	260 g/L at 20 deg C			**Partition Coefficient log Kow**	Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Likely to be an irritant
Eye Irritation	Likely to be an irritant
Skin Sensitisation	No data (but other borates are not skin sensitisers)
Mutagenicity	No evidence of mutagenicity/carcinogenicity
Acute Toxicity	Oral LD50 2330 mg/kg bw (rat)
Repeated Dose Toxicity	No data
Reproductive Toxicity	Probable developmental effects at high concentrations

Environmental Toxicity

Aquatic Toxicity	Fish LC50 63 mg/L (salmon, fresh water). Some further data available on sodium tetraborate include Daphnia EC50 242 mgB/L and Algae EC10 24 mgB/L
Degradation	5. Not applicable
Bioconcentration	Not applicable
Terrestrial Toxicity	Will affect plants as used in defoliants

P? No	**vP?** No	**B?** No	**vB?** No	**T?** Yes	**PBT?** No	**vPvB?** No

Comments on above: *No IUCLID data so data drawn from various sources including: www.chem007.com (Chinese supplier data sheet); www.pesticideinfo.org (Pesticide Action Network (PAN) database); Borax's MSDS for sodium metaborate dihydrate.*

General Information

Project Reference	7		
(EINECS) Name	Sodium perborate monohydrate		
EINECS No.	239-172-9	**CAS No.**	10332-33-9
Synonyms	Disodium-di-u-peroxo-bis-(dihydroxoborate)monohydrate; Sodium perborate monohydrate; Sodium peroxoborate monohydrate; Perboric acid, sodium salt.		
Formula	$[NaBO_2.H_2O_2]_2$ or $NaBO_3.xH_2O$	**Mol. Wt.**	99.8
Classification	See comment below		
Ambient State	Solid	**Melting Point**	60 deg C
Boiling Point	Decomposes		
Relative Density	0.4 to 0.65	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	c15 g/L at 20 deg C	**Partition Coefficient log Kow**	Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Irritating (rabbit)
Eye Irritation	Highly irritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Positive results in vitro
Acute Toxicity	Oral: LD50 1060 mg/kg bw (mouse); LOEL 50 mg/kg bw (dog). Dermal >2000 mg/kg bw. IV: LD50 78 mg/kg bw (dog).
Repeated Dose Toxicity	Tests suggest NOAEL of 200 mg/kg bw but one test suggested changes in growth rates induced at 50 mg/kg bw (rabbit)
Reproductive Toxicity	Tests (with tetrahydrate) on rats found developmental effects suggesting a NOAEL of 100 mg/kg bw for both maternal and developmental toxicity (draft RAR)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 51 mg/L (96hrs fresh water). Daphnia: EC50 11 mg/L (48hrs). Algae: EC50 18 mg/L (96hrs) . *No chronic data.*
Degradation	5. Not applicable
Bioconcentration	Not applicable
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	Yes	No	No

Comments on above:

Main sources: HERA Perborates RA (2002); draft ESR RAR (Umweltbundesamt, 2003)
Proposed classification: O, R8; Repr.Cat 2, R61; Repr. Cat 3, R62; Xn, R20/22; Xi, R37-41 (but see S3.3, main text).

General Information

Project Reference	8

(EINECS) Name	Sodium perborate tetrahydrate		
EINECS No.	No number	**CAS No.**	10486-00-7
Synonyms	Disodium-di-u-peroxo-bis-(dihydroxoborate)hexahydrate; Sodium perborate tetrahydrate; Sodium peroxoborate tetrahydrate; Perboric acid, sodium salt.		
Formula	[NaBO2.H2O2]2.6H2O or NaBO3 x4 H2O	**Mol. Wt.**	153.9
Classification	See comment below		

Ambient State	Solid	**Melting Point**	60 deg C	**Boiling Point**	Decomposes
Relative Density	0.65-0.9	**Vapour Pressure Pa**	Negligible		
Water Solubility mg per L	23 g/L at 20 deg C	**Partition Coefficient log Kow**	Not applicable		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Irritating (rabbit)
Eye Irritation	Highly irritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Positive results in vitro
Acute Toxicity	Oral: LD50 1060 mg/kg bw (mouse); LOEL 50 mg/kg bw (dog). Dermal >2000 mg/kg bw. IV: LD50 78 mg/kg bw (dog).
Repeated Dose Toxicity	Tests suggest NOAEL of 200 mg/kg bw but one test suggested changes in growth rates induced at 50 mg/kg bw (rabbit)
Reproductive Toxicity	Tests on rats found developmental effects suggesting a NOAEL of 100 mg/kg bw for both maternal and developmental toxicity (draft RAR)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 51 mg/L (96hrs fresh water). Daphnia: EC50 11 mg/L (48hrs). Algae: EC50 18 mg/L (96hrs) . *No chronic data.*
Degradation	5. Not applicable
Bioconcentration	Not applicable
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	Yes	**PBT?**	No	**vPvB?**	No

Comments on above:

Main sources: HERA Perborates RA (2002); draft ESR RAR (Umweltbundesamt, 2003)
Proposed classification: O, R8; Repr.Cat 2, R61; Repr. Cat 3, R62; Xn, R20; Xi, R37-41 (but see S3.3, main text).

General Information

Project Reference	9		
(EINECS) Name	N,N'-ethlyenebis[N-acteylacetamide]		
EINECS No.	234-123-8	**CAS No.**	10543-57-4
Synonyms	TAED (tetra acetyl ethylene diamine);		
Formula	C10 H16 N2 O4	**Mol. Wt.**	228
Classification	None		

Ambient State	Solid	**Melting Point**	152 deg C	**Boiling Point**	No data
Relative Density	0.6 (bulk) 1.32 (solid)	**Vapour Pressure Pa**	Negligible		
Water Solubility mg per L	1 g/L at 20 deg C	**Partition Coefficient log Kow**	-0.08 to -2.4		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating (rabbit)
Eye Irritation	Not irritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Negative in vitro and in vivo
Acute Toxicity	Oral LD50 > 2000 mg/kg bw (rat).
Repeated Dose Toxicity	NOAEL 90 mg/kg bw (rat 90 days)
Reproductive Toxicity	No data but teratogenicity NOEL > 200 mg/kg bw(rat)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >250 mg/L (96hrs fresh wtaer). Daphnia: EC50 > 800 mg/L (48hrs). Algae: NOEL >500 mgL (14 days).
Degradation	4. Readily biodegradable (typically around 90% after 28 days) *Note: TAED is rapidly converted to DAED (di acetyl ethylene diamine) during the wash cycle*
Bioconcentration	3 (estimated, HERA)
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main data sources: IUCLID (dated 18 February 2000) & HERA (2002b).*

General Information

Project Reference 10

(EINECS) Name Disodium carbonate, compounds with hydrogen peroxide (2:3)

EINECS No. 239-707-6 **CAS No.** 15630-89-4

Synonyms Carbonic acid disodium salt (with hydrogen peroxide 2:3); Disodium carbonate, hydrogen peroxide (2:3); Sodium Percarbonate;

Formula (CH2 O3)3 (H2 O2)2 Na2 **Mol. Wt.** 314

Classification O, R8; Xn, R22; Xi, R41 (industry standard)

Ambient State Solid **Melting Point** Decomposes **Boiling Point** Not applicable

Relative Density 1 (bulk) 2.1 (solid) **Vapour Pressure Pa** Negligible

Water Solubility mg per L 130-150 g/L at 20 deg C **Partition Coefficient log Kow** Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion Slightly irritating (rat/rabbit).

Eye Irritation Highly irritating (rabbit)

Skin Sensitisation Not sensitising (guinea pig)

Mutagenicity No data

Acute Toxicity Oral LD50 >1034 mg/kg bw (rat) but effects on dogs observed at 300 mg/kg bw. Dermal LDLo >2000 mg/kg bw (rabbit)

Repeated Dose Toxicity No data

Reproductive Toxicity No data

Environmental Toxicity

Aquatic Toxicity Fish: LC50 70.7 mg/L (96hrs fresh water). Daphnia: EC50 100 mg/L (24hrs). Other crustacea: EC50 89 mg/L (96hrs). Algae: LOEC 10 mg/L (21d). *HERA reports EC50s of 4.9 (Daphnia) and 7.7 mg/L (algae) based on hydrogen peroxide tests.* Chronic Daphnia NOEC 0.1 mg/L (21d)

Degradation 5. Not applicable

Bioconcentration Not applicable

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000 & HERA (2002).*

General Information

Project Reference	11		
(EINECS) Name	Etidronic acid		
EINECS No.	220-552-8	**CAS No.**	2809-21-4
Synonyms	(1-hydroxy-1-phosphone-ethyl)-phosphonic acid; (1-hydroxyethylidene)-1,1-diphosphonic acid; 1-hydroxyethane-1,1-diphosphonic acid; acetophosphonic acid; HEDP.		
Formula	$C_2 H_8 O_7 P_2$	**Mol. Wt.**	206
Classification	C, R34; N, R 51/53 (typical)		
Ambient State	Solid	**Melting Point**	c195 deg C
		Boiling Point	>200 deg C
Relative Density	1.44 at 20 deg C	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	680 g/L at 25 deg C	**Partition Coefficient log Kow**	-3.49

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Slightly irritating (rabbit)
Eye Irritation	Varying results up to corrosive (rabbit)
Skin Sensitisation	Not sensitising (SIAM)
Mutagenicity	No evidence of mutagenicity (HERA)
Acute Toxicity	Oral LD50 1100 mg/kg bw (mouse). Dermal LD50 >4764 mg/kg bw (rabbit)
Repeated Dose Toxicity	Effects on respiratory system at 1 mg/m3 (rat, 21d), Cat oral LOAEL 50 mg/kg bw (6 weeks). HERA suggests a NOAEL of 19 mg/kg bw/d (rat, 2yrs)
Reproductive Toxicity	NOAEL c100 mg/kg bw (based on both reproductive and developmental tests) but SIAM suggests a NOAEL of c250 mg/kg bw for reproductive/developmental toxicity.

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 180 mg/L (14d fresh water). Daphnia: EC50 100 mg/L (24hrs). Other crustacea: EC50 89 mg/L (96hrs). Algae: LOEC 10 mg/L (21d) but EC50 3 mg/L (SIAM) Chronic Daphnia NOEC 0.1 mg/L (21d) (HERA)
Degradation	2. Inherently biodegradable - numerous test results ranging from 0% to 33% after 28 days
Bioconcentration	IUCLID: 71 (fish); SIAM suggests BCF<2; HERA suggests <2-18.
Terrestrial Toxicity	Soil dwelling organisms (and plants) LC50 > 960 mg/kg soil dw. Birds LC50 > 284 mg/kg bw (SIAM)

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000; UK/ICCA SIDS Profile on HEDP and Salts at SIAM 18 (April 2004) and HERA draft Phosphonates assessment dated September 2004.*

General Information

Project Reference 12

(EINECS) Name	Tetrasodium (1-hyrdoxyethylidene)biphosphonate		
EINECS No.	223-267-7	**CAS No.**	3794-83-0
Synonyms	(1-Hydroxyethylidene)bisphosphonic acid tetrasodium salt; HEDP-4Na; Tetrasodium etidronate		
Formula	C2 H8 O7 P2.4Na	**Mol. Wt.**	252
Classification	Xi, R36/38; N, R 51/53 (typical)		

Ambient State	Solid	**Melting Point**	>100	**Boiling Point**	Not applicable

Relative Density	1.4?	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	Soluble	**Partition Coefficient log Kow**	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not an irritant (SIAM)
Eye Irritation	Mild irritant (SIAM)
Skin Sensitisation	Not sensitising (SIAM)
Mutagenicity	AS for HEDP, no evidence of mutagenicity (HERA)
Acute Toxicity	Oral LD50 940 mg/kg bw (rat). Dermal LD50 >1650 mg/kg bw (rabbit)
Repeated Dose Toxicity	As for HEDP, HERA suggests a NOAEL of 19 mg/kg bw/d (rat, 2yrs)
Reproductive Toxicity	Tests on HEDP salts suggest NOAEL >447 mg/kgbw/d (rat 2 generation) (HERA(

Environmental Toxicity

Aquatic Toxicity	As for HEDP, Fish: LC50 180 mg/L (14d fresh water). Daphnia: EC50 100 mg/L (24hrs). Other crustacea: EC50 89 mg/L (96hrs). Algae: LOEC 10 mg/L (21d) but EC50 3 mg/L (SIAM) . Chronic Daphnia NOEC 0.1 mg/L (21d) (HERA)
Degradation	2. Inherently biodegradable - based on HEDP results
Bioconcentration	IUCLID: 71 (fish); SIAM suggests BCF<2; HERA suggests <2-18.
Terrestrial Toxicity	As for HEDP, Soil dwelling organisms (and plants) LC50 > 960 mg/kg soil dw. Birds LC50 > 284 mg/kg bw (SIAM)

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *As for HEDP.*

General Information

Project Reference 13

(EINECS) Name Nitrilotrimethylenetris (phosphonic acid)

EINECS No. 229-146-5 **CAS No.** 6419-19-8

Synonyms Amino tris (methylene phosphonic acid) (ATMP);

Formula C3 H12 N O9 P3 **Mol. Wt.** 299

Classification C, R34, R36/38 (typical)

Ambient State Solid **Melting Point** >200 deg C **Boiling Point** Decomposes

Relative Density 1.3 **Vapour Pressure Pa** 101 at 25 deg C

Water Solubility mg per L 500 g/L at 35 deg C **Partition Coefficient log Kow** -3.53

Human/Mammalian Toxicity

Skin Irritation/Corrosion Moderately irritating (rabbit)

Eye Irritation Moderately irritating (rabbit)

Skin Sensitisation Not sensitising (guinea pig)

Mutagenicity Generally negative in vitro and in vivo

Acute Toxicity Oral: LD50 2790 mg/kg bw (rat). Dermal: LD50 >6310 mg/kg bw (rabbit)

Repeated Dose Toxicity Oral NOAEL 150 mg/kg bw/day (rat) (IUCLID). Although HERA suggests similar NOAEL for ATMP salts, that for ATMP is suggested to be >500 mg/kg bw/d (rat, 2yrs)

Reproductive Toxicity Not a reprotoxic substance. For developmental toxicity NOAEL >275 mg/kg bw (rat 3 generation study) (HERA)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 150 mg/L (fresh water); Daphnia: EC50 190 mg/L; Algae: EC50 12 mg/L. Chronic NOEC >23 mg/L (fish & Daphnia); 7.4 mg/L (algae)

Degradation 2. Inherently biodegradable - numerous test results ranging from 0% to 30% after 28 days

Bioconcentration 18 - 24

Terrestrial Toxicity Plants: LC50 >1000 mg/L. Birds: LC50 >565mg/kg bw

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000, HERA (2004).*

General Information

Project Reference 14

(EINECS) Name	[[(phosphonomethyl)imino]bis[(ethylenenitrilo)bis (methylene)]] tetrakisphosphonic acid, sodium salt		
EINECS No.	244-751-4	**CAS No.**	22042-96-2
Synonyms	Diethylene triamine penta (methylenephosphonic acid), sodium salt (DTPMP-xNa)		
Formula	C9 H28 N3 O15 P5 .xNa	**Mol. Wt.**	617
Classification	Xi, R36/38		
Ambient State	Liquid	**Melting Point**	<-20 deg C
		Boiling Point	100 deg C
Relative Density	1.3	**Vapour Pressure Pa**	<2500 at 20 deg C
Water Solubility mg per L	>500 g/L	**Partition Coefficient log Kow**	-3.4

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Slightly irritating (rabbit)
Eye Irritation	Slightly irritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Positive results for some mouse tests in vitro.
Acute Toxicity	Oral LD50 >5000 mg/kg bw (rat); >2510 mg/kg bw (birds). Dermal LD50 >2000 mg/kg bw (rabbit)
Repeated Dose Toxicity	Oral NOAEL 2.5 mg/kg bw/day (rat - 90 days)
Reproductive Toxicity	Reprotox NOAEL c90 mg/kg bw/day for F1 and F2 rat offspring. Developmental NOAEL (re skletal deformation) 500/1000 mg/kg bw/day (rat)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >100mg/L (fresh water); Crustacea: EC50 156 mg/L; Algae: EC50 8.68 mg/L Fish: Chronic NOEC >26 mg/L (60 days). *Note HERA reports lower algae values (EC50 <1 mg/L) for DTPMP.*
Degradation	2. Inherently biodegradable (for example 5-18% after 28 days).
Bioconcentration	No data (but unlikely to be significantly greater than other phosphonates)
Terrestrial Toxicity	Birds: LC50 >454 mg/kg bw (HERA value for DTPMP)

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
Yes	Maybe	No	No	No	No	No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000, HERA (2004).*

General Information

Project Reference 15

(EINECS) Name	Sodium polyacrylate		
EINECS No.	None	**CAS No.**	9003-04-7
Synonyms	2-propenoic acid, homopolymer, sodium salt		
Formula	(-CH2-CH-COONa)n	**Mol. Wt.**	c4000
Classification	Not determined		
Ambient State	Liquid/Solid	**Melting Point**	
		Boiling Point	>100 degC
Relative Density	1.3	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	Miscible	**Partition Coefficient log Kow**	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	May cause mild irritation
Eye Irritation	May cause mild irritation
Skin Sensitisation	Negative (guinea pig) (generic data - see Entry 19)
Mutagenicity	No evidence of mutagenicity
Acute Toxicity	Oral LD50 >5000 mg/kg bw (rat); >2510 mg/kg bw (birds). Dermal LD50 >20000 mg/kg bw (rabbit)
Repeated Dose Toxicity	No data
Reproductive Toxicity	No evidence of reproductive toxicity from various tests (generic data - see Entry 19)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >1000 mg/L; Crustacean: EC50 >1000 mg/L; Algae: EC50 >6.3mg/L (generic data - see Entry 19)
Degradation	2. Inherently biodegradable
Bioconcentration	Unlikely to be significant
Terrestrial Toxicity	No data

P? Yes	**vP?** Maybe	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above: *Main sources: Manufacturer's MSDS.*

General Information

Project Reference 16

(EINECS) Name	Polyacrylic acid		
EINECS No.	None	**CAS No.**	9003-01-4
Synonyms	2-Propenoic acid homopolymer		
Formula	(CH2-CH.COOH)n	**Mol. Wt.**	c4000
Classification	Not determined		
Relative Density	1.3	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	Soluble	**Partition Coefficient log Kow**	No data

Ambient State	Liquid/Solid	**Melting Point**		**Boiling Point**	

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritant (rabbit) (generic data - see Entry 19)
Eye Irritation	Slight effects observed (rabbit) (generic data - see Entry 19)
Skin Sensitisation	Negative (guinea pig) (generic data - see Entry 19)
Mutagenicity	No evidence of genotoxcity from various *in vitro* and *in vivo* tests (generic data - see Entry 19)
Acute Toxicity	Oral LD50 >5000 mg/kg bw (rat); Dermal LD50 >5000 mg/kg bw (rabbit) (generic data - see Entry 19)
Repeated Dose Toxicity	No data
Reproductive Toxicity	No evidence of reproductive toxicity from various tests (generic data - see Entry 19)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >1000 mg/L; Crustacean: EC50 >1000 mg/L; Algae: EC50 >6.3mg/L (generic data - see Entry 19)
Degradation	2. Inherently biodegradable
Bioconcentration	Unlikely to be significant
Terrestrial Toxicity	No data

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *No specific data - based on Entry 19.*

General Information

Project Reference 17

(EINECS) Name 2-Propenoic acid, polymer with 2,5 furandion, sodium salt

EINECS No. None

CAS No. 52255-49-9

Synonyms Copolymer (of acrylic (2-propenoic) acid and maleic anhydride, sodium salt)

Formula (CH2.CH.COONa)x - (CH.COONa.CH.COONa)y

Mol. Wt. c65,000

Classification Not determined

Ambient State Liquid/Solid

Melting Point

Boiling Point

Relative Density 1.3

Vapour Pressure Pa Negligible

Water Solubility mg per L Soluble

Partition Coefficient log Kow No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritant (rabbit) (generic data - see Entry 20)

Eye Irritation Slight effects observed (rabbit) (generic data - see Entry 20)

Skin Sensitisation Negative (guinea pig) (generic data - see Entry 20)

Mutagenicity No evidence of genotoxcity from various *in vitro* and *in vivo* tests (generic data - see Entry 20)

Acute Toxicity Oral LD50 >5000 mg/kg nw (rat) (generic data - see Entry 20)

Repeated Dose Toxicity No data

Reproductive Toxicity No evidence of reproductive toxicity from various tests (generic data - see Entry 20)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 >500 mg/L; Crustacean: EC50 >100 mg/L; Algae: EC50 >30 mg/L .
Chronic data (NOEC): Fish >40 mg/L; Crustacean 1.3 mg/L; Algae >30 mg/L (generic data - see Entry 20)

Degradation 2. Inherently biodegradable

Bioconcentration Unlikely to be significant

Terrestrial Toxicity Earthworm LC50 >1600 mg/kg soil. Oats NOEC 400 mgg/kg soil (generic data - see Entry 20)

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *No specific data - based on Entry 20.*

General Information

Project Reference 18

(EINECS) Name 2-Butenedioic acid (Z), polymer with 2-propenoic acid, sodium salt

EINECS No. None **CAS No.** 29132-58-9

Synonyms P(AA-MA) copolymer of acrylic (or 2-propenoic) acid) and maleic (or 2-butenedioic) acid, sodium salt.

Formula (CH2.CH.COONa)x - (CH.COONa.CH.COONa)y **Mol. Wt.** c65,000

Classification Not determined

Ambient State Liquid/Solid **Melting Point** **Boiling Point**

Relative Density 1.3 **Vapour Pressure Pa** Negligible

Water Solubility mg per L Soluble **Partition Coefficient log Kow** No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritant (rabbit) (generic data - see Entry 20)

Eye Irritation Slight effects observed (rabbit) (generic data - see Entry 20)

Skin Sensitisation Negative (guinea pig) (generic data - see Entry 20)

Mutagenicity No evidence of genotoxcity from various *in vitro* and *in vivo* tests (generic data - see Entry 20)

Acute Toxicity Oral LD50 >5000 mg/kg nw (rat) (generic data - see Entry 20)

Repeated Dose Toxicity No data

Reproductive Toxicity No evidence of reproductive toxicity from various tests (generic data - see Entry 20)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 >500 mg/L; Crustacean: EC50 >100 mg/L; Algae: EC50 >30 mg/L .
Chronic data (NOEC): Fish >40 mg/L; Crustacean 1.3 mg/L; Algae >30 mg/L (generic data - see Entry 20)

Degradation 2. Inherently biodegradable

Bioconcentration Unlikely to be significant

Terrestrial Toxicity Earthworm LC50 >1600 mg/kg soil. Oats NOEC 400 mgg/kg soil (generic data - see Entry 20)

P? Yes **vP?** Maybe **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *No specific data - based on Entry 20.*

General Information

Project Reference 19

(EINECS) Name Polycarboxylates MW 3000-4000 - assumed to be P(AA)

EINECS No. None

CAS No. None

Synonyms Usually P(AA) homopolymers (polyacrylic acid, sodium salt) but may also include P(AA-MAA) copolymers (of acrylic acid and methacrylic acid, sodium salt)

Formula (CH2.CH.COONa)n

Mol. Wt. c4000

Classification Not determined

Ambient State Liquid/Solid

Melting Point

Boiling Point

Relative Density 1.3

Vapour Pressure Pa Negligible

Water Solubility mg per L Soluble

Partition Coefficient log Kow No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritant (rabbit)

Eye Irritation Slight effects observed (rabbit)

Skin Sensitisation Negative (guinea pig)

Mutagenicity No evidence of genotoxicity from various *in vitro* and *in vivo* tests

Acute Toxicity Oral LD50 >5000 mg/kg bw (rat); Dermal LD50 >5000 mg/kg bw (rabbit)

Repeated Dose Toxicity No data

Reproductive Toxicity No evidence of reproductive toxicity from various tests

Environmental Toxicity

Aquatic Toxicity Fish: LC50 >1000 mg/L; Crustacean: EC50 >1000 mg/L; Algae: EC50 >6.3mg/L .
No chronic data

Degradation 2. Inherently biodegradable

Bioconcentration Unlikely to be significant

Terrestrial Toxicity No data

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Sources: P&G Environmental Science Data for Polycarboxylates, ECETOC (1993).*

General Information

Project Reference 20

(EINECS) Name	Polycarboxylates MW 1000-70000 - assumed to be P(AA-MA)		
EINECS No.	None	**CAS No.**	None
Synonyms	Usually P(AA-MA) copolymers (of acrylic acid and maleic acid, sodium salt)		
Formula	(CH2.CH.COONa)x - (CH.COONa.CH.COONa)y	**Mol. Wt.**	c65,000
Classification	Not determined		
Ambient State	Liquid/Solid	**Melting Point**	
		Boiling Point	
Relative Density	1.3	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	Soluble	**Partition Coefficient log Kow**	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritant (rabbit)
Eye Irritation	Slight effects observed (rabbit)
Skin Sensitisation	Negative (guinea pig)
Mutagenicity	No evidence of genotoxcity from various *in vitro* and *in vivo* tests
Acute Toxicity	Oral LD50 >5000 mg/kg nw (rat)
Repeated Dose Toxicity	No data
Reproductive Toxicity	No evidence of reproductive toxicty from various tests

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >500 mg/L; Crustacean: EC50 >100 mg/L; Algae: EC50 >30 mg/L . *Chronic data (NOEC): Fish >40 mg/L; Crustacean 1.3 mg/L; Algae >30 mg/L.*
Degradation	2. Inherently biodegradable
Bioconcentration	Unlikely to be significant
Terrestrial Toxicity	Earthworm LC50 >1600 mg/kg soil. Oats NOEC 400 mgg/kg soil

P? Yes	**vP?** Maybe	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above: *Sources: P&G Environmental Science Data for Polycarboxylates, ECETOC (1993).*

General Information

Project Reference 21

(EINECS) Name	Disodium hydrogen citrate				
EINECS No.	205-622-3	**CAS No.**	144-33-2		
Synonyms	1,2,3-Propanetricarboxylic acid, 2-hydroxy-, disodium salt; Citric acid, disodium salt; Monobasic sodium citrrate; Disodium citrate; Disodium monhydrate citrate				
Formula	C6 H6 O7 . 2Na . (1.5)H20	**Mol. Wt.**	263		
Classification	Not determined				
Ambient State	Solid	**Melting Point**	149	**Boiling Point**	Not applicable
Relative Density		**Vapour Pressure Pa**	Negligible		
Water Solubility mg per L	500 g/L	**Partition Coefficient log Kow**	No data		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	May cause skin irritation
Eye Irritation	May cause eye irritiation
Skin Sensitisation	Not considered a sensitiser
Mutagenicity	Not mutagenic
Acute Toxicity	Low toxicity
Repeated Dose Toxicity	As above
Reproductive Toxicity	Not toxic to reproduction

Environmental Toxicity

Aquatic Toxicity	LC50/EC50 for fish, daphnia and algae >few hundred mg/L
Degradation	4. Readily biodegradable
Bioconcentration	Probably <10
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources include various MSDS data sheets and HERA assessment of Citric Acid and Salts (dated April 2005).*
Note that sodium citrates are EU approved food additive (E331).

General Information

Project Reference 22

(EINECS) Name	Trisodium citrate				
EINECS No.	200-675-3			**CAS No.**	68-04-2
Synonyms	Citrosidine; Citric acid, trisodium salt *Note: Trisodium citrate is also synonym for the dihydrate (C6H807.3Na.2H20, CAS No. 6132-04-3)*				
Formula	C6 H8 O7 . 3Na (anhydrous)			**Mol. Wt.**	258
Classification	Not determined				
Ambient State	Solid	**Melting Point**	150 deg C	**Boiling Point**	No data
Relative Density	1.76 at 18 deg C			**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	425 g/L at 25 deg C			**Partition Coefficient log Kow**	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating (rabbit)
Eye Irritation	Moderately rritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Negative in vitro and in vivo
Acute Toxicity	Oral LD50 >5000 mg/kg bw (rat/mouse).
Repeated Dose Toxicity	Oral NOAEL >600 mg/kg bw/day
Reproductive Toxicity	Reprotox NOAEL >600 mg/kg bw/day

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >18000 mg/L (fresh water). Crustacea: EC50 >1000 mg/L. Algae: EC50 1200 mg/L (growth rate). *No chronic data*
Degradation	4. Readily biodegradable (up to 90% in 48hrs)
Bioconcentration	Probably <10
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main source: IUCLID data sheet dated 19 February 2000*
Note that sodium citrates are EU approved food additive (E331).

General Information

Project Reference 23

(EINECS) Name Edetic acid

EINECS No. 200-449-4 **CAS No.** 60-00-4

Synonyms Acetic acid, (ethylenedinitrilo) tetra-; Ethylene diamine tetraacetic acid; EDTA; Glycine, N,N'-1,2-ethanediylbis (N-(carboxymethyl)-.

Formula C10 H16 N2 O8 **Mol. Wt.** 292

Classification Xi, R36

Ambient State Solid **Melting Point** 220 deg C **Boiling Point** Not applicable

Relative Density 0.8 (bulk 0.65) **Vapour Pressure Pa** Negligible

Water Solubility mg per L c500 at 20 deg C **Partition Coefficient log Kow** -3.34 to -5.01

Human/Mammalian Toxicity

Skin Irritation/Corrosion Moderately irritating (rabbit)

Eye Irritation Irritating (rabbit)

Skin Sensitisation Not sensitising (guinea pig)

Mutagenicity Numerous negative results but also a few positive results

Acute Toxicity Oral LD50 30 mg/kg bw (mouse)

Repeated Dose Toxicity Numerous tests. Lowest NOAEL 15 mg/kg bw/day (mouse).

Reproductive Toxicity NOAEL >250 mg/kg/bw

Environmental Toxicity

Aquatic Toxicity Fish: LC50 41 mg/L (fresh water). Crustacea: LC100 200 mg/L. Algae EC50 1 mg/L (but effects due to metal complexing under test conditions). *No chronic data*
RAR recommends Daphia NOEC of 22 mg/L

Degradation 2. Inherently biodegradable? Numerous results, typically <1% to 20% after 28days

Bioconcentration 1.9 (fish)

Terrestrial Toxicity Some plant data

P? Yes **vP?** Maybe **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000 and RAR (ECB, 2004). Note that EDTA and its salts are used as food additives (E385 is calcium disodium EDTA).*

General Information

Project Reference 24

(EINECS) Name	Tetra sodium ethylene diamine tetra acetate				
EINECS No.	200-573-9		**CAS No.**	64-02-8	
Synonyms	(Ethylenedianitrilo) tetra acetic acid tetrasodium salt; Ethylene diamine tetra acetic acid tetrasodium salt; EDTA tetrasodium salt				
Formula	C10 H16 N2 O8 . 4Na		**Mol. Wt.**	380	
Classification	Xn, R22; Xi, R41				
Ambient State	Solid	**Melting Point**	Decomposes	**Boiling Point**	Not applicable
Relative Density	0.7 (bulk)		**Vapour Pressure Pa**	Negligible	
Water Solubility mg per L	c1000 g/L at 20 deg C		**Partition Coefficient log Kow**	No data	

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Moderately irritating (rabbit)
Eye Irritation	Irritating (rabbit)
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Numerous negative results but also a few positive results
Acute Toxicity	Oral LD50 30 mg/kg bw (mouse)
Repeated Dose Toxicity	Numerous tests. Lowest NOAEL 15 mg/kg bw/day (mouse).
Reproductive Toxicity	NOAEL >250 mg/kg/bw

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 41 mg/L (fresh water). Daphnia EC50 610 mg/L. Algae EC50 1 mg/L. (but effects due to metal complexing under test conditions). *No chronic data* *RAR recommends Daphia NOEC of 22 mg/L*
Degradation	2. Inherently biodegradable? Numerous results, typically <1% to 20% after 28days
Bioconcentration	1.9 (fish)
Terrestrial Toxicity	No data

P?	Yes	**vP?**	Maybe	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*
Very extensive toxicity data (mostly from BASF and in German).

General Information

Project Reference 25

(EINECS) Name Nitrilotriacetic acid

EINECS No. 205-355-7

CAS No. 139-13-9

Synonyms NTA;Triglycine; trimethylamine-alpha,alpha',alpha''-tricarboxylic acid; Nitriloacetic acid;

Formula C6 H9 N O6

Mol. Wt. 191

Classification Xn, R22, R36/37/38, R40

Ambient State Solid

Melting Point >200 deg C

Boiling Point Not applicable

Relative Density >1

Vapour Pressure Pa Negligible

Water Solubility mg per L Slightly

Partition Coefficient log Kow No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion Causes irritation (MSDS data)

Eye Irritation Causes irritation (MSDS data)

Skin Sensitisation Causes irritation (MSDS data)

Mutagenicity Not genotoxic from various *in vitro* and *in vivo* tests but possible human carcinogen (IARC 2B). Recently classified as a Cat. 3 Carcinogen (R40).

Acute Toxicity Oral LD50 1100 mg/kg (rat)

Repeated Dose Toxicity ??

Reproductive Toxicity ??

Environmental Toxicity

Aquatic Toxicity Fish: LC50 75 mg/L (96h fresh water). Crustacean: LC50 75 mg/L. Algae: NOEC c4 mg/L (5d). *Fish: Chronic LC1 c10 mg/L (27 days).*

Degradation 4. Readily biodegradable (typically c100% within 14 days)

Bioconcentration BCF c3

Terrestrial Toxicity No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	Maybe	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: Draft ESR (Environmental) Risk Assessment for Trisodium Nitrilotriacetate (CAS 5064-31-3), dated December 2003; IARC (1999): Nitrilotriacetic Acid and its Salts (Group 2B); and various Material Safety Data Sheets.*

General Information

Project Reference 26

(EINECS) Name Sodium carbonate

EINECS No. 207-838-8 **CAS No.** 497-19-8

Synonyms Bisodium carbonate; Calcined soda; Carbonic acid, sodium salt; Soda ash.
Note: Sodium carbonate is also synonym for the monhydrate (Na2.CO3.H20, CAS No. 5968-11-6)

Formula Na2 CO3 **Mol. Wt.** 106

Classification Xi, R36 (Annex I)

Ambient State Solid **Melting Point** >360 deg C **Boiling Point** Not applicable

Relative Density 2.5 (bulk 0.5 - 1.0) **Vapour Pressure Pa** Negligible

Water Solubility mg per L c220 g/L **Partition Coefficient log Kow** Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion Moderately irritating (human/rabbit) but a range of results

Eye Irritation Highly irritating (rabbit)

Skin Sensitisation Not known to be a sensitiser (but no data)

Mutagenicity No data

Acute Toxicity Oral LD50 4090 mg/kg bw (rat) . Inhalation LC50 0.8 mg/L (guinea pig). Dermal LD50 117 mg/kg bw (mouse).

Repeated Dose Toxicity One reported NOAEL of 0.01-0.02 mg/L (lung changes in rat)

Reproductive Toxicity No data to suggest reprotoxin or developmental effects

Environmental Toxicity

Aquatic Toxicity Fish: LC50 167 mg/L (fresh water). Daphnia: LC50 151 mg/L. Algae: LC50 137 mg/L.
Fish: Chronic LC100 70 mg/L (5 days).

Degradation 5. Not applicable

Bioconcentration Not applicable

Terrestrial Toxicity No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000. It should be boted that the most recent assessmet (HERA, 2002c as revised in 2005) suggests that the properties of sodium carbonate are less harmful than those presented in the IUCLID data sheet.*

General Information

Project Reference 27

(EINECS) Name	Disodium metasilicate				
EINECS No.	229-912-9			**CAS No.**	6834-92-0
Synonyms	Sodium metasilicate; Silicic acid, disodium salt; Disodium silicate				
Formula	Na2 O3 Si (anhydrous)			**Mol. Wt.**	Not applicable
Classification	C, R34; Xi, R37 (Annex I)				
Ambient State	Solid	**Melting Point**	>360 deg C	**Boiling Point**	Not applicable
Relative Density	2.5 (bulk 0.87)			**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	200 g/L			**Partition Coefficient log Kow**	Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion	(Highly) corrosive (rabbit - but 'not irritating' if applied dry as rabbits do not sweat)
Eye Irritation	Corrosive
Skin Sensitisation	Not sensitising
Mutagenicity	Negative
Acute Toxicity	Oral LD50 600 mg/kg bw (rat)
Repeated Dose Toxicity	NOAEL 792 mg/kg bw (2 year study on rats). HERA suggests NOAEL of 159 mg/kg bw/d (180d value for rats)
Reproductive Toxicity	Tests show no effects

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 124 mg/L (fresh water); Daphnia LC50 216 mg/L (based on sodium silicate). *No chronic data*
Degradation	5. Not applicable
Bioconcentration	Not applicable
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000 and HERA (2005a).*

General Information

Project Reference 28

(EINECS) Name Silicic acid, sodium salt

EINECS No. 215-687-4 **CAS No.** 1344-09-8

Synonyms Disodium metasilicate; Sodium silicate; Water glass; Sodium silicate glass; Sodium orthosilicate

Formula Na2 O. nO2 Si (anhydrous) **Mol. Wt.** Not applicable

Classification Xi, R36/37/38 (typical)

Ambient State Solid **Melting Point** >360 deg C **Boiling Point** Not applicable

Relative Density 2.4 (bulk varies 0.6 - 1.5) **Vapour Pressure Pa** Negligible

Water Solubility mg per L 350 g/L at 25 deg C **Partition Coefficient log Kow** Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion Corrosive (rabbit - but a wide range of results)

Eye Irritation Corrosive (rabbit - but as above a wide range of results)

Skin Sensitisation Not sensitising

Mutagenicity Negative

Acute Toxicity Oral LD50 770 mg/kg bw (mouse). Dermal LDlo 200 mg/kg bw (guinea pig)

Repeated Dose Toxicity NOAEL 792 mg/kg bw (2 year study on rats). HERA suggests NOAEL of 159 mg/kg bw/d (180d value for rats)

Reproductive Toxicity Tests show no effects

Environmental Toxicity

Aquatic Toxicity Fish: LC50 >300 mg/L (fresh water); Daphnia LC50 216 mg/L (Other crustacea EC50 160 mg/L). *Very limited chronic data*

Degradation 5. Not applicable

Bioconcentration Not applicable

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000 and HERA (2005a).*

General Information

Project Reference 29

(EINECS) Name Disodium disilicate

EINECS No. 237-623-4

CAS No. 13870-28-5

Synonyms Sodium disilicate; Silicic acid, disodium salt

Formula O5 Si2 . 2Na (anhydrous)

Mol. Wt. Not applicable

Classification Xn, R22; Xi, R38, R41 (typical)

Ambient State Solid

Melting Point 90 deg C

Boiling Point 103 deg C

Relative Density c1.4

Vapour Pressure Pa Negligible

Water Solubility mg per L Fully miscible

Partition Coefficient log Kow Not applicable

Human/Mammalian Toxicity

Skin Irritation/Corrosion Corrosive (rabbit)

Eye Irritation Corrosive (rabbit)

Skin Sensitisation No data

Mutagenicity Negative

Acute Toxicity Oral LD50 >1000 mg/kg bw (mouse/rat).

Repeated Dose Toxicity No specific data but HERA suggests NOAEL of 159 mg/kg bw/d (180d value for rats)

Reproductive Toxicity Insufficient data - but likely to be similar to Entries 27/28

Environmental Toxicity

Aquatic Toxicity Fish: LC50 210 mg/L (fresh water); Daphnia LC50 216 mg/L. *No chronic data*

Degradation 5. Not applicable

Bioconcentration Not applicable

Terrestrial Toxicity No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference	30		
(EINECS) Name	Dyes unspecified		
EINECS No.	No data	**CAS No.**	No data
Synonyms	Understood to cover a diverse range of 150-200 specific dyes		
Formula	Varied	**Mol. Wt.**	Varied
Classification	Not determined		

Ambient State	Not known	**Melting Point**	No data	**Boiling Point**	No data
Relative Density	No data	**Vapour Pressure Pa**	No data		
Water Solubility mg per L	No data	**Partition Coefficient log Kow**	No data		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	No data
Eye Irritation	No data
Skin Sensitisation	No data
Mutagenicity	No data
Acute Toxicity	No data
Repeated Dose Toxicity	No data
Reproductive Toxicity	No data

Environmental Toxicity

Aquatic Toxicity	Understood to be generally low (but no specific data)
Degradation	2. Inherently biodegradable?
Bioconcentration	No data
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
Maybe	Maybe	Maybe	Maybe	Maybe	Maybe	Maybe

Comments on above: *As dyes are used in very low concentrations (<0.1%), there is no requirement (under the Detergents Regulation) to identify them (as concentraions <0.2%).*

General Information

Project Reference 31

(EINECS) Name	Polyvinylpyrrolidone
EINECS No.	None
CAS No.	9003-39-8
Synonyms	PVP; Povidone; Poly(n-vinylbutrolactam); 2-Pyrrolidone, 1-ethyl-, homopolymer *Note: various forms including K15, K30, K60 and K90 in use. PVP-K30 appears to be typical form used in detergents*
Formula	$(C_6H_9NO)_n$
Mol. Wt.	c50,000
Classification	Not determined
Ambient State	Solid
Melting Point	>200 deg C
Boiling Point	Not applicable
Relative Density	0.5 (bulk)
Vapour Pressure Pa	Negligible
Water Solubility mg per L	Soluble
Partition Coefficient log Kow	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	May be irritant but others state non-irritating (based on human repeat insult patch test (RIPT)
Eye Irritation	May be irritant - but some evidence of non-irritation (rabbit)
Skin Sensitisation	May be sensitiser but others state non-sensitising (human RIPT)
Mutagenicity	Not considered to be a mutagen
Acute Toxicity	Oral LD50 1,040 mg/kg bw (rabbit)
Repeated Dose Toxicity	No effects on rats/dogs fed on diet containing 10% PVP
Reproductive Toxicity	No evidence of embryo toxicity or teratogenicity

Environmental Toxicity

Aquatic Toxicity	Limited data suggest marine toxicity very low with LC/EC50 values >1000 mg/L.
Degradation	2. Inherently biodegradable (one reference to 11% in 28 days)
Bioconcentration	Unlikely to bioaccumulate (due to high MW)
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
Maybe	Maybe	No	No	No	No	No

Comments on above: *Main sources: various Material Safety Data Sheets and JECFA (1980).*

General Information

Project Reference 32

(EINECS) Name Subtilisin

EINECS No. 232-755-2 **CAS No.** 9014-01-1

Synonyms Proteae
Other CAS numbers inlude: 1395-21-7, 9073-77-2, 9001-92-7, 79986-26-8, 95979-76-3 and 689-17-1.

Formula Complex **Mol. Wt.** c27000

Classification Xi, R37/38, R41, R42 (Annex I)

Ambient State Solid **Melting Point** Decomposes **Boiling Point** Decomposes

Relative Density 0.6 - 1.3 (bulk) **Vapour Pressure Pa** Negligible

Water Solubility mg per L 1000 g/L **Partition Coefficient log Kow** -3.1

Human/Mammalian Toxicity

Skin Irritation/Corrosion Range of results up to severe irritation

Eye Irritation Can cause eye irritation

Skin Sensitisation Although not considered a skin sensitiser for humans, one study reports positive results for guinea pigs. However can cause respiratory allergenic reactions (esp. asthma)

Mutagenicity Negative genotxicity results (*in vitro* and *in vivo*). No indication of carcinogenicity

Acute Toxicity Oral LD50 >100 mg/kg bw (rats). Inhalation LC50 >0.1 mg/L (rats). *Note concentration as 'active enzyme proteins'*

Repeated Dose Toxicity No significant effects expected

Reproductive Toxicity No significant effects observed

Environmental Toxicity

Aquatic Toxicity Fish LC50 5 mg/L (freshwater, 96hrs); Daphnia EC50 0.1 mg/L (48hrs); Algae EC50 0.39 mg/L (3hrs). *All data have high reliability.*

Degradation 4. Readily biodegrdable (OECD 301D & 301F)
No data on anaerobic degradation

Bioconcentration Insignificant bioaccumulation potential

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: HERA (2005b) Note that production of engineered enzymes involves use of Genetically Modified Microorganisms (GMMs).*

General Information

Project Reference 33.1

(EINECS) Name	Amylase		
EINECS No.	232-565-6	**CAS No.**	9000-90-2
Synonyms			
Formula	Complex	**Mol. Wt.**	58000
Classification	Xn, R42 (Annex I)		
Ambient State	Solid	**Melting Point**	Not applicable
		Boiling Point	Not applicable
Relative Density	0.6 - 1.3 (bulk)	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	<800 g/L	**Partition Coefficient log Kow**	-2.95

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Mild irritant (rabbit) - although effects may be due to protease impurities
Eye Irritation	Mild irritant (rabbit & human) -although effects may be due to protease impurities
Skin Sensitisation	Not sensitising (guinea pig & humans) - *but may induce asthma (respiratory sensitisation)*
Mutagenicity	Not considered genotoxic (but effects observed at high concentrations)
Acute Toxicity	Oral - low toxicity (no observed effects in rats). Respiratory effects observed in rats (but possibly due to protease impurities)
Repeated Dose Toxicity	Not toxic (oral). No data for dermal/inhalation
Reproductive Toxicity	No observed effects (rat study)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >320 mg/L (freshwater, 96hrs); Daphnia: EC50 450 mg/L (48hrs); Algae: EC50 112 mg/L (72hrs). *No chronic data.*
Degradation	4. Readily biodegradable (99% DOC Removal OECD 301E)
Bioconcentration	Expected to be low due to high MW, high water solubility and low logKow
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main source: HERA (2005c): a-Amylases, Cellulases and Lipases dated November 2005.*
Note: physico-chemical data as for protease.

General Information

Project Reference 33.2

(EINECS) Name	Cellulase		
EINECS No.	232-734-4	**CAS No.**	9012-54-8
Synonyms	Cellulase (B-(1,4)-Glucanase)		
Formula	Complex	**Mol. Wt.**	20-80,000
Classification	Xn, R42 (Annex I)		
Ambient State	Solid	**Melting Point**	Not applicable
		Boiling Point	Not applicable
Relative Density	0.6 - 1.3 (bulk)	**Vapour Pressure Pa**	Not applicable
Water Solubility mg per L	<800 g/L	**Partition Coefficient log Kow**	-2.95

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Mild irritant (rabbit)
Eye Irritation	Varied results
Skin Sensitisation	Negative results (guinea pigs)
Mutagenicity	No genotoxic effects observed
Acute Toxicity	Oral LD50 8 g/kg bw (mice). Inhalation LC50 >3.5 mg/L (rats)
Repeated Dose Toxicity	Minor effects in rats observed at doses of 3g/kg bw
Reproductive Toxicity	No data

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >300 mg/L (freshwater, 96hrs); Daphnia: EC50 >1000 mg/L (48hrs); Algae: EC50 >1000 mg/L (72hrs). *No chronic data*
Degradation	4. Readily biodegradable (>75% DOC Removal OECD 301E)
Bioconcentration	Expected to be low due to high MW, high water solubility and low logKow
Terrestrial Toxicity	No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main source: HERA (2005c): a-Amylases, Cellulases and Lipases dated November 2005.*
Note: physico-chemical data as for protease.

General Information

Project Reference 33.3

(EINECS) Name	Lipase, tricylglycerol				
EINECS No.	232-619-9	**CAS No.**	9001-62-1		
Synonyms					
Formula	Complex	**Mol. Wt.**	20-80,000?		
Classification	Xn, R42 (industry standard)				
Ambient State	Solid	**Melting Point**	Not applicable	**Boiling Point**	Not applicable
Relative Density	0.6 - 1.3 (bulk)	**Vapour Pressure Pa**	Not applicable		
Water Solubility mg per L	<800 g/L	**Partition Coefficient log Kow**	-2.95		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Mild irritant (rabbits) but effects possibly due to protease impurities
Eye Irritation	Negative result (rabbit)
Skin Sensitisation	Negative results (guinea pigs)
Mutagenicity	No evidence of genotoxcity
Acute Toxicity	Oral LD50 >5 g/kg bw (rats). Inhalation LC50 >0.74 mg/L (rats)
Repeated Dose Toxicity	NOAEL >5 g/kgbw (rats)
Reproductive Toxicity	No data

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >1000 mg/L (freshwater, 96hrs); Daphnia: EC50 >1000 mg/L (24hrs); Algae: EC50 99 mg/L (72hrs). *No chronic data*
Degradation	4. Readily biodegradable (99% DOC Removal OECD 301E)
Bioconcentration	Expected to be low due to high MW, high water solubility and low logKow
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: HERA (2005c): a-Amylases, Cellulases and Lipases dated November 2005.*
Note: physico-chemical data as for protease.

General Information

Project Reference 34

(EINECS) Name	Disodium 2,2' ([1,1'-biphenyl]-4,4'-diyldivinylene)bis(benzenesulphonate)		
EINECS No.	248-421-0	**CAS No.**	27344-41-8
Synonyms	Tinopal CBS; FWA-5; Distyrylbiphenylsulphonate; DSBP; Benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis-,disodium salt		
Formula	C28 H22 O6 S2 . 2Na	**Mol. Wt.**	563
Classification	Not determined		
Ambient State	Solid	**Melting Point**	>200 deg C
		Boiling Point	Not applicable
Relative Density	1.5	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	15-25 at 20 degC	**Partition Coefficient log Kow**	-1.1 to -2.3 at 25 deg C

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating (rabbit)
Eye Irritation	Irritating (rabbit))
Skin Sensitisation	Not sensitising (guinea pig)
Mutagenicity	Genotoxicity in vitro: Positive (chinese hamsters V79, cells) [but other tests suggest not mutagenic (HERA)]. Carcinogenicity: negative (rats, IUCLID & mice, HERA)
Acute Toxicity	Oral: LD50 >=2000 mg/kg bw (rat); Inhalation: LC50 3.6 mg/L (4hrs rat); Dermal: LD50 >2000 mg/kg bw (rat)
Repeated Dose Toxicity	NOAEL 190 mg/kg bw/day (rat feed study, HERA)
Reproductive Toxicity	Teratogenicity: NOAEL 1000 mg/kg bw (21 days rat)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 76 mg/L (96hrs freshwater); Daphnia: EC50 1000 mg/L (48hrs); Algae EC50 10 mg/L (72hrs); Microorganisms (sludge): EC50 >300 mg/L (3hrs). Chronic NOEC <=1 mg/L (28 days fish, freshwater)
Degradation	1. No biodegradation observed (<1% after 28 days & 20-30% after 28 days)
Bioconcentration	<1 (although earlier studies suggest BCF values of up to 60)
Terrestrial Toxicity	Worm: LC50 >=1000 mg/kg dw (14 days); NOEC 1.37 mg/kg dw

P? Yes	**vP?** Maybe	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above: *Main sources: IUCLID data sheet dated 18 February 2000) and HERA (2003).*

General Information

Project Reference 35

(EINECS) Name Disodium 4,4'-bis[(4-anilino-6-morpholino- 1,3,5-triazin-2-yl]amino]stilbene-2, 2'-disulphonate

EINECS No. 240-245-2 **CAS No.** 16090-02-1

Synonyms FWA-1; Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-(4-morpholinyl)-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-,disodium salt

Formula C40 H40 N12 08 S2 2Na **Mol. Wt.** 925

Classification Not determined

Ambient State Solid **Melting Point** >200 deg C **Boiling Point** Not applicable

Relative Density 1.5 at 20 deg C **Vapour Pressure Pa** Negligible

Water Solubility mg per L 1-3 g/L **Partition Coefficient log Kow** -1.6 (HERA)

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritating (rabbit)

Eye Irritation Not irritating (rabbit)

Skin Sensitisation Not sensitising (guinea pig)

Mutagenicity No effects observed (in vitro and in vivo)

Acute Toxicity Oral: LD50 >500 mg/kg bw (cat) and >1,000 mg/kg bw for other test animals
Dermal: LD50 > 2000 mg/kg bw *Note HERA provides higher values for acute toxicity*

Repeated Dose Toxicity No effects observed

Reproductive Toxicity No developmental effects observed (3 generation study on rats)

Environmental Toxicity

Aquatic Toxicity Fish: NOEC c180 mg/L (96hr to freshwater fish); Daphnia: EC50 > 1000 mg/L (24hr to Daphnia magna); Algae: NOEC/LOEC 25/50 mg/L (96 hrs to Scenedesmus subspicatus). *HERA provides some chronic NOECs 63 mg/L (fish, 14d); 25 mg/L (algae, 72hr) and an unreliable 1 mg/L (daphnia, 21d)*

Degradation 4. Readily biodegradable in activated sludge (>60% after 28days)

Bioconcentration <1

Terrestrial Toxicity Worm: NOEC/LC0 = 1.37 mg/kg dw (14 d)

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: Limited (and potentially unreliable) data on phsyico-chemical properties provided in IUCLID (dated 18 February 2000) with additional information from HERA (2004a).*

General Information

Project Reference 36

(EINECS) Name	Paraffins unspecified - *assumed to be C10-C16 n-paraffins*
EINECS No.	265-233-4
CAS No.	64771-72-8
Synonyms	Note CAS 64771-72-8 comprises larger group of C5-C20 *n*-paraffins
Formula	Mixture Cn H(2n+2) (n = 10-16)
Mol. Wt.	c180
Classification	R10, R36/37/38 (typical examples)
Ambient State	Liquid
Melting Point	-30 to +18 degC
Boiling Point	174-287 degC
Relative Density	0.75 (approx)
Vapour Pressure Pa	1-100
Water Solubility mg per L	<0.1
Partition Coefficient log Kow	>5

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Slightly irritating (rabbit) (C10 & C14)
Eye Irritation	Not irritating (rabbit) (C10 & C14) (*but some labelling of products suggest otherwise*)
Skin Sensitisation	Not sensitising (at least for higher MW *n*-paraffins)
Mutagenicity	Negative genetic toxicity results in vitro (C10 & C14). No evidence of carcinogenicity
Acute Toxicity	Oral LD50 > 5000 mg/kg bw (rat - C10 & C14); Inhalation LC50 >1369 ppm (C10) and 41 ppm (C14) (rat 14d) ; Dermal LD50 >2000 and >5000 mg/kg bw (rat) for C10 & C14.
Repeated Dose Toxicity	Decane: Inhalation 90d NOAEL = 540ppm (rat) Tetradecane: Oral LOAEL 9600 mg/kg bw (mouse 20 weeks)
Reproductive Toxicity	No evidence of reproductive toxicity (C10)

Environmental Toxicity

Aquatic Toxicity	Decane: NOEC (marine fish 96hrs) 500 mg/L; EC50 (daphnia/algae) <0.1 mg/L (various studies 18-96 hrs). Tetradecane:NOEC (various studies on invertebrates/algae) <0.01 mg/L. *No chonric data*
Degradation	4. Readily biodegradable
Bioconcentration	Increases with chain length: C10 = 3636 and C14 = 42153
Terrestrial Toxicity	Few studies suggest limited toxicity to plants

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	Yes	Maybe	Yes	No	No

Comments on above: *Main sources: IUCLID Data Sheets for Decane (CAS 124-18-5), Tetradecane (CAS 629-59-4) and C5-C20 n-paraffins (CAS 64771-72-8).*

General Information

Project Reference	37

(EINECS) Name	Polydimethyl siloxane		
EINECS No.	Not listed	**CAS No.**	9016-00-6
Synonyms	PDMS; Dimethyl polysiloxane; Dimethicone; Polyoxy(dimethylsilylene) *Note: CAS 9016-00-6 is generic reference for PDMS compounds. Specific compounds include CAS Nos 63148-62-9 (formula below) and 70131-67-8*		
Formula	(CH3)3.SiO.[(CH3)2SiO]n.Si(CH3)3	**Mol. Wt.**	c30,000
Classification	Not determined		
Relative Density	0.97	**Vapour Pressure Pa**	Negligible
Water Solubility mg per L	Insoluble	**Partition Coefficient log Kow**	8 or more

Ambient State	Liquid	**Melting Point**	-70 deg C?	**Boiling Point**	>200 deg C

Human/Mammalian Toxicity

Skin Irritation/Corrosion	May cause skin irritation (MSDS)
Eye Irritation	May cause eye irritation (MSDS)
Skin Sensitisation	No data
Mutagenicity	Not identified as mutagen
Acute Toxicity	Not toxic - oral LD50 >35000 mg/kg bw (rat)
Repeated Dose Toxicity	No data
Reproductive Toxicity	Although high MW polymers are generally considered to be non-toxic, relevant MSDSs note: *"adverse reproductive effects have been reported in animals"*

Environmental Toxicity

Aquatic Toxicity	Fish LC50 >1,000 mg/L (generally) (freshwater, 96 hrs)
Degradation	1. Does not biodegrade (but undergoes hydrolysis in some soils)
Bioconcentration	No evidence to suggest significant bioconcentration (Stevens, 2006)
Terrestrial Toxicity	NOEC 230 mg/kg dw (springtail)

P?	Yes	**vP?**	Yes	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: Product Data Sheets, MSDS and Stevens (2006). Note that PDMS is a food additive (E900).*

General Information

Project Reference 38.1

(EINECS) Name	Sodium toluene-4-sulphonate is used as representing toluene sulphonates (unspecified)		
EINECS No.	211-522-5	**CAS No.**	657-84-1
Synonyms	An isomer, sodium toluene sulphonate (CAS 12068-03-0) , is used as the representative salt in the HERA assessment and data from this study have been used here. Toluene sulphonates could also include potassium salts.		
Formula	C7 H8 O3 S . Na	**Mol. Wt.**	194
Classification	Not determined		

Ambient State	Solid	**Melting Point**	>200 deg C	**Boiling Point**	Not applicable
Relative Density	??	**Vapour Pressure Pa**	Negligible		
Water Solubility mg per L	Soluble	**Partition Coefficient log Kow**	-2.4		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Slight irritation (HERA)
Eye Irritation	Moderate irritation (HERA)
Skin Sensitisation	Not sensitising (HERA)
Mutagenicity	No effects of genetic toxicity or chromosomal aberration (GINC)
Acute Toxicity	Oral LD50 >2,000 mg/kg bw (rat) (GINC) (>6,500 - HERA)
Repeated Dose Toxicity	Oral NOAEL >1,000 mg/kg bw (rat 28 days) (GINC)
Reproductive Toxicity	No data - but no developmental effects obseved on xylene sulphonate study (HERA)

Environmental Toxicity

Aquatic Toxicity	No data located - but HERA suggests that data likely to be comprable with cumene (and xylene) sulphonates - i.e. low aquatic toxicity
Degradation	4. Readily biodegradable (HERA)
Bioconcentration	Modelling results suggest BCF of <3 (HERA)
Terrestrial Toxicity	No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main sources: HERA (2005d) assessment on 'Hydrotropes' and mammalian toxicity results from the Japanese Global Information Network on Chemicals (GINC).*

General Information

Project Reference 38.2

(EINECS) Name Sodium cumene sulphonate is used as representing cumene sulphonates (unspecified)

EINECS No. 248-938-7

CAS No. 28348-53-0

Synonyms The HERA assessment also considers an isomer (CAS 32073-22-6) as well as the corresponding ammonium salt (CAS 37475-88-0)

Formula C9 H12 O3 S . Na

Mol. Wt. 222

Classification Not determined

Ambient State Solid

Melting Point >200 deg C

Boiling Point Not applicable

Relative Density ??

Vapour Pressure Pa Negligible

Water Solubility mg per L >300 g/L

Partition Coefficient log Kow -1.5

Human/Mammalian Toxicity

Skin Irritation/Corrosion Varied results from not irritating to moderate irritation

Eye Irritation Nor irritating to mild irritation

Skin Sensitisation Not sensitising

Mutagenicity No indication of genetic toxicity or carcinogenicity observed

Acute Toxicity Oral LD50 >7000 mg/kg bw (rat); Inhalation LC50 >770 mg/L (rat); Dermal LD50 >2000 mg/kg bw (rabbit)

Repeated Dose Toxicity Oral NOAEL >159 mg/kg bw (rat 91 days)

Reproductive Toxicity No data - but no developmental effects obseved on xylene sulphonate study

Environmental Toxicity

Aquatic Toxicity Fish LC50 >450 mg/L (freshwater, 96hrs); Daphnia EC50 >450 mg/L (96hrs); Algae EC50 >1000 mg/L. Limited suggests chronic NOEC 30 mg/L (Daphnia)

Degradation 4. Readily biodegradable

Bioconcentration Modelling results suggest BCF of 3

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: HERA (2005d) assessment on 'Hydrotropes'.*

General Information

Project Reference 39

(EINECS) Name	Polyethylene glycols				
EINECS No.	500-038-2	**CAS No.**	25322-68-3		
Synonyms	PEG200, PEG400 etc.; poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-Ethane-1,2-diol, ethoxylated				
Formula	HO (CH2 CH2 O)n H	**Mol. Wt.**	200-10000		
Classification	None				
Ambient State	Solid	**Melting Point**	c40 degC	**Boiling Point**	Not applicable
Relative Density	1.1	**Vapour Pressure Pa**	Not applicable		
Water Solubility mg per L	c800 g/L	**Partition Coefficient log Kow**	No data		

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating
Eye Irritation	Slightly irritating
Skin Sensitisation	Not irritating
Mutagenicity	No data to suggest mutagencity
Acute Toxicity	Toxicity decreases with increasing MW. Oral LD50 14000 mg/kg bw (rabbit, PEG200)
Repeated Dose Toxicity	NOAEL 8% of feed (rats 90days). NOAEL >60 mgPEG1500/kg/day (rats 2yrs)
Reproductive Toxicity	No data to suggest reprotoxicity

Environmental Toxicity

Aquatic Toxicity	Fish LC50 >5000 mg/L (freshwater, 24hrs), >1000 mgf/L (freshwater, 96hrs)
Degradation	2. Inherently biodegradable (higher MWs) 4. Readily biodegradable (lower MWs)
Bioconcentration	No bioaccumulation expected
Terrestrial Toxicity	No data

P? No	**vP?** No	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above: *Main sources: WHO Food Additives Series 14: Polyethylene Glycols (JECFA, 1980a), various MSDSs from suppliers.*

General Information

Project Reference 40

(EINECS) Name	Carboxylmethylcellulose		
EINECS No.	None	**CAS No.**	9000-11-7
Synonyms	CMC; CM-Cellulose; Carboxylmethyl cellulose ether;		
Formula	Complex	**Mol. Wt.**	800-10,000
Classification	None		
Ambient State	Solid	**Melting Point**	No data
Boiling Point	Not applicable		
Relative Density	1.59	**Vapour Pressure Pa**	Not applicable
Water Solubility mg per L	Soluble	**Partition Coefficient log Kow**	No data

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating
Eye Irritation	Not irritating
Skin Sensitisation	Not irritating
Mutagenicity	Not classified
Acute Toxicity	Not toxic
Repeated Dose Toxicity	Not toxic
Reproductive Toxicity	Not toxic

Environmental Toxicity

Aquatic Toxicity	Not toxic. Fish/Daphnia EC50 > 800 mg/L; Algae NOEC >800 mg/L
Degradation	2. Inherently biodegradable - but limited data
Bioconcentration	Low
Terrestrial Toxicity	Not toxic

P? Yes	**vP?** Maybe	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above:

Main source: P&G data sheet for 'Carboxymethyl Cellulose Ether'
Note that CMC is an EU approved food additive (E466).

General Information

Project Reference 41

(EINECS) Name Anionic derivatives of polymers of terephthalic acid and ethylene glycol

EINECS No. Not known **CAS No.** Not known

Synonyms

Formula **Mol. Wt.**

Classification

Ambient State **Melting Point** **Boiling Point**

Relative Density **Vapour Pressure Pa**

Water Solubility mg per L **Partition Coefficient log Kow**

Human/Mammalian Toxicity

Skin Irritation/Corrosion

Eye Irritation

Skin Sensitisation

Mutagenicity

Acute Toxicity

Repeated Dose Toxicity

Reproductive Toxicity

Environmental Toxicity

Aquatic Toxicity

Degradation

Bioconcentration

Terrestrial Toxicity

P? **vP?** **B?** **vB?** **T?** **PBT?** **vPvB?**

Comments on above: *No specific compounds have been identified on which to base analysis.*

General Information

Project Reference 42

(EINECS) Name Ethanol

EINECS No. 200-578-6

CAS No. 64-17-5

Synonyms Absolute ethanol; alcohol; alcohol anhydrous; ethyl alcohol; ethyl hydrate;

Formula C_2H_6O

Mol. Wt. 46.07

Classification F, R11 (Annex I)

Ambient State Liquid

Melting Point -114 deg C

Boiling Point 78 deg C

Relative Density 0.79 at 20 deg C

Vapour Pressure Pa c5800 at 20 deg C

Water Solubility mg per L Miscible

Partition Coefficient log Kow -0.32

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritating (rabbit) [no data]

Eye Irritation Moderately irritating (rabbit) [no data]

Skin Sensitisation Not sensitising (guinea pig) [GLP]

Mutagenicity Genetic toxicity in vitro: positive (human lymphocytes; aspergillus nidulans; saccharomyces cerevisiae; mouse lymphoma assay; chinese hamster ovary sells; escherichia coli) [no data].

Acute Toxicity Oral LD50 >790 mg/kg bw (mouse); Inhalation LC50 5.9 mg/L (rat); Dermal LDLo 20000 mg/kg bw (rabbit); LD50 933 mg/kg bw (rat)

Repeated Dose Toxicity 13 studies; some show limited effects, usually reduced body weight gain (or weight loss), fatty degeneration of liver and haematological effects; no deaths

Reproductive Toxicity Several tests show evidence of toxicity to reproduction (effects on the testis and other reproduction tissues, adverse effects on ginadal growth and development and sexual behaviour); other tests have shown teratogenic effects and congenital malformations

Environmental Toxicity

Aquatic Toxicity Fish: 8140 mg/L (48hrs freshwater); Other crustacea: 3715 mg/L (48hrs); Algae: EC50 9310 mg/L. Chronic NOEC 2 mg/L (10 days other crustacea)

Degradation 4. Readily biodegradable (75-84% after 20 days in freshwater and synthetic salt water)

Bioconcentration Not expected to bioaccumulate

Terrestrial Toxicity Worm: LC50 0.1 mg/cm2 filter paper (48 hrs)

P? No **vP?** No **B?** No **vB?** No **T?** Maybe **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 43

(EINECS) Name Propan-2-ol

EINECS No. 200-661-7 **CAS No.** 67-63-0

Synonyms 1-methylethanol; 1-methyl alcohol; 2-propanol; iso-propanol; 2-hydroxypropane; dimethyl carbinol; iso-propyl alcohol; sec-propanol; IPA

Formula C3 H8 O **Mol. Wt.** 60

Classification F, R11; Xi, R36, R67 (Annex I)

Ambient State Liquid **Melting Point** c-89 deg C **Boiling Point** 82.5 deg C

Relative Density 0.785 at 20 deg Cq **Vapour Pressure Pa** 4200 at 20 deg C

Water Solubility mg per L Miscible **Partition Coefficient log Kow** 0.05 - 0.11

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritating [no data]

Eye Irritation Irritating [no data]

Skin Sensitisation Not sensitising [no GLP]

Mutagenicity Genetic toxicity in vitro: negative [GLP]; Genetic toxicity in vivo: negative [GLP]

Acute Toxicity Oral: LD50 4396 mg/kg bw (rat); Inhalation: LD50 27.2 mg/L (mouse); Dermal: LD50 12800 mg/kg bw (rat); I.P.: LD50 2050 mg/kg bw (rat); I.V.: LD50 1088 mg/L (rat)

Repeated Dose Toxicity Inhalation: NOAEL 100 ppm (13 wks rat) [GLP];

Reproductive Toxicity Generally no toxic to reproduction effects detected (NOAEL parental 500 mg/kg bw - NOAEL F1 Offspring 500 mg/kg bw - gavage rat. Not teratogenic (NOAEL parental 240 mg/kg bw - NOAEL teratogenicity 480 mg/kg bw - gavage rabbit)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 4200 mg/L (96hrs marine); Other crustacea: LC50 903 mg/L (96hrs); Algae: EC50 >1000 mg/L (96hrs); Microorganisms: EC50 790 mg/L (96hrs). *No chronic data.*

Degradation 4. Readily biodegradable (domestic waste)

Bioconcentration Not expected to bioaccumulate

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 44

(EINECS) Name	2-butoxyethanol		
EINECS No.	203-905-0	**CAS No.**	111-76-2
Synonyms	Ethylene glycol; Monobutyl ether; Monobutyl glycol ether; 2-Butoxy-1-ethanol; 2-n-butoxyethanol; 3-oxa-1-heptanol; Butyl cellosolve; Butyl glycol; Butyl glycol ether; BGE; Butyl oxitol; Ethylene glycol butyl ether; EGBE; Ethylene glycol monobutyl ether; Ethylene glycol n-butyl ether		
Formula	C6 H14 O2	**Mol. Wt.**	118
Classification	Xn, R20/21/22; Xi, R36/38 (Annex I)		
Ambient State	Liquid	**Melting Point**	c-72degC
		Boiling Point	c170 degC
Relative Density	0.90 at 25 degC	**Vapour Pressure Pa**	c100 at 20 degC
Water Solubility mg per L	Miscible	**Partition Coefficient log Kow**	0.74 to 0.83

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating (but non-GLP results suggest irritating)
Eye Irritation	Irritating
Skin Sensitisation	Not sensitising
Mutagenicity	Genetic toxicity in vitro: negative. No data on genetic toxicity in vivo.
Acute Toxicity	Oral LD50 320 mg/kg bw (rabbit) ; Inhalation LD50 1.5-3.4 mg/L (rat) ; Dermal: LD50 99 mg/kg bw (rabbit)
Repeated Dose Toxicity	Inhalation: NOAEL 0.12 mg/L (90 days rat) ; Oral feed: 40 mg/kg bw (102 days rat) Drinking water: NOAEL 223-370 mg/kg bw (13 wks mouse) ; Dermal: 150 mg/kg (90 days rabbit) [
Reproductive Toxicity	Reprotox NOAEL parental 304 mg'kg bw (13 wks rat drinking water). Developmental NOAEL maternal 0.24 mg/L - NOAEL teratogenicity 0.97 mg/L (10 days rat inhalation) ; NOAEL maternal 350 mg/kg bw -NOAEL teratogenicity 650 mg/kg bw (7 days mouse gavage)

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 983 mg/L (7 days freshwater); Other crustacea: LC50 550-950 mg/L (96hrs) ; Algae: 35 mg/L (8 days). *No chronic data available.*
Degradation	4. Readily biodegradable (88% after 20 days domestic sludge)
Bioconcentration	BCF 2.5 (calculated from log Kow)
Terrestrial Toxicity	No data

P? No	**vP?** No	**B?** No	**vB?** No	**T?** No	**PBT?** No	**vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 45

(EINECS) Name Decan-1-ol

EINECS No. 203-956-9 **CAS No.** 112-30-1

Synonyms 1-decanol; 1-hydroxydecane; decyl alcohol; n-decanol

Formula C10 H22 O **Mol. Wt.** 158

Classification Xi, R36/38; N, R51/53 (typical)

Ambient State Liquid **Melting Point** c5 deg C **Boiling Point** c230 deg C

Relative Density 0.83 at 20 deg C **Vapour Pressure Pa** 133 at 69.5 degC

Water Solubility mg per L 37 at 25 deg C **Partition Coefficient log Kow** 4.11 - 4.23

Human/Mammalian Toxicity

Skin Irritation/Corrosion Irritating

Eye Irritation Irritating

Skin Sensitisation Not sensitising

Mutagenicity Genetic toxicity in vitro: negative. Genetic toxicity in vivo: no data.

Acute Toxicity Oral: LD50 >5000 mg/kg bw (rat); Inhalation LC50 4 mg/L (mouse); Dermal: LD50 3560 mg/kg bw (rabbit)

Repeated Dose Toxicity No data

Reproductive Toxicity No effects

Environmental Toxicity

Aquatic Toxicity Fish: LC50 0.6 mg/L (48hrs freshwater); Daphnia: EC50 3 mg/L (48 hrs); Microorganisms: EC50 8.83 mg/L (48hrs protozoa). *No chronic data.*

Degradation 4. Readily biodegradable (86% after 30 days municipal sewage treatment plant effluent)

Bioconcentration No data.

Terrestrial Toxicity No data.

P? No **vP?** No **B?** Maybe **vB?** No **T?** Maybe **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 46

(EINECS) Name 2-(2-butoxyethoxy)ethanol

EINECS No. 203-961-6

CAS No. 112-34-5

Synonyms 1-hydroxy-3,6-dioxadecan; 2-hydroxy-2-butoxy-diethylether; 3,6-dioxa-1-decanol; BDG; BDGE; butadigol; butoxy diglycol; butoxydiethylene glycol; butoxyethoxy ethanol; butyl carbinol; butyl carbitol; butyl dioxitol; diethyleneglycol monobutylether; DEGBE; DGBE; butyl oxitol glycol ether; diethylene glycol n-butyl ether; ethanol 2,2'-oxybis- monobutyl ether

Formula $C_8H_{18}O_3$

Mol. Wt. 162

Classification Xi, R36 (Annex I)

Ambient State Liquid

Melting Point -68 deg C

Boiling Point c230 deg C

Relative Density 0.96 at 20 deg C

Vapour Pressure Pa

Water Solubility mg per L Miscible

Partition Coefficient log Kow 0.15 - 0.91

Human/Mammalian Toxicity

Skin Irritation/Corrosion Irritating

Eye Irritation Irritating

Skin Sensitisation Not sensitising

Mutagenicity Genetic toxicity in vitro: three positive tests (chinese hampster ovary cells and mouse lymphoma assay) . Genetic toxicity in vivo: negative

Acute Toxicity Oral: LD50 1720-2310 mg/kg bw (guinea pig); Inhalation: no data; Dermal: LD50 >2000 mg/kg bw (rabbit); I.P.: LD50 500-1000 mg/kg bw (rat); S.C.: 2417 mg/kg bw (mouse)

Repeated Dose Toxicity Inhalation: NOAEL 0.094 mg/L (90 days rat); Dermal: 30 mg/kg bw (4 wks rabbit); Drinking water: 51 mg/kg bw (30 days rat); Gavage: 50 mg/kg (13 wks rat)

Reproductive Toxicity Inhalation: NOAEL 0.094 mg/L (90 days rat); Dermal: 30 mg/kg bw (4 wks rabbit); Drinking water: 51 mg/kg bw (30 days rat); Gavage: 50 mg/kg (13 wks rat)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 1150 mg/L (7 day freshwater); Daphnia: EC50 >100 mg/L (48hrs); Algae: EC50 >100 mg/L (96hrs); Microorganisms: EC10 1170 mg/L (16hrs bacteria).
No chronic data

Degradation 4. Readily biodegredable (>60% in 28 days activated sludge)

Bioconcentration BCF=0.46 (calculated)

Terrestrial Toxicity No data

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference	47

(EINECS) Name	Propane-1,2-diol		
EINECS No.	200-338-8	**CAS No.**	57-55-6
Synonyms	1,2-dihydroxypropane; 1,2-propylene glycol; 2,3-propanediol; 2-hydroxypropanol; isopropylene glycol; methylethyl glycol; methylethylene glycol;MPG; PG		
Formula	C3 H8 O2	**Mol. Wt.**	76
Classification	None		

Ambient State	Liquid	**Melting Point**	-60 deg C	**Boiling Point**	185-190 deg C

Relative Density	1.038 at 20 deg C	**Vapour Pressure Pa**	11-30 at 20 deg C
Water Solubility mg per L	Miscible	**Partition Coefficient log Kow**	-1.4

Human/Mammalian Toxicity

Skin Irritation/Corrosion	Not irritating
Eye Irritation	Not irritating
Skin Sensitisation	Not sensitising
Mutagenicity	Genetic toxicity in vitro: negative. Genetic toxicity in vivo: negative
Acute Toxicity	Oral: LD50 >10400 mg/kg bw (rat); Inhalation: no data; Dermal: LD50 20800 mg/kg bw (rabbit); I.P.: LD50 6660 mg/kg bw (rat); S.C.: LD50 13000 mg/kg bw (mouse); I.V.: LD50 3099 mg/kg bw (rabbit)
Repeated Dose Toxicity	Inhalation: NOAEL 1 mg/L (90 days rat); Oral feed: NOAEL 80 mg/kg bw (94 days cat); Drinking water: NOAEL 10% drinking water (140 days rat)
Reproductive Toxicity	No effects

Environmental Toxicity

Aquatic Toxicity	Fish: LC50 >1000 mg/L (48hrs freshwater); Other crustacea: EC50 10000mg/L (24hrs); Algae: EC50 19000 mg/L (14 day). *No chronic data*
Degradation	4. Readily biodegradable (100% after 24hrs activated sludge)
Bioconcentration	BCF <1
Terrestrial Toxicity	No data.

P?	No	**vP?**	No	**B?**	No	**vB?**	No	**T?**	No	**PBT?**	No	**vPvB?**	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 48

(EINECS) Name Glycerol

EINECS No. 200-289-5 **CAS No.** 56-81-5

Synonyms 1,2,3-trihydroxy propane; 1,2,3-propanetriol; grycerin

Formula $C_3 H_8 O_3$ **Mol. Wt.** 92

Classification None

Ambient State Liquid **Melting Point** 18deg C **Boiling Point** 290 deg C

Relative Density 1.26 **Vapour Pressure Pa** 0.33at 20 deg C

Water Solubility mg per L Miscible **Partition Coefficient log Kow** -1.8 (measured) ;-2.5 (calc)

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritating

Eye Irritation Not irritating

Skin Sensitisation Not sensitising

Mutagenicity Genetic toxicity in vitro: negative. Genetic toxicity in vivo: ambiguous

Acute Toxicity Oral: LD50 4090 mg/kg bw (mouse); Inhalation: no data; Dermal: LD50 >18700 mg/kg bw (rabbit); I.P.: LD50 4420 mg/kg bw (rat); S.C.: 91 mg/kg bw (rat); I.V.: 1976 mg/kg bw (rat)

Repeated Dose Toxicity Inhalation: NOAEL 0.167 mg/L (13 wks rat); Oral feed: NOAEL >=2000 mg/kg bw (50 days human)

Reproductive Toxicity Effects on fertility of rats and monkeys have been reported. No developmental effects (teratogenicity) have been reported.

Environmental Toxicity

Aquatic Toxicity Fish: LC50 >5000 mg/L (24hrs freshwater); Daphnia: EC50 >500 mg/L (24hrs); Algae: Toxic threshold concentration(3%) 2900 mg/L (8 days).
No chronic data.

Degradation 4. Readily biodegradable

Bioconcentration No data

Terrestrial Toxicity No data.

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 49

(EINECS) Name 2-aminoethanol

EINECS No. 205-483-3 **CAS No.** 141-43-5

Synonyms 1-amino-2-hydroxyethane; 2-amino-1-ethanol; 2-hydroxyethanamine; beta-aminoethyl alcohol; glycinol; MEA

Formula C2 H7 N O **Mol. Wt.** 60

Classification Xn, R20/21/22; C, R34 (Annex I)

Ambient State Liquid **Melting Point** 10.5 deg C **Boiling Point** 170deg C

Relative Density 1.013at 20 deg C **Vapour Pressure Pa** 58 at 27 deg C

Water Solubility mg per L Miscible **Partition Coefficient log Kow** -1.91 to -1.31

Human/Mammalian Toxicity

Skin Irritation/Corrosion Corrosive/irritating

Eye Irritation Corrosive/irritating

Skin Sensitisation Unclear

Mutagenicity Genetic toxicity in vitro: negative. Genetic toxicity in vivo: negative

Acute Toxicity Oral: LD50 >500 mg/kg bw (rat & rabbit); Inhalation: LC50 0.58 mg/L (guinea pig); Dermal: LD50 1025 mg/kg bw (rabbit); I.P.: LD50 50-100 mg/kg bw (mouse)

Repeated Dose Toxicity Oral feed: NOAEL 320 mg/kg bw (rat)

Reproductive Toxicity Fertility: NOAEL parental >351 mg/kg bw - NOAEL F1 offspring >351 mg/kg bw (8 wks rat oral feed): Developmental toxicity: NOAEL maternal 10 mg/kg bw - NOAEL teratogenicity 75 mg/kg bw (13 days rabbit) - no teratogenic effects reported

Environmental Toxicity

Aquatic Toxicity Fish: LC50 150 mg/L (96hrs freshwater); Daphnia EC50 65 mg/L (48hrs); Algae: EC50 15 mg/L (72hrs); Microorganisms EC50 13.7 mg/L (30 mins bacteria). Chronic NOEC 1.77 mg/L (100 days fish freshwater)

Degradation 4. Readily biodegradable (domestic waste)

Bioconcentration No data

Terrestrial Toxicity No data

P? No **vP?** No **B?** No **vB?** No **T?** No **PBT?** No **vPvB?** No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000.*

General Information

Project Reference 50

(EINECS) Name 2,2',2''-nitrilotriethanol

EINECS No. 203-049-8 **CAS No.** 102-71-6

Synonyms Ethanol-2,2',2''-nitrilotris-; 2,2',2''-trihydroxy-triethylamine; triethanolamine (TEA); tris(2-hydroxyethyl) amine

Formula C6 H15 N O3 **Mol. Wt.** 149

Classification Xi, R36/38; Xn, R48, R22 (typical examples)

Ambient State Liquid/Solid **Melting Point** 21deg C **Boiling Point** 335 deg C

Relative Density 1.124 at 20 deg C **Vapour Pressure Pa** <1 at 25 deg C

Water Solubility mg per L Miscible **Partition Coefficient log Kow** -1.3 to -2.5

Human/Mammalian Toxicity

Skin Irritation/Corrosion Not irritating - *but labelling of marketed products suggests otherwise*

Eye Irritation Not irritating- *but labelling of marketed products suggests otherwise*

Skin Sensitisation Not sensitising

Mutagenicity Genetic toxicity in vitro: negative. Genetic toxicity in vivo: negative

Acute Toxicity Oral: LD50 2200 mg/kg bw (rabbit/guinea pig); Inhalation: no data; Dermal: >11 mg/kg bw (rabbit); I.P.: LD50 1450 mg/kg bw (mouse)

Repeated Dose Toxicity Inhalation: NOAEL 0.25 mg/L (28 days rat); Oral feed: NOAEL 80 mg/kg bw (90 days rat); Dermal: NOAEL 1000 mg/kg bw (90 days mouse); Drinking water: NOAEL 1667 mg/kg bw (14 days rat); Drinking water + dermal: NOAEL 1.4-13 mg/L (180 days rat)

Reproductive Toxicity No data on toxicity to reproduction. No developmental effects have been reported - NOAEL maternal 1125 mg/kg bw - NOAEL teratogenicity 1125 mg/kg bw (10 days mouse gavage)

Environmental Toxicity

Aquatic Toxicity Fish: LC50 11.8 mg/L (96hrs freshwater); Daphnia: EC50 1386 mg/L (24hrs); Algae: EC50 169 mg/L (96hrs); Microorganisms: EC50 525 mg/L (30 mins bacteria). Chronic NOEC 16 mg/L (21 days Daphnia)

Degradation 4. Readily biodegradable? but some tests suggest
2. Inherently biodegradable

Bioconcentration BCF < 4 (fish, freshwater)

Terrestrial Toxicity No data

P?	**vP?**	**B?**	**vB?**	**T?**	**PBT?**	**vPvB?**
No	No	No	No	No	No	No

Comments on above: *Main source: IUCLID data sheet dated 18 February 2000, Numerous biodgradation tests results giving varying degrees of biodgradability.*

Annex 4

Waste Water Treatment

A4.1 Introduction

A4.1.1 Waste Water Treatment

Most of the chemicals used in detergents find their way into waste water (sewage) treatment plants. The degree to which these chemicals and other contaminants are removed from the effluent discharged to river or sea depends on the level of treatment as illustrated in Figure A4.1.

As can be seen, the removal of phosphorus requires tertiary treatment and this forms the key requirement of the Urban Waste Water Directive (Council Directive 91/271/EEC).

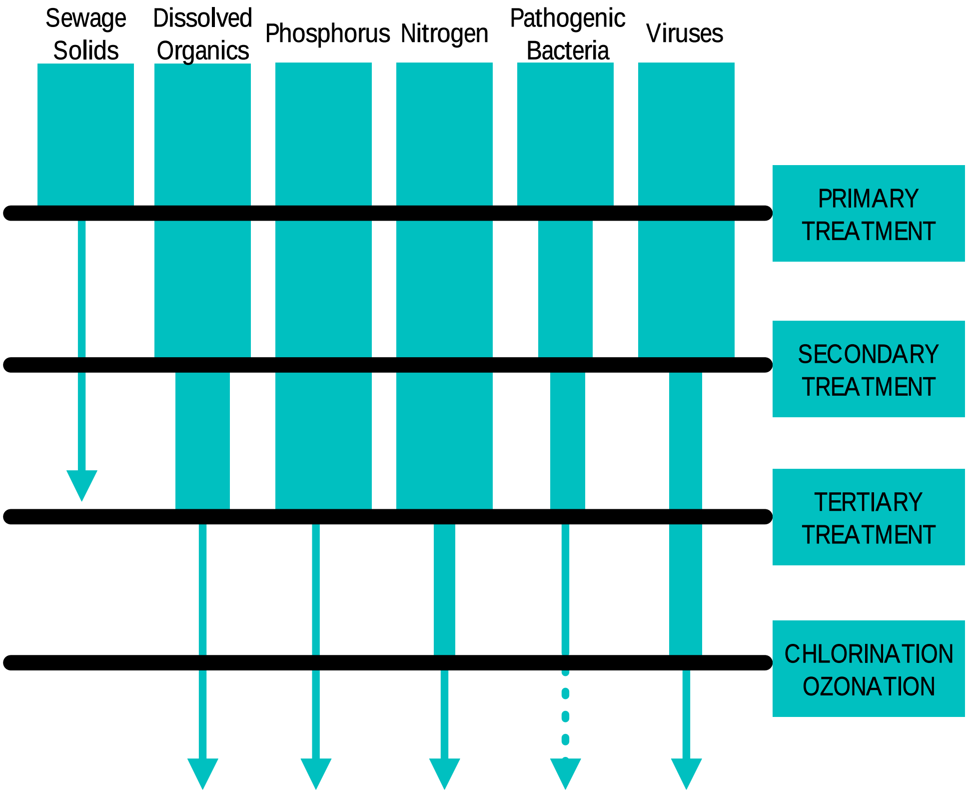

Figure A4.1: Removal of Contaminants by Waste Water Treatment
(after Figure 13.6, ReVelle & ReVelle, 1988)

Although most EU citizens are now connected to mains sewerage and waste water treatment plants, there is a considerable degree of variation as shown in Table A4.1 (overleaf).

In respect of tertiary treatment, there is still room for considerable progress as illustrated in Table A4.2 (overleaf).

Table A4.1: %Population Connected to Waste Water Treatment Plants (for EU-25)

Country	%Population	Country	%Population
Netherlands	98.1	Italy	63.1
United Kingdom	94.6	Greece	56.2
Germany	90.5	Poland	54.7
Denmark	89.0	Slovakia	48.8
Luxembourg	87.5	Spain	48.3
Sweden	86.0	Portugal	46.1
Austria	81.4	Belgium	38.1
Finland	81.0	Cyprus	34.5
France	76.9	Hungary	32.2
Ireland	74.8	Slovenia	30.0
Estonia	69.0	Malta	13.0
Czech Republic	65.1	Latvia & Lithuania	No data

Source: Eurostat, 2004a

Table A4.2: %Population Connected to Tertiary Treatment (for EU-25)

Country	%Population	Country	%Population
Denmark	84.0	Poland	22.7
Germany	83.1	Luxembourg	19.1
Finland	81.0	Belgium	16.1
Sweden	81.0	Greece	9.6
Netherlands	80.0	Hungary	5.5
Austria	63.7	Spain	3.3
Estonia	40.0	Portugal	2.3
Cyprus	34.5	Ireland	1.8
United Kingdom	27.0	Slovenia	0.0
Italy	24.1		
Malta, Czech Republic, Lithuania, Latvia, France, Slovakia			No data

Source: Eurostat, 2004a

A4.1.2 Primary Treatment

The first stage of waste water treatment essentially involves the physical separation of non-dissolved material from the influent in a settlement tank. Material that is less dense than water is skimmed off the surface whilst denser material is drawn from the bottom of the tank. The remaining waste water (or primary effluent) is then transferred to secondary treatment.

A4.1.3 Secondary Treatment

Secondary treatment usually involves biological treatment and further settlement. The most common process is ‘activated sludge’ in which a microbial culture consumes organic material (from the primary effluent) in an aerated tank. The resultant mixture is then passed to a clarifier (a further settlement tank) to separate the secondary effluent from the remaining sludge which is returned to the aerated tank.

Clearly, the effectiveness of secondary treatment on a particular (organic) contaminant is closely related to the rate at which the contaminant biodegrades under aerobic conditions.

The secondary effluent is then transferred to tertiary treatment (where provided).

A4.1.4 Tertiary Treatment

Tertiary treatment is the generic term given to further treatment. The treatment may involve biological treatment (such as that used to remove nitrogen) or chemical treatment (such as the use of ferric chloride to remove phosphorous through precipitation).

Finally, the tertiary effluent may be disinfected (usually through chlorination, ozonation or use of ultra-violet light) before being discharged to the environment.

A4.1.5 Sludge Treatment

Contaminants removed from the liquid stream form sewage sludge. The sludge can undergo further biological treatment under aerobic (with air as in the activated sludge process) or anaerobic conditions before disposal. Sludge may be disposed of to landfill, incineration or directly to agricultural land. Data on sludge re-use (i.e. application to land) are available for the EU-15 countries (bar Italy) which indicate that most of these countries re-use about half of the sludge as shown in Table A4.3.

Table A4.3: %Sludge Re-Use across EU-15 (bar Italy)

Country	**%Sludge Re-Use**	**Country**	**%Sludge Re-Use**
Luxembourg	86%	United Kingdom	52%
Finland	60%	Germany	40%
Portugal	60%	Ireland	24%
France	56%	Netherlands	23%
Spain	54%	Belgium	16%
Denmark	54%	Austria	12%
Sweden	52%	Greece	6%

Source: CEC, 2004

A4.2 Treatment of Phosphates and Zeolites

The relative significance of sludge arisings from the use of phosphate and zeolite based detergents has been the subject of past debate. Some studies have shown that the use of zeolites leads to an increase in sludge suspended solids (see, for example, Piirtola *et al*, 1998) and such studies have been seized upon by the phosphates industry (see, for example, CEEP (undated)). However, such arguments have been countered by the zeolites industry that, if the additional sludge due to phosphorous removal is accounted for, the sludge quantities are indistinguishable (see, for example, Hauthal, 1996). This issue was considered in the WRc report (Appendix F, WRc (2002)) which came to the same conclusion.

Although CSTEE (2003) initially supported the view that the use of zeolite based detergents leads to greater suspended solid concentrations than the use of STPP detergents, this argument was not sustained under further examination as CSTEE subsequently reported (CSTEE, 2003a) that the use of zeolites in detergents should not increase the volume of sewage sludge produced.

A4.3 Treatment of Ingredients of Potential Concern

An indication of whether or not particular (organic) detergent ingredients are likely to be removed from a typical municipal waste water treatment works (provided with primary and secondary treatment only) can be derived by consideration of the event tree shown in Figure A4.2.

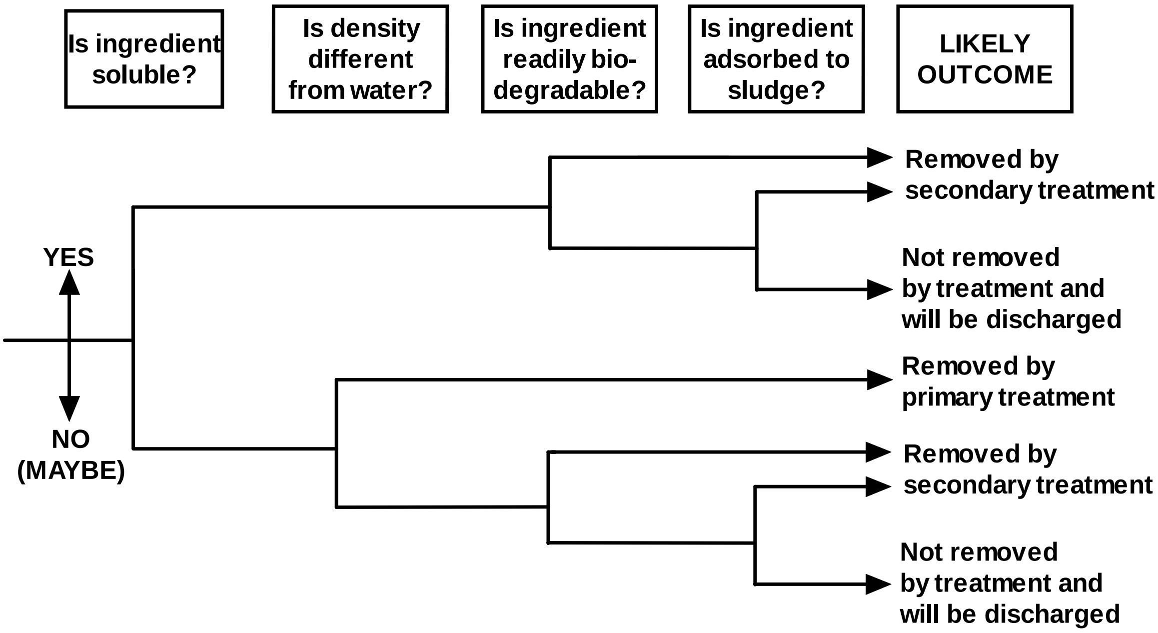

Figure A4.2: Event Tree indicating Waste Water Treatment Outcomes

By way of example, phosphonates are soluble but not readily biodegradable suggesting that removal is dependent on sludge adsorption. As discussed in the main text (see Section 4.2), available data indicate that phosphonates are substantially removed from waste water treatment through sludge adsorption. On the other hand, *n*-paraffins are barely soluble and are significantly less dense than water and would expect to be removed by primary treatment. Since *n*-paraffins are readily biodegradable, residual concentrations would tend to be removed in secondary treatment.

This exercise was repeated for each of the 'ingredients of potential concern' considered in Section 4 of the main text and the results are summarised in Table A4.4. In several cases, there were insufficient monitoring data to indicate whether a specific ingredient would be removed during waste water treatment. However, the degree to which a material is adsorbed to sludge will be a function the organic carbon-water partition coefficient (Koc) which depends on the octanol-water partition (Kow). In short, substances with a log Kow value in excess of four (which will include most polymers) are likely to be adsorbed (ICON, 2001).

Table A4.4: Waste Water Treatment and Ingredients of Potential Concern

Ingredient of Potential Concern	**Soluble?**	**Density**	**Readily bio-degradable?**	**Adsorbed to sludge?**	**Likely Outcome and Comment**
Phosphonates	Y	n/a	N	Y	Phosphonates are adsorbed to sludge giving substantial removal
Polycarboxylates	Y	n/a	N	Y	Polycarboxylates are adsorbed to sludge (and may be removed by ferric chloride treatment)
EDTA and EDTA tetrasodium salt	Y	n/a	N	N	EDTA and its salts are not generally removed (but increased pH results in removal)
Nitrilotriacetic acid (NTA)	N?	>1	Y	N?	Monitoring data suggest NTA is substantially removed during treatment
Detergent dyes	?	?	N	?	Dyes may not be removed by treatment but insufficient data to comment
Dye transfer inhibitors (PVP)	Y	n/a	N?	Y?	PVP may well be adsorbed to sludge (but insufficient data to comment further)
FWA-5	Y	n/a	N	Y	Monitoring data indicate that FWA-5 is substantially removed due to sludge adsorption
Foam regulators: - *n*-paraffins	N	0.75	Y	Y?	Would expect substantial removal by primary & secondary treatment. Furthermore, high logKow values (>5) would indicate that any residual paraffins would be adsorbed to sludge.
- PDMS	N	0.97	N	Y	Monitoring data indicate that PDMS is adsorbed to sludge (and to suspended solids) leading to substantial removal.
Formulation aids (PEG - higher MWs)	Y	n/a	N	Y?	PEG may well be removed during treatment due adsorption to sludge (but insufficient data to comment further)
Anti-redeposition agents (CMC)	Y	n/a	N	Y?	As for PEG above.
Solvents: - 1-decanol	Y	n/a	Y	Y?	Would expect substantial removal during treatment. Residual 1-decanol likely to be adsorbed to sludge (as log Kow >4).
- Triethanolamine	Y	n/a	N?	N?	May not be removed by waste water treatment (depending on biodegradability).

A4.4 Commentary

Waste water treatment (with an emphasis on primary and secondary treatment) is likely to result in the substantial removal of many of the ingredients of potential concern which will limit discharges to the aquatic environment.

However, EDTA is not removed by waste water treatment and triethanolamine may also not be substantially removed depending on its biodegradability (which is discussed further in Annex 5). There are insufficient data to comment on whether dyes will be removed by waste water treatment.

Although there are insufficient monitoring data to provide confirmation, it is likely that PVP, PEG and CMC will be removed during waste water treatment due to adsorption to the sludge.

Clearly, there remain a number of uncertainties over whether ingredients will, in practice, be removed. Furthermore, where ingredients are removed by treatment, their subsequent fate in sewage sludge may require further consideration - particularly where sludge is re-used on agricultural land.

Annex 5

Biodegradation Testing

A5.1 Introduction

Chemical compounds may break down (degrade) in various ways. Compounds may undergo chemical reactions with water (hydrolysis) or with other agents or be degraded by natural sunlight (photodegradation). However, for many organic compounds, particular attention is given to biodegradation in which compounds are broken down by micro-organisms[1].

When oxygen (air) is present, this process is referred to as ***aerobic biodegradation*** and the resultant degradation products usually include carbon dioxide and water. In the absence of oxygen (air), ***anaerobic biodegradation*** may occur and the resultant degradation products usually include carbon dioxide and methane.

In relation to organic detergent ingredients, aerobic biodegradation is of particular importance as this has a direct influence on whether such ingredients are likely to be removed in waste water treatment (as discussed in Annex 4) and to persist in the environment.

For a particular ingredient, the two key parameters of interest are the degree to which the ingredient will (ultimately) biodegrade and the rate of biodegradation. These two parameters can be measured using a wide range of standard tests as discussed further below.

A5.2 Biodegradation Testing Regimes

A5.2.1 Overview of Testing Strategy

As part of a tiered strategy for testing the biodegradability of organic chemicals, the OECD (OECD, 2005) defines readily biodegradable and inherently biodegradable chemicals as follows:

- *Readily Biodegradable*: an arbitrary classification of chemicals which have passed certain specified screening tests for ultimate biodegradability; these tests are so stringent that it is assumed that such compounds will rapidly and completely biodegrade in aquatic environments under aerobic conditions; and

- *Inherently Biodegradable*: a classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability.

The tiered testing strategy involves:

- firstly, carrying out an appropriate, relatively inexpensive but stringent screening test for ready biodegradability. If the chemical passes the ready test, it is readily biodegradable;

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[1] Other routes (which do not involve biodegradation) are collectively referred to as abiotic degradation.

- if the chemical is shown not to be readily biodegradable, then a test for inherent biodegradability may be carried out. If the chemical passes the inherent test, it is inherently biodegradable; and
- simulation testing, a higher tier of testing which simulates removal of the chemical in specific environments such as a biological sewage treatment plant, or sediment, or soil, or seawater, may also be carried out, to determine whether and to what extent removal will occur in the specified environment. Simulation testing may be carried out for chemicals which pass a ready test, to demonstrate a higher level of removal in the specific environment than the default level given, for example, in the Technical Guidance Document (European Commission, 2003). Alternatively, simulation testing may be carried out for chemicals which fail a ready test but indicate a significant level of ultimate biodegradability, to demonstrate their level of removal in the specific environment.

This approach is shown diagrammatically in Figure A5.1.

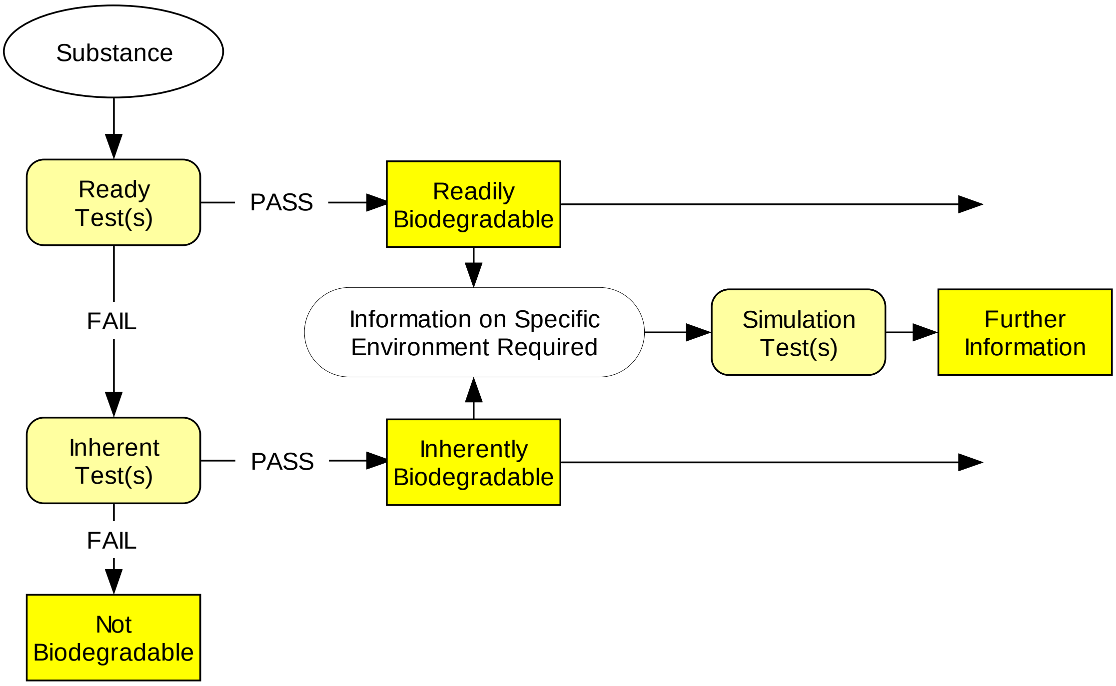

Figure A5.1: Tiered Approach to Biodegradation Testing

Standardised tests are available for use at all three tiers of the OECD testing scheme, although simulation tests are not yet available for some specific environments. The three types of standardised tests which are of particular relevance to this study are the OECD tests, ISO tests and those prescribed in Annex V of Directive 67/548/EEC[2] as summarised in Table A5.1.

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[2] Council Directive 67/548/EEC of 27 June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (OJ 196 16/8/1967, p1) (as amended).

Table A5.1: Summary of OECD/EC Biodegradation Tests

OECD Test	Title	ISO Test	Title	EC Test	Title
301	**Ready Biodegradability:**		**Water quality - Evaluation in an aqueous medium of the (ultimate) aerobic biodegradability of organic compounds:**	**C.4**	**Determination of the "Ready" Biodegradability:**
301A	DOC Die-Away Test	7827	Method by analysis of dissolved organic carbon (DOC)	C.4-A	Dissolved Organic Carbon (DOC) Die-Away Test
301B	CO_2 Evolution Test	9439	CO_2 Evolution Test	C.4-C	CO_2 Evolution Test
301C	Modified MITI Test (I)			C.4-F	M.I.T.I. Test
301D	Closed Bottle Test	10707	Method by analysis of biochemical oxygen demand (closed bottle test)	C.4-E	Closed Bottle Test
		10708	Method by determining the biochemical oxygen demand in a two-phase closed bottle test		
301E	Modified OECD Screening Test			C.4-B	Modified OECD Screening Test
301F	Manometric Respirometry Test	9408	Determination of oxygen demand in a closed respirometer	C.4-D	Manometric Respirometry Test
310	CO_2 in Sealed Vessels (Headspace Test)	14593	Method by analysis of inorganic carbon in sealed vessels (CO_2 headspace test)		
302	**Inherent Biodegradability:**				
302A	Modified SCAS Test	9887	Semi-continuous activated sludge method (SCAS)	**C.12**	Biodegradation: Modified SCAS Test
302B	Zahn-Wellens/ EMPA Test	9888	Static test (Zahn-Wellens method)	**C.9**	Biodegradation: Zahn-Wellens Test
302C	Modified MITI Test (II)				
303	**Simulation Test - Aerobic Sewage Treatment:**				
303A	Activated Sludge Units	11733	Activated sludge simulation test	**C.10**	Biodegradation: Activated Sludge Simulation Test
303B	Biofilms				
304A	Inherent Biodegradability in Soil				
306	Biodegradability in Seawater	16221	Water quality - Guidance for determination of biodegradability in the marine environment		
307	Aerobic and Anaerobic Transformation in Soil				

Table A5.1: Summary of OECD/EC Biodegradation Tests					
OECD Test	**Title**	**ISO Test**	**Title**	**EC Test**	**Title**
308	Aerobic and Anaerobic Transformation in Aquatic Sediment Systems				

As far as can be determined, there are few significant differences amongst the OECD and corresponding ISO and EC tests. Although different tests provide similar results for many chemicals, there are also numerous inconsistencies and the selection of an appropriate test and correct interpretation of the results is an important consideration, particularly for more 'difficult' chemicals (such as those with low solubility or those toxic to the inoculum) (OECD, 2005; Falck *et al*, 2005).

A5.2.2 Biodegradation Testing and the Detergents Regulation

In relation to the Detergents Regulation, biodegradation testing requirements relate solely to surfactants and involve consideration of two parameters: 'primary biodegradation' and 'ultimate aerobic biodegradation'. The definitions of each are presented in Table A5.2.

Table A5.2: Definitions of Primary and Ultimate Biodegradation		
Parameter	**OECD 301/EC.4 Guidelines**	**Article 2, Detergents Regulation**
Primary Biodegradation	The alteration in the chemical structure of a substance, brought about by biological action, resulting in the loss of a specific property of that substance.	The structural change (transformation) of a surfactant by micro-organisms resulting in the loss of its surface-active properties due to the degradation of the parent substance and consequential loss of the surface-active property as measured by test methods listed in Annex II.
Ultimate Aerobic Biodegradation	The level of degradation achieved when the test compound is totally utilised by micro-organisms resulting in the production of carbon dioxide, water, mineral salts and new microbial cellular constituents (biomass).	The level of biodegradation achieved when the surfactant is totally used by micro-organisms in the presence of oxygen resulting in its breakdown to carbon dioxide, water and mineral salts of any other elements present (mineralisation), as measured by test methods listed in Annex III, and new microbial cellular constituents (biomass).

The essential differences between the two sets of definitions are that, for the Detergents Regulation, the focus is on the surface-active properties of surfactants and specific test methods are referenced.

In relation to non-surfactant (organic) detergent ingredients, it has been assumed that attention will tend to focus on 'ultimate aerobic biodegradation' (as discussed in the remainder of this Annex) rather than on 'primary biodegradation'. The ultimate aerobic biodegradation tests listed in Annex III (of the Detergents Regulation) comprise all the EC C.4 (i.e. OECD 301) tests listed in Table A5.1 together with the reference method ISO 14593 (*Water quality - Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium - Method by analysis of inorganic carbon in sealed vessels (CO_2 headspace test)*) which is the basis of the new OECD 310 test (*Ready Biodegradability: CO_2 in Sealed Vessels (Headspace Test)*).

A5.2.3 Biodegradability Criteria

Ultimate aerobic biodegradation is measured in both ready and inherent biodegradation tests. The ready biodegradability tests use organic test compounds as the sole source of carbon and energy for an inoculum of mixed aerobic micro-organisms. They are carried out under well defined aerobic conditions in which the amount of test substance is high (in the range of 2 to 100 mg/L) and the amount of available biomass is low. The time available for biodegradation to occur is limited, with the total test time limited to 28 days, and generally a further restriction that, after evidence of biodegradation (generally 10% biodegradation of the substance) is obtained in the test, the pass level must be reached within 10 days. This restriction is known as the 10-day window.

In some circumstances, the 10-day window is not considered necessary. The Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE, 1999) has delivered an opinion that, for surfactants used in detergent preparations, the 10-day window is not necessary to achieve the stringency desired in a ready test (and this was carried forward to the tests specified in Annex III to the Detergents Regulation). The reasons for this include the multiphase kinetics generally observed for surfactants, which may be multi-component and also may degrade to intermediates which may have different degradation rates from the parent substance. The necessity for the 10-day window in ready tests for non-surfactant organic substances used in detergent products will depend upon the kinetic information available for each specific group of these substances.

In the ready tests, the extent of ultimate biodegradation is measured by non-specific, summary parameters such as Dissolved Organic Carbon (DOC), Biochemical Oxygen Demand (BOD) and CO_2 production. Domestic sewage, activated sludge or secondary effluent is the typical source of micro-organisms (or inoculum) in tests for ready biodegradability. The inoculum should not have been pre-adapted to degradation of the test substance by previous exposure to the test substance or to structurally related chemicals. The pass levels for ready tests depend upon the parameter being measured (OECD, 2005).

The pass criteria for ready biodegradability tests OECD 301/EC C.4 and ISO 14593 are summarised in Table A5.3.

Table A5.3: Criteria for Ready Biodegradability

Test	**Title**	**Criterion for Ready Biodegradability**[1]
OECD 301A/EC C.4-A	DOC Die-Away Test	70% in 28 days
OECD 301B/EC C.4-C	CO_2 Evolution Test	60% in 28 days
OECD 301C/EC C.4-F	Modified MITI Test (I)	60% in 28 days
OECD 301D/EC C.4-E	Closed Bottle Test	60% in 28 days

Table A5.3: Criteria for Ready Biodegradability

Test	**Title**	**Criterion for Ready Biodegradability**[1]
OECD 301E/EC C.4-B	Modified OECD Screening Test	70% in 28 days
OECD 301F/EC C.4-D	Manometric Respirometry Test	60% in 28 days
ISO 14593 (OECD 310)	CO_2 Headspace Test	60% in 28 days

Note: 1) Generally, the criterion of 60 or 70% biodegradation is to be reached within a 10 day window (which is deemed to commence once 10% biodegradation has been reached). However, in some cases (including surfactants), the 10 day window is not applied so that the criterion of 60 or 70% biodegradation is to be reached within 28 days (which is equivalent to the test period).

Unlike the stringent ready biodegradability tests, inherent biodegradation tests are carried out under conditions that encourage biodegradation. The test procedures allow prolonged exposure of the test substance to micro-organisms and have a high amount of available biomass and a low ratio of test substance to biomass. Some of these tests may be conducted using micro-organisms that have previously been exposed to the test substance, which frequently results in adaptation leading to a significant increase of the degradation rate (OECD, 2005). A substance yielding a positive result in a test of this type may be classified as “inherently biodegradable”, which, preferably, should be qualified by one of the terms "with pre-adaptation” or “without pre-adaptation” as appropriate. Because of the favourable conditions employed in these tests, rapid biodegradation of inherently biodegradable chemicals in the environment cannot generally be assumed (OECD, 2005).

Of the three main inherent aerobic biodegradability tests considered here, the Semi-Continuous Activated Sludge (SCAS) test provides the most suitable conditions for allowing biodegradation to take place (OECD, 2005). However, as the conditions in this test are considered to be more favourable than the conditions in an activated sludge sewage treatment plant, it is difficult to predict the degree of biodegradation in the environment, or during sewage treatment, based on biodegradation observed in the SCAS test (European Commission, 2003). The TGD does allow significant biodegradation in either the Zahn-Wellens/EMPA test (OECD 302B; ISO 9888) or in the MITI II test (OECD 302C) to be correlated with some biodegradation during sewage treatment and in the environment, if other specific test conditions are met (European Commission, 2003). The MITI II test is considered to be more stringent than the Zahn-Wellens/EMPA test (OECD 2005).

Since inherent biodegradability can be considered to be a specific property of a chemical, it is not necessary to define limits on test duration or biodegradation rates. However, for practical reasons (i.e. sludge viability) the duration of most tests does have a finite limit. Biodegradation above 20% of theoretical (measured as BOD, DOC removal or COD) may be regarded as evidence of inherent, primary biodegradability, whereas biodegradation above 70% of theoretical (measured as BOD, DOC removal or COD) may be regarded as evidence of inherent, ultimate biodegradability (OECD, 2005) as summarised in Table A5.4. The use of a compound-specific analytical technique or a ^{14}C-labelled test substance may allow greater test sensitivity, which may result in a lower substance removal level being accepted as evidence of inherent biodegradability.

Table A5.4: Summary Criteria for Inherent Ultimate Biodegradability

Test	**Title**	**Criterion for Inherent Ultimate Biodegradability**
OECD 302A/ISO 9887/EC C.12	SCAS Test	70% BOD, DOC, or COD removal
OECD 302B/ISO 9888/EC C.9	Zahn-Wellens Test	70% BOD, DOC, or COD removal
OECD 302C	MITI II Test	70% BOD, DOC, or COD removal

Finally, simulation tests, in which environmentally relevant conditions including environmentally relevant concentrations of the chemical are used, constitute the highest tier of testing methodology. For many substances, the concentrations present in the environment can be up to several orders of magnitude lower than the concentrations necessary for measurement of summary parameters such as BOD, evolved CO_2, and DOC in the ready and inherent biodegradability tests used for screening purposes. Both substance toxicity and substance solubility may be suitable to enable biodegradation at environmental concentrations, either in the sewage treatment plant, in surface waters, or in soil, even though the substance does not pass either the ready or the inherent biodegradability tests. Thus simulation tests, which are carried out under controlled laboratory conditions intended to approximate a realistic natural or technological environment such as surface water, soil, or the sewage treatment plant, are the next tier in the process of establishing the biodegradability of a substance in the environment.

Detection methods using summary parameters may be used in simulation tests if the environmental concentration of the specific substance is high enough to allow measurement under the conditions of the test. However, for many substances, specific analytical detection methods which are valid for the test environment or radiotracer methods requiring specially synthesised substances containing ^{14}C at suitable positions to reflect ultimate biodegradation will be required. The need to use the more expensive detection methods must be decided for the specific substance, depending on the order of magnitude of the predicted environmental concentration and the availability/sensitivity of appropriate analytical methods.

For the aquatic environment, the OECD guideline for the testing of chemicals states that if it can be demonstrated that the chemical is **ultimately degraded by more than 70% in 28 days under realistic conditions in the aquatic environment**, then the definition of **“rapid degradability”** in relation to aquatic hazard classification will have been met (OECD, 2005). If first order degradation[3] occurs, which is normal for low concentrations of chemicals, then this corresponds to a half-life of 16 days for ultimate biodegradation (OECD, 2005). Realistic conditions in the environment include:

- substance concentration which is realistic for the environment (within an order of magnitude);
- realistic concentration of inoculum (e.g.10^3 - 10^6 cells/ml in surface water);
- inoculum from a relevant environment; and
- realistic environmental temperature (e.g. 5°C to 25°C).

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[3] First order degradation is exponential decay based on the formula $C = C_0 e^{-kt}$.

A5.3 Overview of Ready Biodegradability Tests

A5.3.1 DOC Detection (OECD 301A/E; ISO 7827; EC C.4-A/B)

The simplest tests to carry out experimentally involve detection of DOC remaining in the aqueous solution. The carbon content and, preferably, the purity or relative proportions of major components of the test substance should be known. The amount of DOC in the test flasks, which contain DOC from both the substance to be degraded and the biodegrading matter (inoculum), is compared with the DOC from control flasks containing the inoculum alone. As the inoculum may contain significant DOC levels, at least 10mg/L of DOC due to the test substance must be used to enable meaningful subtraction of the DOC in the controls from the other DOC in the test solutions. Measurements in both test and control flasks taken over time will show a decreasing DOC due to the substance being tested, if biodegradation occurs. At least 70% of the DOC must be removed from the test flasks to achieve the pass level required for ready tests using DOC detection.

Problems with the DOC detection will occur if the substance being tested is volatile, or if it adsorbs significantly to the biomass in the test medium. In both cases a lower amount of DOC will remain in solution and be measured by the test than the amount of substance which has not yet biodegraded. Thus the DOC detection method should not be used for volatile substances, or for substances which would be expected to adsorb significantly to biomass. In addition, this detection method is not suitable for poorly soluble substances.

Relevant tests include OECD 301A (ISO 7827, EC C.4-A) and the more stringent OECD 301E (EC C.4-B) (which uses a significantly lower inoculum level). The tests are all carried out in conical flasks (250 mL to 2L, depending on the DOC detection method), with the test substance dissolved in a mineral medium to support inoculum growth. In OECD 301E, supplemental minerals and vitamins are added to the standard mineral medium, as the low initial inoculum concentration will require greater inoculum growth to achieve sufficient removal of the test substance by biodegradation. The test (test substance plus inoculum) and various controls are run in parallel. Ideally, tests for abiotic decomposition, adsorption to sludge, and toxicity to sludge will determine whether the test method is suitable for the substance to be tested before the biodegradation test is carried out. It should always be remembered that DOC elimination is not always a clear indicator for biodegradation.

A5.3.2 CO_2 Evolution (OECD 301B/310; ISO 9439/14593; EC C.4-C)

It is possible to measure the carbon dioxide evolved in the biodegradation process, by using test apparatus in which CO_2 free air (i.e. the air contains no carbon dioxide) is bubbled through the test and control solutions, where it picks up CO_2 released by biodegradation. The air then flows through traps containing a CO_2 absorber such as barium hydroxide. The amount of CO_2 adsorbed is determined by titration of the residual hydroxide in the trap, or alternatively as inorganic carbon. In all cases, controls are run to determine the amount of CO_2 released in the absence of the test substance. Controls for inhibition due to the test substance and for abiotic degradation, and use of a reference substance to check the test procedure are also recommended. The amount of CO_2 released by the test substance is determined by subtraction of the amount of CO_2 released by the control from the CO_2 released by the flasks which also contain the test substance. The net CO_2 released is then compared to the theoretical amount of CO_2 release due to ultimate biodegradation of the substance, to determine the percentage biodegradation. The degree of biodegradation may also be calculated from supplemental DOC analysis made at the beginning and end of incubation.

Problems with this CO_2 evolution method are concerned with the experimental difficulty of establishing and maintaining the apparatus required. Also, the method may give low results if inorganic carbon builds up in the test medium, especially during the time in the middle of the test when the 10-day window criterion is being determined (Weytjens *et al*, 1994). Larson *et al* (1996) indicates that inorganic carbon build-up is dependent on the design of the test apparatus, with negligible inorganic carbon build-up using the shaken (rather than stirred) flasks used in his modification of the test method. However, the revised ISO test for the CO_2 evolution method (ISO 9439, 1999) caries the caveat that the test may not fully represent the true microbial kinetic rate. In addition, although the method is capable of detecting the CO_2 evolved due to cell metabolism, the carbon incorporated into the biodegrading organisms due to cell growth is not detected. To account for this, a lower pass rate, 60%, is set for all ready tests using the CO_2 detection technique, compared with the 70% pass rate required for ready tests using DOC detection. The CO_2 detection method described above is considered suitable for poorly soluble and adsorbing compounds, but not for volatile substances. In addition, the carbon content of the test substance must be known, to allow the theoretical CO_2 release to be calculated.

To overcome problems with possible inorganic carbon build-up in the test medium during the biodegradation of some substances, and to provide a method suitable for volatile substances, closed bottle tests in which the oxygen needed for biodegradation is in a gaseous headspace accounting for one third of the volume of the bottle have been developed. The test bottles are sacrificed in triplicate, at sufficient intervals throughout the 28 days of the test to determine the 10-day window. At each measurement occasion, either inorganic carbon (CO_2) measurements of the headspace gas are carried out after acidification and shaking, which drive the remaining dissolved inorganic carbon (DIC) into the headspace, or DIC is measured in solution after CO_2 in the headspace is converted to carbonate using alkali. These procedures ensure that all the inorganic carbon present in the system at the time of the measurement is measured, and give a much better description of the course of the biodegradation process than the earlier methods, which only release residual DIC by acidification on one occasion, at the end of the test period. Appropriate blanks and inhibition controls are specified in the test guidelines. Percentage biodegradation is calculated from a comparison of the net CO_2 released at appropriate stages in the headspace test to the theoretical amount of CO_2 release due to ultimate biodegradation of the substance. The pass rate for this test is set at 60%, as carbon incorporated into the biodegrading organisms due to cell growth is not detected.

If a substance is found to be toxic to the inoculum at the substance concentration normally used in ready tests, it may be possible to prepare a radio-labelled analogue of the substance for use at much lower concentrations. In this case, special test apparatus suitable for use with radioactive materials must be used, generally in a laboratory adapted for radio-tracer work. In order to allow ultimate biodegradation to be measured, the radio-labelled substance should contain ^{14}C either at all carbons, or at the last carbon expected to be removed in the biodegradation process. Primary biodegradation could be measured from $^{14}CO_2$ evolution from a substance containing ^{14}C only at the carbon whose removal will result in the loss of the specific property under consideration. The biodegradation tests discussed above which measure CO_2 evolution are suitable tests to be adapted for this purpose. Radio-labelled substances are also used, especially in simulation tests, if it is necessary to carry out the test at substance concentrations similar to those found in the environment.

Relevant tests include OECD 301B (EC C.4-C) which is carried out in flasks from which the CO_2 generated by microbial respiration is trapped and analysed. The test results may be dependent on the test design, and especially the rate at which CO_2 can be removed from the test solution. Although the tests may give low estimates of biodegradability, they are still useful as screening tests, especially as they can be used for both poorly soluble and adsorbable substances. The tests are not suitable for volatile substances, however.

Ready tests ISO 14593 (and OECD 310) have been developed to overcome some of the disadvantages of the earlier CO_2 evolution tests. They are closed bottle tests in which the oxygen needed for biodegradation is in a gaseous headspace accounting for one third of the volume of the bottle. These headspace tests are generally suitable for volatile substances, and for poorly soluble substances in a suitable dispersion, as well as for water soluble and adsorbable substances. A test is considered to be valid if the mean percentage degradation in the vessels containing the reference compound is >60% on the 14th day of incubation, and the mean amount of total inorganic carbon (TIC) produced from the blank controls at the end of the test is <15% of the organic carbon added initially as the test compound. Although the headspace test, by an increased frequency of analysis which includes the driving of released CO_2 to either the solution or to the headspace, overcomes many of the problems with inorganic carbon build-up, ISO 14593 still carries a warning that the test conditions do not always correspond to the optimal conditions for allowing the maximum degree of biodegradation to occur.

A5.3.3 Oxygen Depletion Measurements from Solution (OECD 301D; ISO 10707/10708; EC C.4-E)

It is also possible to measure the oxygen required to oxidise the carbon and other elements in the test substance. As carbon incorporated into cellular material will not be oxidised until the death of the cell, which may not occur during the 28 days of the test, the pass rate for ready tests using oxygen depletion or consumption (see below) methods has been set at 60% of the theoretical oxygen demand, as for the CO_2 evolution methods.

In the closed bottle tests, biodegradation is carried out in completely filled closed bottles with no gaseous headspace, and oxygen depletion from the test solution is attributed to biodegradation of the test substance after allowing for oxygen depletion in the control. These tests are suitable for volatile substances. Oxygen in the test and control flasks is measured using either the Winkler method or an oxygen-specific electrode, with flasks for both test and control being sacrificed each time a measurement is made. The chemical structure of the test substance should be known, to enable the theoretical oxygen demand to be calculated. If the test substance contains nitrogen, it is necessary to determine whether or not nitrification will occur under the test conditions, and if so to adjust the theoretical oxygen demand accordingly. As the oxygen level in the closed bottle must not fall below 0.5 mg/L in order to ensure that inoculum activity is not limited, the initial concentration of test substance must be low, generally about 2 mg/L but depending upon the theoretical oxygen demand of the test substance. If the chemical structure of the test substance is not known, it is possible, but less satisfactory, to calculate the test substance biodegradation percentage using the chemical oxygen demand (COD) of the substance, as falsely high values may be obtained if the test substance is incompletely oxidised in the COD test.

Relevant tests include OECD 301D (ISO 10707, EC C.4-E) which is carried out in glass BOD bottles of approximately 250-300 mL volume, with glass stoppers made airtight by use of a non-carbon based sealant. OECD 301D points out that a strict cleaning procedure must be followed out for the bottles if the electrode detection method is to be used. As the oxygen needed for biodegradation comes entirely from the solution, the concentration of the test substance is generally low, about 2 mg/L. A test is considered valid if:

- oxygen depletion in the inoculum blank control does not exceed 1.5 mg/L after 28 days; and
- the residual concentration of oxygen in the test bottles does not fall below 0.5 mg/L at any time.

A more recent variation (ISO 10708) is based on a two phase closed bottle test in which the oxygen needed for biodegradation is in a gaseous headspace accounting for one third of the volume of the bottle. The two-phase closed bottle test is especially suitable for poorly soluble substances, using simple equipment but is not suitable for volatile substances. Furthermore, this test is favoured by industry as it is relatively simple and is claimed to be less expensive than other tests. For this reason, the Scientific Committee on Health and Environmental Risks was invited to consider whether the use of this test would provide equally valid results to those tests prescribed in Annex III of the Detergents Regulation (see Section A5.2.2). In its Opinion, SCHER (2005) concluded that ISO 10708 provides an equivalent level of reliability and stringency to the prescribed tests.

A5.3.4 Oxygen Uptake Measurements (OECD 301C/F; ISO 9408; EC C.4-D/F)

Respirometric methods allow continuous recording of the oxygen taken up in the biodegradation process. This is very advantageous for determining the course of the biodegradation, including the onset of the 10-day window. The method, which requires precise temperature control, uses stirred, closed flasks with a trap for CO_2 removal, and an oxygen-generating electrode which is activated by the pressure drop in the system caused by CO_2 removal. The amount of oxygen taken up by the microbial population during biodegradation of the test substance (corrected for uptake by blank inoculum, run in parallel) is expressed as a percentage of the theoretical oxygen demand or, less satisfactorily, COD. Alternatively, in the absence of a suitable system for oxygen generation, in some tests, continuous pressure measurements can determine the amount of CO_2 lost from the system.

Relevant tests include OECD 301C (EC C.4-F) and OECD 301F (ISO 9408, EC C.4-D). OECD 301C has been adapted from the MITI I test developed in Japan. The temperature of the test, at 25°C, is at the upper limit of other ready tests. The inoculum is freshly collected from no fewer than ten sites, mainly in areas where a variety of chemicals are used and discharged, including sewage treatment works, industrial waste-water treatment works, rivers, lakes, and seas. It is then conditioned by aeration and daily supernatant replacement and feeding with glucose, peptone and potassium orthophosphate solution, for one month, before being used as inoculum in the test. The sludge stock may be maintained for three further months before being replaced by a freshly collected and conditioned sludge mixture.

The test is carried out using six respirometric flasks, three of which contain test substance plus inoculum. The other three flasks consist of one inoculum control, one reference substance control, and one abiotic control containing the test substance in water. The concentration of the test substance is determined at the beginning of the test by specific analysis, and the DOC may also be determined for water soluble substances. At the end of incubation, normally 28 days, the pH of the contents of the bottles is measured and the concentration of the residual test substance and any intermediates is determined by specific analysis. For water soluble substances, the DOC may also be determined. Special care is to be taken for volatile substances. If nitrification is anticipated, nitrate and nitrite concentrations should be determined, if possible. If nitrification has taken place, corrections must be made for the additional oxygen consumption. If any loss of test substance is shown in the abiotic control, the amount of test substance remaining in that control is used to calculate percentage biodegradation.

OECD 301C is considered to be valid if the amount of BOD in the inoculum controls at the end of the test, which is usually at about 20 mg/L to 30 mg/L, does not exceed 60 mg/L after 28 days. If the pH value is outside the range 6-8.5 (which may indicate nitrification of nitrogen-containing test compounds) and the oxygen consumption by the test substance is less than 60%, the test should be repeated with a lower concentration of test substance. The general validity criterion that the duplicate results agree within 20% does apply, and the percentage degradation required by the reference compound is somewhat more stringent, with more than 40% degradation of aniline calculated from the oxygen consumption required after 7 days, and more than 65% degradation required after 14 days.

OECD 301F uses duplicate test and inoculum control flasks, and one flask containing the reference compound plus inoculum. In addition, controls for abiotic degradation and toxicity to the inoculum can be included. When an automatic respirometer is used, a continuous record of oxygen uptake is obtained, enabling the 10 day window to be accurately determined. For non-automatic respirometers, daily readings are adequate. At the end of incubation, normally 28 days, the pH of the contents of the flasks is determined. If the pH value is outside the range 6-8.5 (which may indicate nitrification of nitrogen-containing test compounds) and the oxygen consumption by the test substance is less than 60%, the test should be repeated with a lower concentration of test substance.

Oxygen uptake due to nitrification is a possibility if the test compound contains nitrogen. This can be detected by using a qualitative spot test procedure for nitrite and nitrate on a small volume of reaction mixture taken from each vessel, followed, if needed, by a quantitative determination of nitrate and nitrite. If nitrification has taken place, corrections must be made for the additional oxygen consumption.

The tests are considered to be valid if the amount of BOD in the inoculum controls at the end of the test, which is usually at about 20 mg/L to 30 mg/L, does not exceed 60 mg/L after 28 days. For these tests, the general requirement that the duplicate results agree within 20% does not apply, but test results should be reported individually rather than averaged if the agreement is outside this range. If inhibition is indicated by degradation of the reference compound by less than 40% at the end of the test, it is advised to repeat the test with a lower concentration of the test compound.

A5.3.5 Summary

Table A5.5 summarises the applicability of the various ready biodegradability tests.

Table A5.5: Applicability of Ready Biodegradability Tests

Test	**Applicability**	**Recommendation for Test Use**
DOC Detection: OECD 301A/ISO 7827/EC C.4-A DOC Die-Away Test	Only applicable to organic compounds which are: – water-soluble (>100 mg/L); – of known carbon content and purity; – non-volatile; and – not significantly adsorbed on glass and activated sludge.	Only for non-volatile, water-soluble test compounds. Test substances with a low level of sorption to test media may be tested, but a sorption control must be included. Not suitable for highly sorbing substances. DOC elimination is not always a clear indicator for biodegradation.
DOC Detection: OECD 301E/EC C.4-B Modified OECD Screening Test	Only applicable to organic compounds which are: – water-soluble at the test concentration (10-40 mg/L DOC); – non-volatile; and – not significantly adsorbed on glass and activated sludge.	
CO_2 Evolution: OECD 301B/ISO 9439/EC C.4-C CO_2 Evolution Test	The standard is applicable to organic compounds which are: – water-soluble at the test concentration (20 mg/L DOC); – water-insoluble at the test conditions, though good dispersion is needed; – non-volatile; and – not inhibitory to the test micro-organisms at the test concentration.	Useful for poorly soluble and strongly adsorbing chemicals. Useful for soluble chemicals, as CO_2 evolution is a good indicator of microbial activity. With the additional DOC measurement a good differentiation is possible between biodegradation and abiotic elimination e.g. adsorption.
CO_2 Evolution: ISO 14593/OECD 310 CO_2 Headspace Test	The standard is applicable to organic compounds which are: – water-soluble at the test concentration (20 mg/L DOC); – water-insoluble at the test conditions, though good dispersion is needed; – volatile (provided less than 1% of the substance is in the headspace); and – not inhibitory to the test micro-organisms at the test concentration.	Test method for water-soluble, poorly soluble and volatile test compounds using an analytical parameter which has a strictly biological origin.

Table A5.5: Applicability of Ready Biodegradability Tests

Test	**Applicability**	**Recommendation for Test Use**
Oxygen Depletion: OECD 301D/ISO 10707/ISO 10708/ EC C.4-E Closed Bottle Test	The test substance should be dissolved in the test medium. Also suitable for poorly soluble substances and, possibly for toxic substances.	Test method for low test concentrations of substances which can be dissolved in the test medium. Also suitable for poorly soluble substances. Degradation values for insoluble substances may be falsely low unless the bottles are agitated periodically during the incubation. May be suitable for toxic substances (Annex II, OECD 1992).
Oxygen Uptake: OECD 301C/EC C.4-F Modified MITI Test (I)	Suitable for water soluble substances. Insoluble and volatile substances may be assessed provided precautions are taken. The formula of the test substance and its purity, or relative proportions of major components, should be known so that the theoretical oxygen demand (ThOD) may be calculated. Respirometric methods with oxygen uptake as the analytical procedure may be influenced significantly by the oxygen uptake resulting from ammonium oxidation.	Suitable for water soluble substances. Insoluble and volatile substances may be assessed provided precautions are taken (Annex III, OECD 1992). N-containing test substances may be nitrified, and this has to be considered in determining the test result.
Oxygen Uptake: OECD 301F/ISO 9408/ EC C.4-D Manometric Respirometry Test	Suitable for water soluble substances. Insoluble and volatile substances may be assessed provided precautions are taken. Respirometric methods with oxygen uptake as the analytical procedure may be influenced significantly by the oxygen uptake resulting from ammonium oxidation.	

A5.4 Overview of Inherent Biodegradability Tests

A5.4.1 Semi-Continuous Activated Sludge (SCAS) Test (OECD 302A; ISO 9887; EC C.12)

The SCAS test uses activated sludge from a sewage treatment plant, pre-conditioned in aeration vessels for up to 2 weeks until a clear supernatant containing less than 12 mg/l DOC is obtained. The daily test/preconditioning cycle consists of 23 hours aeration, ceasing aeration and allowing the sludge to settle for 45 minutes, withdrawing 2/3 of the contents of the vessel from the supernatant liquor, and replacing the volume withdrawn with the supernatant from freshly settled domestic sewage, to which the test compound is added for the test units, but not to control units or during the initial sludge preconditioning procedure. The carbonaceous material in the sewage feed is oxidised extensively within 8 hours of the start of each aeration cycle. Thereafter, the sludge respires endogenously for the remainder of the aeration period, during which time the only available substrate is the test compound unless this is also readily metabolised. These features, combined with daily reinoculation of the test when domestic sewage is used as the medium, provide highly favourable conditions for both acclimatisation and biodegradation.

DOC detection or, alternatively, specific chemical analysis or radio-tracer methods using ^{14}C labelled substances may be used to determine the percentage biodegradation. If DOC detection is used, the DOC results in the supernatant liquors of the test units and the control units are plotted against time. As the sludge becomes acclimatised and biodegradation is achieved the DOC level found in the test will approach that found in the control. Once the difference between the two levels is found to be constant over three consecutive measurements, three further measurements are made and the percentage biodegradation of the test compound is calculated. Test chemicals with greater than 20% loss of DOC may be regarded as inherently biodegradable, whereas greater than 70% loss of DOC is evidence of ultimate inherent biodegradability. The use of a compound-specific analytical techniques or ^{14}C-labelled test substances may allow greater sensitivity. In these last cases, a lower level may be regarded as evidence of inherent biodegradability.

The test is suitable for organic compounds which are water-soluble at the test concentration; non-volatile, not lost by foaming, not significantly adsorbable on glass or activated sludge, and not inhibitory to the test micro-organisms at the test concentration. The organic carbon content of test substance must be established. The length of the test for compounds showing little or no biodegradation is indeterminate, but experience suggests that this should be at least 12 weeks (OECD, 1981).

If, from the outset, there is no difference between the control and the test, or the difference between the two remains constant at a level less than would be expected if no degradation had taken place, further tests are necessary to distinguish between biodegradation and adsorption. This may be done by using the supernatant liquors as a source of adapted inoculum for suitable ready tests.

A5.4.2 Zahn-Wellens/EMPA Test (OECD 302B; ISO 9888; EC C.9)

The Zahn-Wellens/EMPA test is a static test, carried out using DOC or alternatively COD (chemical oxygen demand) as the detection system. The test is only suitable for substances which are water soluble at the test concentration. In addition, the test substance must not be volatile, or capable of being lost by foaming from the test solution. Generally, duplicate vessels containing the test substance as the sole source of organic carbon, mineral nutrients and a relatively large amount of activated sludge in aqueous medium are agitated and aerated at 20-25°C in the dark or in diffuse light for up to 28 days. Blank controls, containing activated sludge and mineral nutrients but no test substance, are run in parallel, as is a procedure control containing a reference substance plus inoculum.

The DOC (or COD) is measured after about three hours have elapsed. This initial measurement is made to detect any adsorption of the test substance onto the activated sludge. Subsequent measurements are taken at regular intervals, on at least four occasions in the interval between days 1 and 27, and on days 27 and 28 (or, if the plateau is reached earlier, on the last 2 days of the test). If sludge adaptation is to be monitored, more frequent, preferably daily, sampling should be carried out. The percentage biodegradation at sampling occasions after the first 3 hours is calculated using the 3 hour value obtained after any adsorption has taken place, corrected by any adsorption in the control, as the reference value. Biodegradation curves are analysed to show any significant difference between the expected and measured DOC (or COD) values. If necessary, the test may be repeated using pre-adapted sludge, but this must be stated in the test report.

The test is considered valid if the procedural control shows the removal of the reference compound by at least 70% within 14 days and if the removal of DOC (or COD) in the test suspension took place relatively gradually over days or weeks, since this indicates biodegradation. However, physico-chemical adsorption can, in some cases, play a role and this is indicated by complete or substantial removal in the first 3 hours, with the difference between blanks and test solutions remaining at an unexpectedly low value. In such cases additional information can be obtained from a comparison between the DOC left in solution after 3 hours, the expected initial DOC value calculated from the amount of test substance added and the value measured before the inoculum is added. If a more precise distinction between biodegradation (or partial degradation) and adsorption is to be drawn, further tests need to be carried out. A suitable test would be based upon a respirometric test for ready biodegradation, using the supernatant of the acclimatised sludge as inoculum.

Zahn-Wellens tests which show rapid biodegradation can be used in EU risk assessment models to indicate some biodegradation during sewage treatment and in the environment (European Commission, 2003). The specific additional test criteria which must be met are that the pass rate of 70% biodegradation must be met within 7 days, that the percentage removal before biodegradation begins should be below 15%, and that the biodegradation phase of the test should take no longer than 3 days. It is necessary to obtain several test measurements during the first 7 days of the test in order to demonstrate that these conditions have been met, and thus some older tests on substances which would be expected to meet these test criteria may not be useful for this purpose.

A5.4.3 MITI II Test (OECD 302C)

The MITI II test is designed to determine the Biochemical Oxygen Demand (BOD) and to carry out an analysis of residual chemicals in order to evaluate the inherent biodegradability of chemical substances which have been found by the MITI I method (discussed in Section A5.3.4) to have low degradability. The MITI II test is carried out in apparatus similar to that used in the MITI I ready biodegradation test, using a BOD meter to measure and record the oxygen uptake, and using the same specially prepared inoculum. The MITI II inherent test uses a lower level of test substance and a higher level of inoculum, however, giving a test substance to inoculum ratio increased by more than a factor of 10 over that used in the MITI I test. The MITI II test can also be used with a BOD measuring device which is especially adapted for use with volatile substances. The test apparatus contains six test vessels, three of which contain the test substance, basal culture medium, and inoculum, and the three controls, one with basal culture medium and inoculum, a reference control with aniline or a similar reference substance, basal culture medium, and inoculum, and an abiotic degradation control containing the test substance and water. The test is suitable for water-soluble substances, and for insoluble substances if they can be suitably pulverised and dispersed. Volatile substances are measured with the modified dissolved oxygen meter, which uses capillary tubing to connect the agitated test unit to the oxygen generator. The test is only applicable to materials which, at the concentration used in the test, are not inhibitory to the inoculum, and do not reach and react with the CO_2 adsorbent.

The test has two outputs. The first is a determination of the BOD of the test solution as a function of time, over the 28 days of the test. The method gives a continuous record of the oxygen uptake, which will indicate slow increases due to sludge adaptation to the test substance as the sole source of organic carbon, and more rapid increases as the substance is degraded by the adapted sludge. Finally, the BOD will decrease as the test substance is depleted from solution. The percentage biodegradation is determined from the average of the total BOD values determined from the test solutions, corrected by the BOD in the control, relative to the theoretical oxygen demand (ThOD) for the test substance.

The second output, the amount of residual test substance, can be determined by specific analysis of the test substance remaining in the supernatant of the test flasks compared with the amount remaining in the abiotic control. Alternatively, for water-soluble substances the amount of carbon remaining in the test solutions can be determined using a total organic carbon (TOC) analyser.

If a pass level of 70% is reached within 14 days, and the biodegradation phase which follows the sludge adaptation phase lasts for no longer than three days, then the result of passing the MITI II test can be used in risk assessment models to indicate that the substance is considered to show some biodegradation during sewage treatment and in the environment (European Commission, 2003).

The applicability of the inherent biodegradability tests is summarised in Table A5.6. Note that only the SCAS and the Zahn-Wellens test are mentioned as suitable for use under the Detergents Directive.

Table A5.6: Applicability of Ultimate Inherent Biodegradability Tests

Test	**Applicability**	**Recommendation for Test Use**
SCAS: OECD 302A ISO 9887 EC C.12	Organic compounds which are: – water-soluble at the test concentration; – non-volatile, or having a negligible vapour pressure; – not lost by foaming from the test solution; – not significantly adsorbable on glass and activated sludge; and – not inhibitory to the test micro-organisms at the test concentration. *Note: organic carbon content of test substance must be established.*	Test with high biodegradation potential: – especially for compounds not easily degradable; and – for waste water including co-metabolic degradation. Useful method for attempting the pre-adaptation of an inoculum, for use in other tests.
Zahn-Wellens/EMPA: OECD 302B ISO 9888 ECC.9	Organic compounds which are: – water-soluble at the test concentration – non-volatile, or having a negligible vapour pressure; – not lost by foaming from the test solution; and – not inhibitory to test micro-organisms at the test concentration. *Note: organic carbon content of test substance must be established.*	Batch method for the evaluation of elimination and biodegradation of test compounds. Also suitable for waste water.
MITI II: OECD 302C	Only applicable to organic substances which, at the test concentration: – have negligible vapour pressure, unless modified BOD meter used for volatile substances; – are not inhibitory to test micro-organisms; – do not reach and react with the CO_2 adsorbent; – have available an analytical method appropriate for use in the test solution; – have a known empirical formula so that the ThOD may be calculated; *Note: poorly soluble substances may require special measures, e.g. ultrasound dispersion, for dispersal*	Respirometric method for determining biodegradation under relatively stringent inherent test conditions. Suitable for volatile substances. Care in BOD determination needed, due to high inoculum to test substance ratio.

A5.5 Overview of Simulation Tests

A5.5.1 Sewage Treatment (OECD 303A; ISO 11733; EC C.10)

Simulation tests for removal during sewage treatment are based on the standards ISO 11733 and OECD 303A. The tests, initially developed for surfactants, are used if detailed information on removal in waste water treatment plants, such as percentage removal, is required. Such results can be used directly as input into risk assessment models such as EUSES (European Commission, 2003). Because of the relatively high cost and effort of applying these simulation tests, simpler and cheaper screening tests were investigated in parallel. Experience with many surfactants and other chemicals has shown that those which were found to be readily biodegradable also degraded in the simulation tests for removal during sewage treatment. Some of those failing the screening tests passed the inherent biodegradability tests (e.g. OECD 302A and 302B) but only some of this latter group were degraded in these simulation tests, while those chemicals which failed tests for inherent biodegradability did not degrade in these simulation tests (OECD 303A, 2001). Thus the simulation tests described below may indicate removal for substances which have not passed the inherent biodegradability tests, but this removal will be due processes other than biodegradation (e.g. removal due to adsorption or volatilisation).

Simulation tests for removal during sewage treatment are designed to determine both the removal and the primary and/or ultimate biodegradation of water-soluble organic compounds by aerobic micro-organisms in a continuously operated test system simulating the activated sludge process. An easily biodegradable organic medium and the organic test compound are the sources of carbon and energy for the micro-organisms. The purity, water solubility, volatility and adsorption characteristics of the test substance should be known to enable correct interpretation of results to be made. Normally volatile and insoluble substances cannot be tested unless special precautions are taken. The chemical structure, or at least the empirical formula should also be known in order to calculate theoretical values and/or to check measured values of parameters, e.g. ThOD, DOC and COD. Information on the toxicity of the test substance to micro-organisms may be useful for selecting appropriate test concentrations and may be essential for the correct interpretation of low biodegradation values.

The tests use two types of laboratory apparatus designed to simulate an activated sludge sewage treatment plant, and which operate continuously for the period of the test (up to 12 weeks). The Husmann apparatus consists of connected reactor and settler (or clarifier) vessels, with test and control units running in parallel. The aerated reactor contains activated sludge at between 1 and 3 g/l dry solids, which is in the lower to middle portion of the sludge range used in operational sewage treatment facilities. If nitrification is desired, a nitrifying sludge should be chosen. Solution from the reactor is fed into the clarifier at a rate giving a hydraulic retention time of 6 hours, which is appropriate for older activated sludge treatment plants. The treated supernatant is removed from the top portion of the clarifier and analysed for the specific substance or DOC (or, for higher concentrations, COD) remaining. The sludge at the bottom of the clarifier is returned to the reaction vessel. The sludge retention time, of between 6 and 10 days, is achieved by periodic (at least daily) removal of an appropriate amount of sludge from the system. The test solution, an organic medium of synthetic or preferably settled domestic sewage containing the test substance at a concentration normally between 10 and 20 mg/l DOC, with an upper limit of 50 mg/l DOC, is added to the reaction vessel of test unit, while only the organic medium is added to the control unit, at an addition rate chosen to maintain the 6 hour hydraulic retention time of the system. The difference between the effluent concentrations of DOC in the test and control units is assumed to be due to the test substance or its organic metabolites. The percentage removal of the test substance is calculated by comparing the DOC in the test effluent, after subtraction of the DOC in the control effluent, with the initial DOC due to the substance in the influent.

Adsorption of the test substance may normally be distinguished from biodegradation by careful examination of the elimination-time curve. Conformation of adsorption can be obtained by carrying out a suitable (i.e. CO_2 evolution, or oxygen uptake) ready test using an acclimatised inoculum from the unit receiving the test substance, which should degrade the substance in the ready test if biodegradation has been occurring in the simulation test.

The second type of laboratory apparatus, the porous pot, is very useful for investigations which require careful control of the sludge retention time, such as tests investigating biodegradation mechanisms. The porous pot system consists of an inner, porous cylinder with a conical bottom held in a slightly larger vessel of the same shape, but made of an impervious plastic material. The treated organic medium passes through the pores in the inner pot, but the sludge is largely retained. Effluent collects in the annular space between the inner and outer pots, and overflows into the collecting vessel. As no settlement occurs, there is no sludge return needed. A control pot without test substance is run in parallel to the test pot(s). Detection methods, sludge sources, nutrient media and treatment of data are similar to those described above for the Husmann apparatus. Both types of apparatus need good temperature control. The porous pot is generally easier to operate than the Husmann apparatus, but the Husmann apparatus is preferred if sludge samples as well as effluent samples are to be analysed.

Tests using these laboratory scale activated sludge sewage treatment plants may be suitable for some non-surfactant organic substances used in detergent products, especially if these substances are present in the environment at concentrations approaching the concentrations typically found for surfactants, for which the simulation tests were developed. Typical sewage treatment influent concentrations for surfactants used as the major surfactant in a washing powder, for example, might range from 2 mg/l up to approximately 10 mg/l (see, for example, Holt *et al,* 1998), or up to approximately 6 mg/l as DOC. This is within an order of magnitude of the substance concentration used in the simulation tests, with DOC detection, of 10-20 mg/l DOC. However, substances present with an expected environmental concentration lower than 1 mg/l DOC would not be suitable for the simulation test using the DOC detection method. It is advantageous to be able to use DOC detection, as the DOC remaining in the effluent after subtraction of DOC in the control can be attributed to both the parent compound and any remaining metabolites, and thus measures the ultimate biodegradation required for hazard assessment. However, specific substance detection or tests with appropriately radio-labelled substances could be carried out, if desired. The tests would be useful for risk assessment of substances which pass a ready test, in order to be able to use the measured elimination percentages in the risk assessment, rather than lower default values based on a ready test pass. The tests might also be useful for inherently biodegradable substances for the same purpose, especially if the level of ultimate biodegradation in the inherent test is high. The tests might also be useful for substances which are not ultimately biodegradable, if the object of the test is to measure removal, not biodegradation. In this case, it would be necessary to extend the test to the measurement of the substance associated with the activated sludge, which would require either a specific analytical method or an appropriate ^{14}C-labelled substance. In all cases, the substance must not be toxic to the degrading medium at the concentration present in the test.

A5.5.2 Other Simulation Tests

Other simulation tests may be useful to indicate biodegradation of organic substances at environmentally relevant concentrations in environments to which they may be delivered after sewage treatment. Soil is the main environment in which biodegradation may take place by means unavailable in a sewage treatment plant. For example, fungal enzymes are instrumental in the degradation of lignin and cellulose present in plant material. In this example, as the soil in simulation soil tests may not include fungal enzymes, field tests would be necessary to measure degradation in a variety of soil environments. In all cases, analytical techniques would need to be appropriate to the test medium.

Several standardised simulation tests are listed in Table A5.1. If specific needs arise, the use of these tests could be considered for non-surfactant organic substances used in detergent preparations, in the specific environment of interest.

A5.6 Selection of Appropriate Tests

A5.6.1 Selection of Tests

The suitability of specific ready tests for non-surfactant organic substances used in detergents depends on the detection method used in the ready test and on the physical and chemical properties of the test substance. Note that ready tests will not be valid if the substance, at the concentration used in the test, is toxic to the inoculum. Other aspects of note relate to polymers and chelating agents as discussed below.

Most polymers contain a spread, or distribution, of polymeric ‘molecules’ composed of different numbers of monomers, and thus with different molecular weights. This is a consequence of the polymerisation processes used in their synthesis. A ‘typical’ molecular weight distribution for a polymeric substance will usually contain a distribution of polymeric material with a fairly low molecular weight, due to premature termination of the polymerisation reaction, as well as the distribution of higher molecular weights which is intended as the main product of the specific polymerisation process. As the lower molecular weight material is often more easily biodegradable than the higher molecular weight material, these polymers may show evidence of some biodegradability in either inherent or even ready biodegradation tests, due to biodegradation of this lower molecular weight material alone. This should be taken into account when interpreting the results of ready and inherent biodegradation testing of polymeric substances.

Chelating agents may also be problematic. Several non-surfactant organic substances are used in detergent products to sequester calcium and magnesium cations. These can be responsible for toxic effects in ecotoxicity tests, as they effectively remove trace minerals needed to sustain growth. The mineral media used in ecotoxicity and biodegradation tests are not the same, however. Table A5.7 shows the mineral levels that are present in the mineral media recommended for different OECD tests. In addition, low levels of vitamins and supplemental minerals such as Mn, B, Zn, Fe, and Mo are added to the mineral medium in OECD 301E, as the low initial inoculum level will require significant growth in order to remove the test substance.

Table A5.7: Levels of Mineral Nutrients for OECD Tests

Mineral Element	Mineral Concentration (mg/mL) in Nutrient Medium for		
	OECD 301A, 301B, 301E and 301F	OECD 301C (MITI)	OECD 301D (Closed bottle)
P	116	29	11.6
N	1.3	1.3	0.13
Na	86	17.2	8.6
K	122	36.5	12.2
Mg	2.2	6.6	2.2
Ca	9.9	29.7	9.9
Fe	0.05–0.1	0.15	0.05–0.1

In theory, sequestrants are initially present in biodegradation tests at levels which, although capable of complexing significant amounts of Ca^{++} and Mg^{++}, would still leave a significant level of these ions, especially Ca^{++}, remaining. However, iron and trace elements could be complexed to a significant extent. The toxicity control that is optional for all ready tests should easily detect any toxicity due to removal of essential elements, as the degradation of the reference substance would be reduced. This control would be particularly useful for OECD 301E.

Taking account of the properties of the ‘ingredients of potential concern’ (as identified in the main text with the additional points on whether ingredients are likely to be adsorbed to the sludge as presented in Annex 4) and the comments on the suitability of the various tests outlined above enabled Table A5.8 to be constructed. Whilst it is not the intention that this table should provide a definitive guide to the selection of a valid test for a particular ingredient, it does allow for consideration of whether the use of a particular test is likely to provide meaningful results.

Table A5.8: Biodegradation Testing Methods for Ingredients of Potential Concern			
Ingredient of Potential Concern	**Soluble?**	**Adsorbs to sludge?**	**Potential OECD test method and comment (corresponding ISO/EC tests can be derived from Table A5.1)**
Phosphonates	Y	Y	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to sorption)
Polycarboxylates	Y	Y	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to sorption)
EDTA and EDTA tetrasodium salt	Y	N	Suitable: 301D Not suitable: 301A, 301B, 301C, 301E, 301F, 310 (assuming some toxicity to inoculum due to chelating action)
Nitrilotriacetic acid (NTA)	N?	N?	Suitable: 301B, 301C, 301D, 301F (assuming non-toxic to inoculum) Not suitable: 301A, 301E, 310 (due to insolubility) *However, trisodium NTA is soluble and all tests would apply*
Detergent dyes	?	?	Insufficient data to comment
Dye transfer inhibitors (PVP)	Y	Y?	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to (likely) sorption)
FWA-5	Y	Y	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to sorption)
Foam regulators: - n-paraffins	N	Y?	Suitable: 301B, 301C, 301D, 301F (assuming non-toxic to inoculum) Not suitable: 301A, 301E, 310 (due to insolubility and/or sorption)
- PDMS	N	Y	Suitable: 301B, 301C, 301D, 301F (assuming non-toxic to inoculum) Not suitable: 301A, 301E, 310 (due to insolubility and/or sorption)
Formulation aids (PEG - higher MWs)	Y	Y?	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to (likely) sorption)
Anti-redeposition agents (CMC)	Y	Y?	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to (likely) sorption)
Solvents: - 1-decanol	Y	Y?	Suitable: 301B, 301C, 301D, 301F, 310 (assuming non-toxic to inoculum) Not suitable: 301A, 301E (due to (likely) sorption)
- Triethanolamine.	Y	N?	Suitable: 301A, 301B, 301C, 301D, 301E, 301F, 310 (assuming non-toxic to inoculum and minimal sorption)

A5.6.2 A Chemical Requiring Three Tiers of Testing

For most of the chemicals considered in this report, there is little uncertainty as to whether they should be classified as readily biodegradable or not based on test results. However, one borderline example is triethanolamine (or TEA) for which several different types of results are presented in the IUCLID data sheet.

The ready biodegradation test results, with the possible exception of one result which is not well enough described to determine whether a ready or an inherent test has been carried out, confirm that TEA does not biodegrade in a standard stringent ready biodegradability test. However, the inherent test results all indicate substantial ultimate biodegradation. In addition, some tests carried out under ready test conditions but with an adapted inoculum (i.e. an inoculum which has been pre-exposed to TEA and learned to use it as a food source), or tests carried out for more than 28 days, such as the 42 day French AFNOR test, show high levels of biodegradation. However, these test results constitute an inherent test pass, rather than a ready test pass, because one of the stringent conditions of the ready test has been relaxed.

Simulation test results also appear in the IUCLID. These show rapid disappearance of TEA under environmental conditions. For example, radio-labelled TEA rapidly degraded in dilute activated sludge, with the parent compound typically disappearing in 24 hours. Metabolite degradation was also followed in this study. TEA in soil disappeared completely within one day at a low concentration (0.7 ppm), but took 14 days to disappear completely at a high concentration (1000 ppm). Note, however, that these rates are much faster than the 30 day half-life which the TGD (European Commission, 2003) gives as a default value for readily biodegradable compounds. TEA disappearance in several river water and sediment systems was also reported, with complete disappearance taking from 2 to 3 days in water/sediment systems. In river water samples without sediment a lag time of up to two weeks was observed, with complete biodegradation taking up to 35 days for the slowest system studied. However, these times are comparable to the TGD defaults for bulk river water, with half-lives ranging from 5 days at 25°C to 15 days at 12°C (the temperature of the simulation experiments is not given in the IUCLID). Information on the adaptation of the environmental inocula to TEA is not given in the IUCLID entry, but one can expect that adaptation would take place in the sewage treatment plant if significant amounts of TEA were present in the STP influent and in the river downstream of the treatment plant if significant amounts of TEA were present in the effluent.

Thus, although TEA does not fulfil the conditions for ready biodegradability, the simulation test results show that it does degrade rapidly in the environment. It would be expected that such findings would be carried forward to any risk assessment work to provide a realistic estimate of the associated risks to the environment.