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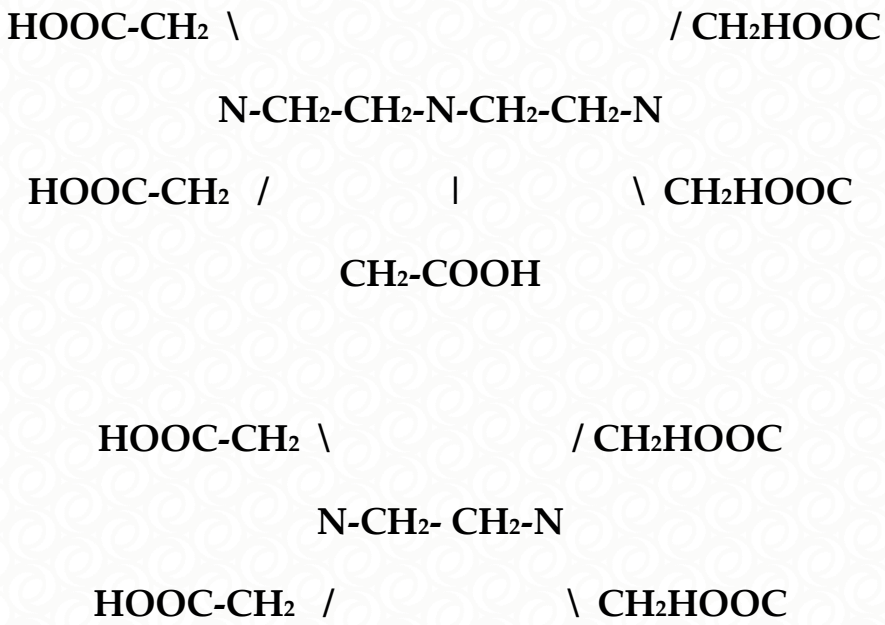
Chelators and eco-labelling of paper products



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This report has been reviewed and approved in accordance with IVL's audited and approved management system.

Preface

This document is a translation of an original report written in Swedish, entitled “Komplexbildare och miljömärkning av pappersprodukter”. Both the Swedish original and the English version can be downloaded from the website of IVL Swedish Environmental Research Institute, www.ivl.se.

The original report was written in 2015. Some dates in this document, regarding e.g. deadlines for response from the industry on the proposed ban of DTPA by the Nordic Swan Ecolabel have therefore already passed.

This document is a translation of the original report. No further work has been performed – neither practical nor on the text. No adjustments of the content taking into account recent development in the issue of use of chelators in the pulp and paper industry have been made.

As the study originally was targeted for a Swedish speaking group, many of the references are in Swedish.

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Summary

This report describes the role and use of and the risks associated with the chelating agents DTPA and EDTA in the production of pulp and paper. The background for the present study is the criteria set by the Nordic Swan Ecolabel for the use of chemicals in the pulp and paper processes, valid since 2014. According to these criteria, the use of certain chemicals classified with specified risk labels is prohibited in the production process in amounts exceeding 0.05 kg/tonne product if the product is to be labeled with the Swan. An exception for DTPA and its salts is given until June 2016. Companies who use DTPA and who need to continue doing so and still be able to label their products with the Swan, must present data supporting the necessity of DTPA in their processes.

In the present report, DTPA and EDTA are described from several aspects: chelating functions, their role in the pulp and paper making process, degradation, effects in aquatic environment and teratogenic effect.

Analyses of DTPA and EDTA in several pulp and paper products are presented. The results show that <2% of added chelating agent is found in the final products. An exception is when DTPA is added at the last stage of the process with the aim of reducing formation of odor and flavor generating substances that can harm what is packaged in the product. In this type of product, all added DTPA is found in the final product.

Earlier performed studies on aqua-toxicity of DTPA and EDTA show no observed effects from the low amounts emitted to recipient from pulp and paper mills in Sweden.

To protect pregnant women working in the pulp and paper mills, there are already regulations in place that include actions such as changing to work tasks not presenting certain risks. Exposure to DTPA and EDTA can easily be included among such risk factors.

Calculations performed on earlier results regarding DTPA and EDTA in recipient water together with results from reproductive toxicity tests show that a volume of 700 L of water in immediate proximity to a mill effluent has to be ingested in order to pose any risk to the unborn child.

Calculations based on DTPA content in paper-based food packaging (paper mug) regarding DTPA intake through hot beverage consumption show that such exposure is by far below levels supposed to present any risks to the unborn child.

No technically feasible alternatives to EDTA and DTPA are available today – despite intense research. Furthermore, these two chelating agents are not completely exchangeable with each other.

The economic consequence of a ban of DTPA above 0.05 kg/tonne in the production process is estimated to be between 5 and 10 billion SEK for the Swedish pulp and paper sector.

Based on the above, the authors recommend that a continued exception for DTPA and its salts is given in the Nordic Ecolabel criteria for use of chemicals in pulp and paper products.

1 Aim and background

The aim of the present study is to describe the importance of and certain risks associated with the commonly used chelators DTPA and EDTA in the production of pulp, paper and board products. The report points at the importance of these substances for modern production processes, their environmental impacts and toxicities. It also describes the environmental and other consequences of a withdrawal or a significant limitation in the use of these chelators in said applications.

The Nordic Swan Ecolabel has set criteria for the use of chemicals for paper and board products that can be labelled with the Nordic Swan Ecolabel (Svanen, 2014). These criteria are listed in the so called Chemical Module document (available in Swedish). In version 2.2, an adjustment regarding criteria K2, the classification of production chemicals, was made.

The criteria regarding production chemicals apply to the manufacturing of pulp and paper as well as conversion. Criteria K2 specifies risk phrases and hazard classes for chemicals which must not be used in the production process in amounts exceeding 0.05 tonnes/kg of final product. According to the Chemical Module, chemicals with such classification are not to be used if the product is to be labelled with the Nordic Swan Ecolabel.

The chelator DTPA has been classified in the CLP Regulation (EG nr 1272/2008) as reproductive toxicant of category 2, H361d, i.e. “Suspected of damaging the unborn child”. In the Dangerous Substance Directive (67/54/EEG), it is classified as R63, i.e. “Possible risk of harm to the unborn child”. DTPA and its salts are to be exempted from this classification until June 2016.

The chelator EDTA has not been classified in the same categories but it has been proposed in the daughter directive (2008/105/EG) of the EU Water Framework Directive that it should be a so called prioritized compound.

The Nordic Swan Ecolabel has investigated the use of DTPA and first came to the conclusion that DTPA can be replaced by EDTA in the production of pulp, paper and board products. As a result of objections to this conclusion, the Nordic Swan Ecolabel decided to allow for the use of DTPA until 2016. However, companies who use DTPA in their production of these goods and want to continue to do so after this date have until this date to provide the Nordic Swan Ecolabel with documentation of economic and environmental reasons supporting such a continued use.

As chelators are used by a majority of pulp and paper manufacturers, the issue of DTPA use is of a general concern to the whole sector, both for mechanical and chemical pulp producers. DTPA and EDTA are definitely not exchangeable in all cases and applications.

2 Properties and functions of DTPA and EDTA

DTPA (Diethylene-triamine-penta-acetic acid), $C_{14}H_{23}N_3O_{10}$ and EDTA (Ethylene-diamine-tetra-acetic acid), $C_{20}H_{16}N_2O_8$, are both synthetically produced organic chelators. They consist of several carboxylic acids bound to one or several nitrogen atoms. They exist as acids in solution or as solid salts.

EDTA and DTPA have both been in wide use by the industry during the last 60 years. They have earlier been more widely used as additives in detergents, soap, water purification, in textile and paint industries, for

production of cosmetics, rubber, pulp and paper and also in the petroleum, gas and food industries. Their use has decreased in recent years but they are still important compounds for the pulp and paper industry.

2.1 The function of DTPA and EDTA

The most important property of chelators, making them so attractive in a wide variety of processes is their ability to form stable, water soluble, complexes with metal ions. Each carboxylic acid in the chelator molecule can bind one ligand. Since these chelators have several carboxylic groups, they can bind different metal ions with different charges. This chelating function prevents the metal ions to form other, undesired complexes or catalyzing undesired chemical reactions. Furthermore, the polar nature of the complexes formed keeps the complexes in solution. The stability of the complex increases with the number of chemical bonds that can be formed (Naturvårdsverket, 2011).

The formation of the metal complex is pH dependent. Different chelators act in different pH intervals and have different optima. DTPA is the chelator with the broadest activity pH span. It also forms complexes of different strength with different metals.

Another important factor in the chelating process is the strength of the bond between the chelator and the metal ion. This factor decides whether a certain complex will be formed in a given mixture of other, competing, anions. This bond strength is expressed as pK-value: the higher the pK, the stronger the complex and thus the higher the probability of the complex to be formed.

Stability constants (pK) for certain complexes of DTPA and EDTA are given in Table 1 below.

Table 1 Stability constants (pK) for DTPA and EDTA metal complexes (Landner, 1998)

	Ca	Mg	Mn	Cd	Cu	Fe(II)	Fe(III)	Hg	Pb	Zn
DTPA	10.7	9.0	15.1	18.9	21.1	16.,5	28.6	26.7	18.8	18.3
EDTA	10.,7	8.7	14.0	16.3	18.6	14.3	25.1	21.,2	18.7	16.,9

The stability of a given complex depends also on the pH of the solution and competing chelating systems; in solid form (e.g. cellulose fiber) and in dissolved form. This is better described using stability constants, see Figure 1 and Figure 2.

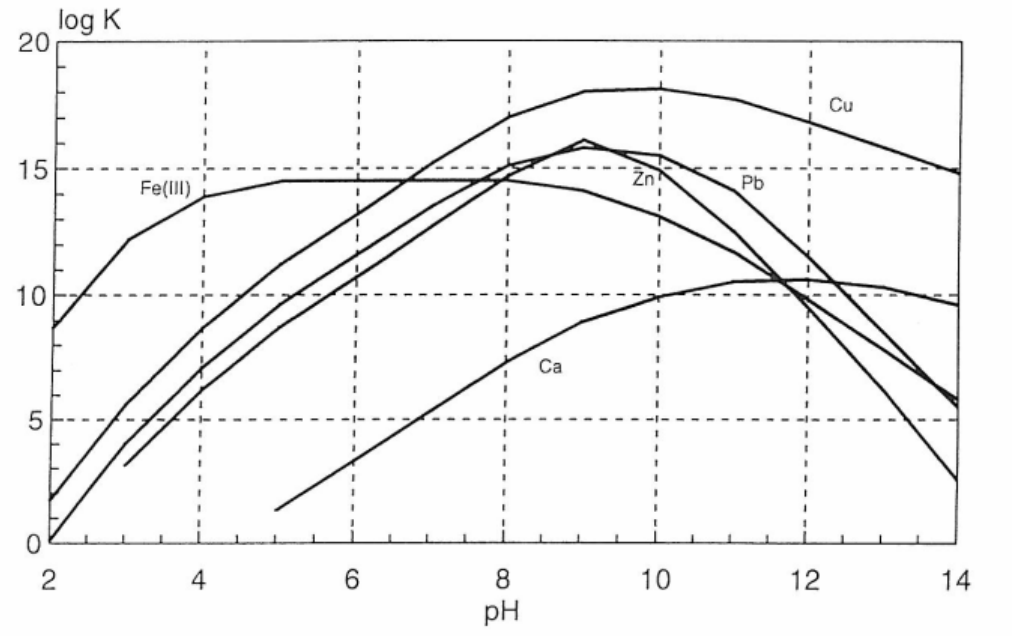

Figure 1 Stability constants for selected metal complexes of DTPA and metals, as a function of pH (Landner, 1998)

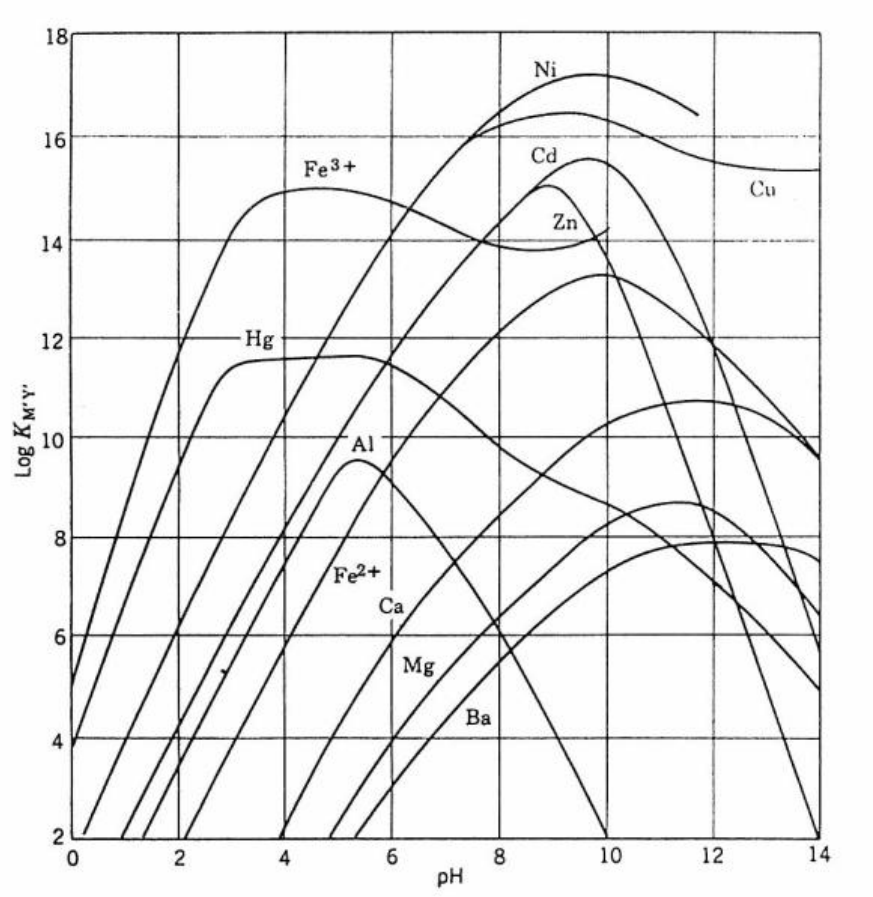

Figure 2 Stability constants for selected metal complexes of EDTA and metals, as a function of pH (Landner, 1998)

As can be seen in the figures above, there is a difference between the maximal values of stability constants and the concentration stability constants. These differences occur since the concentration stability constant require that all metal ions are dissolved and that the chelator is completely ionized.

2.2 The use of DTPA and EDTA and their history

In 1992, the total use of EDTA and DTPA was 2 500 tonnes each. In 2012, the use had increased to 5 500 tonnes of DTPA and 11 000 tonnes of EDTA, according to statistics from the Swedish Chemical Agency. These figures can be compared to the global use of the chelators DTPA, EDTA and NTA (another common chelator) which can be estimated to approximately 200 000 tonnes in 1998.

Chelators (EDTA and DTPA) are since long used by the pulp and paper industry in the peroxide based bleaching process where there is a need to remove metal ions which otherwise will degrade the peroxide. Hydrogen peroxide was, until the end of the 1980s, used only in the mechanical and thermomechanical pulping processes. During the 1990s, hydrogen peroxide bleaching was

developed also for chemical pulp as a part of the process to replace chlorine (Cl_2) bleaching with more environmentally friendly technology. Today, the use of hydrogen peroxide (and therefore also of chelators) is a necessary prerequisite for the production of pulp of both so called ECF (elementary chlorine free, i.e. chemical pulp bleached with ClO_2) and TCF (totally chlorine free, i.e. chemical pulp bleached without any chlorine containing substances) pulp. There are, today, no available alternatives to EDTA or DTPA for modern bleaching technology.

The use of strong chelators has increased in the pulp and paper industry over the recent 30 years (Naturvårdsverket, 2011). This is mostly due to the increased production of TCF pulp but also to the increased quality of newsprint made from TMP (Thermomechanical pulp) and increased production of board.

In 1986, the use of chelators in the Swedish pulp and paper industry was 1000 tonnes of DTPA and 250 tonnes of EDTA. In 1993, the consumption had increased to 1 500 tonnes and 2000 tonnes, respectively (Naturvårdsverket, 2011). In 2013, the consumption was around 1000 tonnes DTPA and 10 500 tonnes of EDTA according to a survey conducted within the frame of this project and the estimation by the project group, based on earlier, unpublished, work.

The dominating diffusion route for DTPA and EDTA to the environment is through water. The diffusion is supposed to be through household and industrial sewage to wastewater treatment plants. The degree of elimination of EDTA and DTPA in the treatment plant depends on the state of the compounds, the pH of the water, water hardness and the content of salts and metal ions. The process of the treatment plant is of course crucial to the elimination and what is not eliminated in the plant will eventually spread to the environment and natural recipients.

3 DTPA and EDTA and their use in production of pulp, paper and board

Today, the Pulp and Paper Industry is the main user of the organic chelators DTPA and EDTA. The role of the chelators is mainly to deactivate manganese(II) ions but also ions of other heavy metals, originating from the wood. These metals would otherwise cause a catalytic oxidation of hydrogen peroxide and ozone, common delignification chemicals used for production of both mechanical and chemical pulp. To achieve this inactivation of metals, the approximately 0.5-2- kg DTPA or EDTA (in acid form) per tonne pulp is added.

Metal ions catalyse the formation of aldehydes in the final board product, which can lead to changes in odour and taste of the packaged product. Addition of chelator to the board product prevents such aldehyde formation.

Until the 1990s, DTPA was prevailing, but nowadays EDTA is used also in CTMP processes and on the board machines. This shift has led to decreased emissions of nitrogen since EDTA contains less nitrogen than DTPA. DTPA is still used after the pulping, in the bleaching and in the distribution of unbleached pulp to the board machines as the alkaline conditions are unsuitable for EDTA, for which a pH <6 is recommended. When DTPA is used after the pulping step, it is also used in the subsequent steps.

In almost all cases where DTPA is used on the "brown side", i.e. before the bleaching, it will be returned and burned in the recovery boiler.

Adding DTPA on the brown side, i.e. after the pulping but before the oxygen delignification, has proven to lead to lower amount of chelator required in the subsequent open bleaching steps. As a consequence of this, the emission of chelator from the process is kept down and more can be incinerated in the boilers.

Both EDTA and DTPA are usually delivered to the plants as sodium salts in aqueous solution. This solution is completely miscible with the different mixtures of fibers, chemicals and water that occur in a pulp and paper mill.

3.1 The role of the chelator and its importance in production of TCF and ECF pulp

Wood contains, beside cellulose, hemicellulose, lignin and extractives, also small amounts of metals. The metal content varies between species and between loci. There is also some formation of metals through corrosion of equipment due to the various process chemicals. In spite of their low amounts, these metals have significant impact on the pulping process.

There are several different delignification and bleaching chemicals used in the production of chemical pulp: For the production of ECF pulp, bleaching is performed with chlorine dioxide. Hydrogen peroxide, H_2O_2, can also be used in an ECF bleaching process. For the production of TCF pulp, the brightness is achieved through the use of hydrogen peroxide or ozone, O_3.

3.1.1 The effect of metals in bleaching with hydrogen peroxide

The metals present in the pulp (mainly manganese but also copper and iron) catalyse unwanted degradation of hydrogen peroxide. If a large share of the peroxide is degraded, only a small fraction of it is available for the actual bleaching reactions, which leads to poor bleaching results and/or larger amounts of chemicals required to achieve acceptable results.

Furthermore, the degradation of the peroxide can generate reactive intermediates such as superoxide anions and hydroxide radicals that react with both lignin and carbo hydrates. This has a positive impact on the solubilisation of lignin but at the same time, hydroxyl radical reacctions lead to cuts in the cellulose chains. Therefore, this degradation of hydrogen peroxide must be kept to a minimum so that pulp with desired strength can be produced.

There are metals that have a positive impact on the bleaching result. Magnesium ion is one example of that as it aids in the stabilization of the hydrogen peroxide. The reason behind this is believed to be that in the alkaline process conditions, the magnesium ions form hydroxide ions that either absorb or otherwise incapacitate the other metal ions that otherwise destroy the peroxide.

When EDTA or DTPA is added to oxygen bleached kraft pulp at pH 5-7, the amount of manganese is decreased from approximately 50 ppm to 1-2 ppm. The contents of magnesium and calcium are not affected to the same extent (Theliander et al., 2001).

There are today no efficient alternatives to EDTA or DTPA for modern bleaching technology. The alternative, degradable, chelators tested are not as potent, resulting in poor brightness of the final pulp or paper. This loss of brightness cannot be compensated for by use of higher amounts of chelators. Furthermore, the alternative chelators are significantly more costly to produce than EDTA and DTPA.

3.1.2 The impact of metals in the formation of aldehydes

Metal ions can also catalyse the formation of aldehydes in products like board (Grahn, 2004). This concerns mainly manganese as it promotes the formation of hexanal in the board product. Hexanal is the result of oxidation of the fatty acids and resins (extractives) in the wood and is an aldehyde that can give rise to unwanted changes in flavour and odour of the food product in the package.

The hexanal content is in fact used as an indicator of how much the package can result in such changes to the food (Umeland, 2001).

Another important function of chelators is thus to eliminate or incapacitate metals that can induce the problems described above.

3.2 The distribution of chelators in pulp and paper processes

Many studies have been performed to investigate the ability of EDTA and DTPA to adsorb to earth, sediments and organic matter such as biosludge. The overall assessment is that such adsorbtion is very low (Grahn, 2004). There are, to our knowledge, no study performed on the adsorbtion of EDTA or DTPA to fibers from chemical or mechanical pulp. However, measurements on the pulping process as a whole and on final pulp and paper products indicate that such adsorbtion of EDTA and DTPA to fibrous material is very low. Chapter 5 of this report presents results that show that this is in fact the case.

The amount of chelator that can be found in the final pulp or paper product is probably mostly what follows the final product from the wet pulp and that is “dried onto” the pulp or paper. The pulp and paper that enters the drying machine has a moisture content of approximately 50% and the amount of chelator in this water will not evaporate but stay in the final, dried, product. See analysis results in Table 2, chapter 5.

4 Elimination of DTPA and EDTA during the production process and in the water treatment plant

Earlier studies on the degradability of chelators and the project group's own experience from previous investigations and test runs (unpublished results) show varying results concerning the degradation of chelators during the process and the external water treatment.

4.1 Elimination during the production process

Test runs and mappings of plants that produce mechanical pulp and use EDTA or DTPA in their peroxide or dithionite bleaching processes show that approximately 20-40% of the amount of added chelator is not retrieved in the waste water. It is believed that the chelator is degraded during the bleaching steps or follows the product.

As mentioned before, if DTPA is added to chemical pulp only before the bleaching but in the oxygen delignification process, approximately 90% of it will follow the process liquor to the evaporation and subsequently burned in the recovery boiler and thereby eliminated.

If EDTA or DTPA is used in the open bleaching process, e.g. in the treatment of the pulp in the Q step, most of it will leave with the process water. It has, however, been shown that by adding approximately 60% of the chelator to the closed part of the bleaching and the rest in the slightly more acidic, open, Q step, the total amount of chelator required is lower.

The amount of chelator leaving the process is probably associated to the reject streams containing fiber bundles, bark residues, etc. that, sometimes after dewatering, leave the process. EDTA and DTPA degradation products have been found in products and waste water from mills (project group's own, unpublished, results), indicating that a degradation of the chelator by e.g. used bleaching chemicals such as oxygen and peroxide during the process cannot be precluded.

The amount of chelator eliminated in this way is, however, limited. Results from numerous measurements indicate that 20-40 % of added chelator "disappear" during the process (ÅF Industry, 2014) – probably through the mechanisms described here.

4.2 Photochemical degradation

Chelators can be eliminated through photochemical oxidation. As EDTA and DTPA form complexes with Fe^{3+} they become photo-chemically labile and are oxidised to smaller compounds by exposure to UV light.

Such photolysis does not result in a complete mineralisation but the metabolites are more susceptible for biological breakdown than the original chelators. It is mostly the Fe(III) complexes of EDTA and DTPA that are subject to photochemical degradation. Also the Mn complexes can photolyze but the resulting metabolites are more stable and are further degraded over a much longer period of time than the iron complexes. Complexes with other metals, such as Mg, Ca, Cu, Cd an Zn are not susceptible to photochemical degradation (Umeland, 2001). The photochemical degradation thus depends on the transformation velocity of photo-stable complexes to labile iron complexes. This process, in turn, is pH dependent. It has been shown that iron complexes are formed more easily at lower pH.

4.3 Biological degradation

The susceptibility of chelators to biological degradation depends on the number of substituents, their nature and the nitrogen compounds, chemical and biochemical properties. Tetra-substituted derivatives of ethylene diamine with two tertiary nitrogen atoms and carboxy-methyl groups, such as EDTA and DTPA, are biologically stable (Pitter and Sykora, 2001). This means that they are quite biologically stable. This said, biological degradation of EDTA in biological water treatment plants has been observed, with a higher degree of degradation when the biological process works under optimal conditions (van Ginkel et al., 1997 and van Ginkel et al., 1999).

The availability of free nitrogen is believed to have a significant role in the degradation of chelators in the biological water treatment plant. Plants run with excess nitrogen have lower degree of chelator reduction than plants run with limited amounts of nitrogen (Grahn, 2004). It is reasonable to assume that in a nitrogen rich environment, the microbial flora degrades the chelators only to a limited extent whereas their 10% nitrogen content will be valuable and subject to biological attack in a nitrogen limited environment.

Ek and Remberger (1999) investigated the biological degradation of EDTA at various pH, sludge load and sludge age. They found that the highest degree of degradation occurred at pH 8.5, low sludge load and high sludge age. The reduction of COD was as high as when pH was at 7. These conditions are also the most favourable for sludge properties. Both sludge volume index and the residual content of suspended solids were lower than at normal conditions at pH7 (Alén & Virtapohja, 1998; van Ginkel & Virtapohja, 1999; Ek, Remberger & Allard, 1999).

4.4 Degradation of chelators in the mills' water treatment plants

EDTA has been shown to be eliminated in the process wastewater treatment plants at favourable conditions.

In the external water treatment plants of the forest industry, such elimination is mostly due to biological breakdown. The water solubility, the low adsorbtion to solid material and the low volatility of the chelators make them unsuitable for elimination through aeration, precipitation or other chemical treatment.

It has been shown possible to reduce the amounts of EDTA with up to 85-90% at optimal operating conditions in a biological treatment plant at steady supply of EDTA. When EDTA was supplied

intermittently, the degree of elimination increases when the supply starts and reaches the above mentioned degree after 24 hours.

DTPA is not degraded in a biological treatment plant. In a conventional active sludge plant, the EDTA-reducing microbes can disappear if the plant runs alternating campaigns with ECF and TCF. This is due to the thus non-stable amounts of chelators reaching the treatment plant.

In a process with biofilm (MBBR; Moving Bed Biofilm Reactor), there is a possibility for the specialized micro-organisms breaking down EDTA to grow on the carriers. Since they grow in the biofilm, they are to a larger extent retained in the system and are thus less affected by a varying supply of chelator resulting from such campaigns. The MBBR therefore gives a more stable degree of elimination.

The sludge age in an MBBR plant is comparable to that obtained in an active sludge plant with low load – but with a better running stability. The high sludge age in these systems allows for a high degree of elimination of EDTA.

Thus, a high and stable degree of elimination of EDTA is obtained when the following parameters apply:

- High sludge age >15-20 days. (Note that this can be achieved with the BAS process, biofilm active sludge, even though the actual sludge age is only approximately 6 days.)

- Sludge age is controlled also taking into account other factors such as sludge loss, low TSS (Total Suspended Solids) and high COD (Chemical Oxygen Demand) reduction. A good sludge quality and good sedimentation properties are desired.

- pH>8

- High oxygen availability (>0.5 g/L in the whole system)

- Stable temperature (30-35°C)

- Stable and continuous supply of EDTA (campaigns with and without bleaching or variations as a consequence of altering between ECF and TCF processes result in lower EDTA elimination on a yearly basis).

Below are a few examples of elimination degrees from various plant processes:

Example 1

Type of pulping process:	TMP and recycled fibers
Type of waste water treatment	Low-load active sludge with LSP (low sludge production) and chemical precipitation
Chelating agent	EDTA
Reduction rate in WWTP	approximately 80%

Example 2

Type of pulping process:	TMP
Type of waste water treatment	Biological pre-treatment on TMP back waters and treatment of total water in a low-load active sludge
Chelating agent	EDTA
Reduction rate in WWTP	approximately 80%

Example 3

Type of pulping process:	Kraft, 30% bleached, 70% unbleached
Type of waste water treatment	Low-load active sludge
Chelating agent	EDTA
Reduction rate in WWTP	>70%

Example 4

Type of pulping process:	Bleached CTMP, 40% at ISO 70% and 60% at ISO 80% brightness
Type of waste water treatment	High-load active sludge + chemical precipitation
Chelating agent	DTPA
Reduction rate in WWTP	Mainly in the pulping process; overall max 30%

Example 5

Type of pulping process:	Kraft, TCF
Type of waste water treatment	BAS on bleach effluents
Chelating agent	EDTA
Reduction rate in WWTP	approximately 70% but varying between 7 and 99%

Example 6

Type of pulping process:	Bleached CTMP
Type of waste water treatment	Multi-step biological treatment
Chelating agent	EDTA
Reduction rate in WWTP	approximately 50% but varying from month to month

A high and stable elimination of EDTA requires steady and constant inflows to the water treatment plant. An illustrating example to this is when a mill runs TCF and ECF in campaigns. In a conventional active sludge plant, the EDTA degrading micro-organisms will disappear if the ECF campaign is too long, resulting in a long period of recovery of this flora when the next TCF campaign starts and therefore also before the EDTA elimination has recovered.

It has also been shown that high concentration of chelators in the drain can cause small flocks of biomaterial, resulting in high TSS emitted to recipient.

In summary, regarding the process elimination of chelating agents:

- Up to 40%, but most commonly 20%, “disappear” during the pulp and paper process. As only a small fraction is retained in the final product (see Table 2, Chapter 5) and other streams, it seems plausible that significant amounts are degraded in the production process.
- The up to 80% of the added EDTA that enters into the biological water treatment plant are eliminated during this process when conditions are favourable. Results of up to 95% elimination of EDTA have been observed in actual cases.

5 Chelators in the final products

For this work, a number of pulp, paper and board products from various mills have been analysed for their contents of EDTA and DTPA.

5.1 Methodology

Samples of pulp and finely cut board were placed in Falcon tubes (polypropylene). 0.02 M phosphate buffer was added and the samples were shaken on a shaker for 30 minutes and then left over night at 4°C.

The samples were pressed with nitrogen through a glass sinter and all buffer solution was collected. The extraction was repeated with deionized water for 30 minutes and the two extracts pooled and centrifuged to remove all particulate matter such as fibers.

A sample of the extract was weighed and filtered through a solid phase C18 column as a cleaning pre-treatment before evaporation of the sample at 95° C (Rudling, 1972). The evaporated residue was esterified with propylene alcohol/HCl at 95° C for 1 hour (Wanker et al., 1992, Nguyen et al., 1994). The reagent was removed by washing with carbonate buffer before the final analysis using GC-NPD (nitrogen-phosphorous detector).

In order to be identified as EDTA and DTPA, the substances retention times must be within +/- 0.1 minute from the references (i.e. standards used for calibration). EDTA and DTPA were further identified using "full scale" GC-MS. Both retention times and MS spectra confirmed the identities of the samples as EDTA and DTPA in the samples.

In one of the samples, a third extraction was performed in order to analyse how effective the first two extractions were. The residual amounts of water in the sample were determined after the extract was pressed from the sample and was found to be 10-12% of added amount. The third extract was found to contain 1.1% of totally extracted EDTA and DTPA, respectively. This means that each extraction could yield a maximum of 90% of the EDTA and DTPA contents and that two such consecutive extractions gave a total yield of 99% leaving 1% in the sample, which is in line with earlier empirical results. The conclusion is that the chelators have very weak or no interaction with the fibers and exist only in the water phase, which is consistent with earlier studies (Allard et al., 1996, Kari et al., 1996 and Ek et al., 1999).

5.2 Results

The samples analysed represent different types of processes, products and stages of the production process. Most of them are final products with a moisture content <10%. Samples D2-D4 are, however, wet pulps. The results of the analyses of EDTA and DTPA contents in the products are shown in Table 2.

Table 2 Analysis of reminiscences of chelators EDTA and DTPA in different types of pulp and board products. The values refer to free acid.

Prov	Dry matter content of sample (%)	Amount of EDTA added in the process (kg/tonne)	Amoount of DTPA added in the process (kg/tonne)	EDTA in sample (µg/kg TS)	DTPA in sample (µg/kg TS)	Share of added chelator found in the sample (%)
A1	95	0	1.5	5.2	0	0.0003
B1	94	3.5	0	240	0	0.007
C1	96	2		350	0	0.2
D1	95		0.05	5000	53000	116
D2	26	6		370	170	1.1
D3	26	6		2000	5600	0.1
D4	32	1.1		46000	0	4.2

The results of this study thus confirm earlier assumptions, described in section 3.2, that if the chelator is added to a fiber suspension with relatively low dry matter content, i.e. a large amount of liquid per amount of fiber, which is the case for the different bleaching steps, a very low share of chelator will be found in the final product. See samples A to C and D3.

Sample D1 is a dry sample, to which the chelator was added to the almost finished product as a flavour and odour preventing agent. Therefore, the amount of chelator that is found in D1 is very high. The value of 116% in the case of sample D1 is probably due to the large amount of chelator added and that the analysis method is not adapted to such high amounts and the uncertainty of the method is high (+/- 20% for EDTA and somewhat higher for DTPA) for such high concentrations.

To summarize, the main conclusion regarding the distribution of chelators in the process systems of the pulp and paper mills are:

- A very small share, often <2%, of added amount of chelator follows the final product (pulp, paper or board) if it is added to any type of suspension.
- A large share, up to 100%, of the chelator is found in the final product if the chelator is added to the almost finished and dried paper or board product.
- Neither EDTA nor DTPA binds to the fiber. Whatever amount of chelator found in the final products is solubilized in the remaining water.

6 Chelating agents in the recipient

Numerous studies have been conducted to clarify to what extent chelators are bound to sediments in the recipients (Svensson & Kaj, 1994; Bolton et al., 1993; Allard et al., 1996). These authors all

came to the conclusion that the studied complexes to a very small extent are adsorbed to the sediments. A few studies of the degradability of chelators have been evaluated by Landner (1998) and can be summarized as follows (translation in italic font of the original report in Swedish):

DTPA and EDTA are, on one side, not easily degraded but, on the other hand, not persistent if the right conditions prevail. It has been clearly shown that EDTA can be degraded (mineralized) both biotically and a-biotically even if a phosphate-stable fraction of the EDTA shows high persistency in the natural aquatic environment. DTPA has not yet been studied in detail to the same extent as EDTA regarding its biodegradation in aquatic environment. It has, however, been indicated that the forms of DTPA encountered in effluents from forest industry are somewhat more easily degradable [at the conditions prevailing in the recipient, remark of the project group] *than the corresponding forms of EDTA and it has also been clearly shown that DTPA exists in – or can be more easily than EDTA transformed into – a photo-labile form that can be degraded photlytically. It is therefore not believed that EDTA, and in particular not DTPA, will accumulate in the environment as a consequence of ongoing emissions of these compunds.*

Strong polar hydrophilic compounds such as DTPA and EDTA cannot be expected to bio-accumulate through the body fat of aquatic organisms (Wolf & Gilbert, 1992). In tests using the North American fish bluegill, the bio-accumulation factor of EDTA was found to be 1, i.e. no accumulation occurs in fish (Bishop & Maki, 1980). There are no corresponding tests with DTPA but the results can be assumed to be equivalent.

During the 1970s and 1080s, there were fears from the authorities that the chelators would solubilize or otherwise mobilize metals from contaminated sediments, so a few initiatives were launched to investigate this. During trials with EDTA and free metals in the concentrations in which they can occur in recipients, no significant increase in mobility of heavy metals was observed (Wolf & Gilbert, 1992). Numerous subsequent studies have, after that, clearly showed that metal mobilization does not occur to any quantitative extent.

In 1995-96, the content of DTPA in both Sörviken, which is a recipient close to the pulp mill Aspa Bruk in Sweden, and in the open parts of the north of lake Vättern, into which the water in Sörviken falls. The concentrations were measured during both winter and summer (Remberger & Svensson, 1997). Close to the bottom and at the proximity of the mill, the concentrations of DTPA were 1.1. mg/L whereas the debouching area had concentrations of 0.07 µg/L. During summer, the DTPA concentrations in the bottom water close to the mill were 0.2 µg/L and no detectable DTPA (<0.002 µg/L) at the surface in the same area. A report from WSP (Sternbeck & Osterås, 2012) reports higher concentrations: 0.6 – 3.9 µg/L close to the mill and 0.43-0.66 µg/L as background concentration.

7 Effect of chelators on water-living organisms

The acute and chronic aquatic toxicity of DTPA and EDTA have been examined numerous times. Jackson & Morgan (1978), as well as other authors, have found that EDTA and other chelators do not pass over the cell membranes of marine algae and invertebrates. This means that these substances do not accumulate in these types of organisms.

A number of studies have shown that the aquatic, acute, toxicity of Fe (III)DTPA/EDTA is low (Lindström, 1994). Van Dam et al. (1995) examined the mortality of *Daphnia carinata* after exposure

to free DTPA in a well-buffered medium at pH 7.63 and total hardness of 20 mg/L CaO_3. The mortality increased from 6 % in the control group to 39 % for a DTPA content of 100 mg/L. This means that LC_{50} was >100 mg/L.

Förlin & Lindeström (1988) exposed juvenile rainbow trout for 23 days in aquariums with flowing water from the river Dalälven to DTPA in the concentrations 0.08; 0.3; 1.0 and 4.1 mg/L. At the end of the trial, it was concluded that the DTPA had not affected neither the liver somatic indices (LSI) of the fishes nor the enzymes alcohol dehydrogenase nor EROD. However, a statistically significant inhibition of the hepatic enzyme cytochrome oxidase after exposure to the highest concentration was detected. DTPA can thus affet the energy turnover in fish liver cells at prolonged exposure to DTPA $\geq$ 4 mg/L (Förlin & Lindeström, 1998). At the trial, the chelator was added in its free form and not as metal complex. In recipients exposed to chelator containing effluents, these are exclusively in the forms of complexes with either iron or manganese, why the observed effect in the study by Förlin & Lindeström probably was, at least partly, due to the fact that a large share of available copper was bound to the DTPA. This would not be the case in natural aquatic systems.

The chelators can thus contribute to the detoxification of heavy metals if they occur in high levels. At the same time, essential metals can, through the same mechanisms, be withdrawn from normal metabolism in exposed organisms and cause deficiency symptoms. The "toxic" effects of chelators that are described in the literature and based on tests conducted at laboratories can probably be attributed to the fact that essential trace elements bind to the chelator, causing trace element deficiencies. This mechanism has been repeatedly proven in laboratory environment but not in field tests as free metal ions do not occur in natural aquatic systems.

Table 3 summarizes some toxicity data for EDTA and DTPA to a number of species, accounted for in Landner (1998) and ECB (2004), respectively.

Table 3 Acute and chronic toxicity of DTPA towards different species. From Landner (1998) and ECB (2004).

Test organism	Substance	Value	Reference
Acute toxicity			
Leopmis macrochirus (fish)	DTPA	LC_{50}, (96 h) = 450 mg/L	Batchelder et al., 1980
Leopmis macrochirus (fish)	EDTA	LC_{50}, (96 h) = 160 mg/ L	Batchelder et al., 1980
Pimephales promelas (fish)	EDTA	LC_{50}, (96 h) = 60 mg/ L	Curtis & Ward, 1980
Daphnia Magna (crustacean)	DTPA	EC_{50} (24 h) = 12 000 mg/ L	Sillanpää & Oikari, 1996; Sorvari & Sillanpää, 1996
Daphnia Magna (crustacean)	EDTA	EC_{50} (24 h) = 610 mg/ L	Sillanpää & Oikari, 1996; Sorvari & Sillanpää, 1996
Microtox	DTPA	EC_{50} (15 min) = 125 000 mg/ L	Sillanpää & Oikari, 1996; Sorvari & Sillanpää, 1996
Microtox	EDTA	EC_{50} (15 min) = 3 170 mg/ L	Sillanpää & Oikari, 1996; Sorvari & Sillanpää, 1996
Chronic toxicity			
Oncorhynchus mykiss (rainbow trout)	DTPA	LOEC (23 d) = 4.1 mg/ L	Förlin & Lindeström, 1988
Oncorhynchus mykiss (rainbow trout)	DTPA	LOEC (4w) = 10 mg/ L	Förlin, 1987
Oncorhynchus mykiss (rainbow trout)	DTPA	LOEC (7 w) = 4 mg/ L	Grotell, 1996
Daphnia magna (crustacean)	EDTA	NOEC = 22 mg/ L	ECB, 2004

Based on the above mentioned trials, threshold level can be determined to 3.2 mg DTPA /L, under which no effects can be expected.

In a toxicological context, it is worth mentioning that strong chelators reduce the bioaccumulation as well as toxicity of heavy metals compared to when these metals occur as free ions. This detoxification effect has been demonstrated at most of the organism levels of the aquatic ecosystem (Landner, 1998).

EDTA has been shown to be able to stimulate algal growth. The mechanism behind this is not fully elucidated but one hypothesis is that a balanced feed of chelator reduces the growth inhibition mediated by high levels of one or more heavy metals. Experimetal studies (Eklund et al., 2002) have shown that growth of algae in waters exposed to effluents from forest industry plants increased with the addition of 4–8 mg/L of EDTA. It must be mentioned that for nitrogen deprived environments, the nitrogen content of EDTA and DTPA can contribute to this increased growth as the nitrogen becomes biologically available.

The toxicity of the chelators EDTA and DTPA has been examined in numerous studies since the 1970s. The results show that on a general level, the toxicity of these compounds to aquatic organisms is low. The concentrations of chelators measured in the primary recipients of pulp and paper mills using these as added chemicals are significantly below the levels where effects have been observed. The chelators do not bio-accumulate and they are degraded over time. There are, thus, no signs that the residual emissions of chelators that occur from the Swedish cellulose industry present any risk for adverse effects on aquatic organisms in the recipients.

8 Basis for classification of DTPA and EDTA

8.1 DTPA

In the REACH system, DTPA is classified as a reproductive toxicant, with the risk term H361 (R63 according to earlier directive, 67/548/EC), see Chapter 1. The classification has been done based on literature data. Three studies are given as basis for the classification:

- A non-identified study from 1994 with a reliability factor of 1, i.e. no restrictions
- Brummet & Mays, 1997, reliability factor of 2, i.e. reliable but with certain restrictions
- Fukuda & Iida, 1983, reliability factor 2

Both DTPA and EDTA bind mainly to divalent metal ions. As described in Chapter 2 different metals are bound with different strengths, which is used in for example treatment of heavy metal poisoning, when Ca-DTPA is administered to the patient. Ca-DTPA will release its calcium ions in favour of forming complexes with the heavy metals and then be secreted. Also other metals in the body will be chelated, such as Zn^{2+}, with which DTPA forms a stronger complex than with Ca^{2+} (see Table 1). Such zinc depletion in a pregnant female can result in the foetus not receiving enough zinc which has shown to cause damage to the unborn offspring. For this reason, in treatment of

pregnant women who need DTPA, the first dose is given as Ca-DTPA and subsequent treatment will be made with Zn-DTPA which is less efficient than Ca-DTPA but shown to be safe for the foetus.

It is this zinc depletion risk that is the reason behind the classification of DTPA as a reproductive toxicant – not DTPA in itself.

There is data to be found in the literature on which amounts of DTPA that can cause these adverse effects on foetuses (Domingo, 1998). Most of the studies examine the effect of injected DTPA and only a few use orally administered DTPA. In the discussions and calculations in this report, data based on trials with injected DTPA have been used as they are – without any recalculation to orally administered doses. A summary of results found in the literature on the adverse effects of DTPA on foetuses is shown in Table 4. Most of the studies on this issue, including the teratogenic effects, are conducted with the aim of evaluating treatment of heavy metal poisoning which means that the aim has not been to determine the highest safe doses but rather the determine the lowest doses at which a detoxification effect can be observed but without adverse side effects. This, in turn, also results in that the results spread more than for NOAEL (No Observed Adverse Efecct Level) studies. Most of the results indicate that doses of 300-400 µmol DTPA/kg body weight and day will have effect on foetuses. There is, however, also studies indicating that 200-300 µmol DTPA/kg body weight will not have any such effects. May's result from 1976 does stand out as they report that there are risks for adverse effects at doses as low as 35 µmol/kg bodyweight and day.

Data indicate that the effects of DTPA are the same in all animal species (Fukuda & Haruzo, 1988), why data obtained on rats and mice have been used as they are for the discussions and calculations in this study.

Table 4 Literature data on reported teratogenic doses of DTPA

Organism	Form of DTPA	Administration	Harmful level	Reference
Mouse	Ca-DTPA	Injection	720 µmol/kg	Fisher et al., 1978
		Injection	360 µmol/kg	Fukuda, 1983
Mouse	Ca-DTPA	Injection	360 µmol/kg is OK	Fischer, 1976
Mouse	Ca-DTPA	Injection	35.6 µmol/kg	Mays, 1976
Rat	Na-DTPA	Oral	254 µmol/kg är OK	Unidentified REACH-reference
Rat	Na-DTPA	Oral	1016 µmol/kg	As above
Mouse	Ca-DTPA	Injection	1440 µmol/kg	Brummett, 1977

8.2 EDTA

Also the REACH consortium for EDTA have searched the literature for data on teratogenicity. The references constituting the basis for classification are:

- ✓ Schardein, J.L. et al, 1981, studies on rat
- ✓ Schardein J.L. et al , 1982, studies on rat
- ✓ Swenerton, H. et al, 1971, studies on rat

- ✓ Kimmel, C.A., 1977, studies on rat

Doses of 3.5 mmol/kg body weight/day were used without any observed adverse effects. This dose is therefore considered as NOEL since no studies using higher doses could be found.

There is, however, expressed in the literature, that EDTA can present risk for foetuses and that it is the same zinc depletion mechanism that cause such effects. In the EU Risk Assessment Document for EDTA (2004), it is stated that no such effects can be seen for doses of 250 mg/kg body weight/day (no reference given) and that at doses of 3 g/kg/day, no offspring survived (no reference given). The reason for these injuries is supposed to be zinc depletion; either due to EDTA chelating the zinc or due to the severe diarrhea in the mothers, caused by the doses of EDTA that coincide with the possibly harmful levels of EDTA.

In the Risk Document, EDTA is not classified as teratogenic, which is also how it is classified in the REACH system, i.e. not teratogenic.

9 Human exposure to DTPA and EDTA from use in pulp and paper industry

The exposure of DTPA and EDTA to humans from pulp and paper products that the project group assessed as relevant for pregnant women are, as mentioned earlier, oral. Such exposure can happen in three ways:

- Exposure during work at the process plant
- Exposure from the external water treatment plants to the recipient
- Exposure through paper products in everyday life. Since it is the oral ingestion that can cause the teratogenic effects, the sources for this exposure can be limited to paper and board being in contact with food, i.e. different types of packaging.

The calculations and discussions in this chapter will be made for DTPA. Since DTPA is harmful in lower doses than EDTA and also is handled much in the same way as EDTA, calculations and discussions made for DTPA will thus constitute a worst case scenario. The calculations and discussions will be based on the highest reported DTPA levels in recipient and product and the lowest doses reported to result in harmful effects on the foetus.

9.1 Exposure in the mill

There are already legislation and rules in place in Sweden related to occupational health and safety as there are also other risks for pregnant women working in pulp and paper mills. This legislation often results in that pregnant women are given work outside the premises where the actual process takes place. It is thus easy to include risk for exposure to chelators as a reason for such measures. Handling of chelators is usually done in closed system which further minimizes the risk of actual exposure.

9.2 Exposure via recipient

For the risk of exposure to harmful doses of chelator through the recipient water, a straight forward calculation on DTPA can be made:

The highest reported DTPA content reported in any recipient outside a pulp and paper mill is 1.4 mg/L (Lindeström & Kind, 1988).

According to the literature, the lowest dose of DTPA reported to give rise to adverse effects is 35.6 µmol/kg and day, which is equivalent to 0.014 g/kg and day (Mw of DTPA = 393.5 g/mol), i.e. in total approximately 1 g for a person with a body weight of 60 kg.

Thus, with a DTPA content of 1.4 mg/L, a volume of 700 L of recipient water in close proximity of a pulp mill is required to reach a harmful dose.

9.3 Exposure via consumer paper products

For the third type of exposure, i.e. through paper and board consumer products, the risk is somewhat more complex to assess. For this reason, the calculations are made using all worst case assumptions. Since both EDTA and DTPA are highly hydrophilic and extremely lipophobic, it is reasonable to assume that paper cups for hot beverages are the paper product that contributes the most to an oral DTPA exposure.

Results presented in Table 2, Chapter 5, show the analyses for DTPA and EDTA perfomed on various pulp and board that can come in contact with food or beverages.

The calculation below is made for coffee served in a paper cup, which is assumed to be a good estimate for the highest risk of oral exposure to DTPA in food. The following assumptions were made:

- The highest level of DTPA content was chosen, i.e. 53 000 µg DTPA/kg product (cup), see Table 2.
- The weight of a standard paper cup was measured to be 8 g.
- All DTPA is assumed to leach into the coffee. (In practice, this is not true since paper cups have liquid barrier coatings.)

This means that a paper cup contains 425 µg DTPA. In order to reach the lowest dose of DTPA reported to give rise to adverse effects, i.e. 35.6 µmol/kg/day, a person weighing 60 kg must consume 1 g DTPA/day. In order to reach that dose, he or she will need approximately 2 350 cups of coffee per day.

In summary, the risks for a pregnant woman being exposed to harmful levels of DTPA through the amounts used in modern Swedish pulp and paper mills can be considered negligible.

10 Technically possible alternatives to DTPA and EDTA and exchangeability of these chelators

There are today no available biologically degradable chelators as effective as EDTA and DTPA. Producers of chelators have for long worked to develop alternatives that are both effective and "environmentally friendly".

Over time, SSVL (Swedish Forest Industries Water and Air Pollution Research Foundation) has conducted several studies evaluating alternatives to EDTA and DTPA for their function in bleaching and other applications, e.g. in a number of projects, e.g. SSVL Project 21, "Chelators in the Forest Industry – Technical significance and environmental aspects" (SSVL, 1979) and SSVL project 52, "Use of chelators in the Forest Industry" (SSVL, 1984).

A number of full scale mill trials have been conducted having the same objective and using alternative chelators. The conclusions in each case have been that none of these "new" chelators can measure up to EDTA or DTPA when it comes to performance and biodegradability.

As an example, the chelator NTA does not bind heavy metals such as manganese to the required extent. Other potential, synthetic and biologically degradable, chelators show similar inadequacy. The consequences of using a weaker and less effective chelator are that the consumption of other bleaching chemicals increase, which in turn has adverse environmental effects, affects the quality of the product in a negative way and substantially increases operational costs of the process.

There have also been attempts performed with alternative technology to remove metal ions from the pulp, such as acid wash but no such trial has had anyway near the performance of conventional treatment with EDTA or DTPA. These alternative technologies also showed to have negative impacts on the quality of the produced pulp, such as tensile strength.

Therefore, it can be stated that there are today no chelators or alternative technologies available that can, for relevant applications, replace EDTA and DTPA.

The reasons for the mills' challenges in replacing DTPA for, e.g., EDTA are to a large extent individual and linked to the proper process, the raw material, the desired quality properties of the product and the technical design of the systems.

Each individual mill normally chooses an application and process solution based on the total environmental impacts from the effluents and their effect on the nearby recipient. In the cases where part of the chelator is added on "the brown side" and thereby can be recirculated and finally incinerated in the boiler, DTPA is often a first choice.

In each individual case, the choice of chelator is preceded by a thorough impact analysis including aspects such as environmental impact, technical applicability and cost efficiency. This means that DTPA is used only when required by the overall benefit.

The amount of added chelator required is individual and depend on factors such as

- Quality and heavy metal content of the wood/chips
- Which cooking method is used and therefore also metals present in the cooking liquors
- Required brightness of final product
- Seasonal variation, affecting maturity of the raw material and impurities of the raw water feed

The conclusion is thus that the amount of chelator used varies between the mills. In order to minimize the use of chelator used and therefore possibly emitted each plant has to be optimized through the following measures:

- Mapping and mass balancing the chelator used
- Optimization of pH, temperatures, retention times and dosages in the process
- Enabling recirculation and incineration of the chelator
- Optimization of external water treatment plant in order to maximally facilitate degradation of the chelator

Again: the choice of suitable chelator is individual and varies from mill to mill.

11 Economic, technical and environmental consequences of a ban of DTPA

As it is the zinc binding property of DTPA and not the substance itself that is the reason for the risk classification as teratogenic, it is reasonable to assume that also potential alternative chelators will have the same function and thereby present similar risks. The discussion below might therefore apply to other chelators than DTPA and prove relevant also for the future alternatives.

11.1 Economic and technical consequences

Chelators are used in the manufacturing of many paper and board products. The amount used is regulated by the Environmental Court for each mill, usually allowing for amounts up to 1-2 kg chelator (calculated as acid) per tonne pulp. The addition of a chelator is a cost for the mill why, for more than 20 years, there has been a constant effort to minimize their use. For most applications, the technical and economic most favourable dosage is in the mentioned interval.

There are today no other chelator than DTPA and EDTA that display equivalent high performance regarding bleaching and prevention of flavour and odour in different types of paper and board used for packaging.

The current proposition from the Nordic Swan Ecolabel in their criteria is to allow a maximum of 0.05 kg of DTPA per tonne pulp in the production process for a paper product labelled with the Nordic Swan. If this proposition would be implemented, no high quality paper or board can be labelled with this label (or possibly even produced) and for all products in which chelators are used, the cost and use of resources would increase.

The Swedish pulp and paper industry is today world leading among the higher quality segments of paper products and a continued focus on these segments is necessary for the future of this industry in Sweden.

If such products cannot be manufactured in Sweden, not only the Swedish pulp and paper industry will be affected. It would also have impact on the industries "downstream" along the value chains, such as printers, packaging industry, tissue producers who will lose the possibility to label their products with the Nordic Swan since they use pulp, paper or board produced in Sweden as their raw material.

To assess the economic consequences of a loss of this crucial product segment is of course very difficult – especially within the frame of this study. However, to give an estimate of the scale of such a loss, one can start with the approximately 9 million tonnes of pulp and paper products manufactured in Sweden in 2014, in which EDTA and/or DTPA were used. The economic value of the export of pulp and paper products from Sweden was 82 billion SEK in 2012. An attempt to make an economic estimation could be to assume that the proposed limit for DTPA affects 10-20 % of the production at the mills that use these chelators today. This would mean a loss of 5-10 billion SEK in income for these mills.

11.2 Environmental consequences

In neither in this nor earlier studies of potential environmental or health impacts of EDTA or DTPA has there been any indication that these chelators could exert any adverse effects through the applications and amounts in which they are used today in the Forest Industry.

Introducing a criterium according to the current suggestion by the Nordic Swan Ecolabel would lead to a stop of the use of DTPA and that the industry, wherever possible, would compensate by adding more bleaching chemicals, preferably peroxides and chlorine dioxide. This would in turn lead to increased use of resources such as peroxides, chlorine dioxide, sodium hydroxide, oxygen, sodium silicate and also energy.

Significant shares of products with high brightness would not be possible to produce at all even with such compensation with peroxide and oxygen.

In the production of TCF, addition of chelator is essential to reach the desired product qualities. A ban of chelators in amounts exceeding 0.05 kg/tonne pulp in the production would result in TCF mills either transferring to ECF process, i.e. introduce chlorine dioxide, or use increased amounts of peroxides which would lead to increased use of resources in the forms of energy and chemicals.

Chelators have important functions also in ECF process in that they keep the required amount of chlorine dioxide down. Without chelators, more chlorione dioxide is required, leading to an increased use of resources – in particular energy – and also to an increased emission of AOX.

The use of EDTA and DTPA contributes somewhat to the emission of nitrogen. This contribution can often partly, but rarely entirely, be compensated by a reduction of required amounts of nutrients in the biological external water treatment plant. This contribution is, however, mostly low.

If EDTA and DTPA were to be banned from the production of pulp and paper, all evidence point to that the overall environmental impact would be negative.

11.3 Concluding remarks

There are, today, no chelators available displaying the same or equivalent good properties as EDTA and DTPA when it comes to efficiency in bleaching processes and preventing flavour and odour in different types of paper and board packaging materials.

If EDTA and DTPA were to be banned from use, it would have severe impact on the important and high quality product segments which is of high importance to the Swedish pulp and paper industry.

An attempt to estimate the economic effect indicates that such a limitation would result in a loss of value of approximately 5-10 billion SEK per year in revenue for the affected companies.

There is no evidence indicating that neither EDTA nor DTPA constitute any environmental or health related risks in the amounts in which they are used today in the forest industry.

Everything points in the direction that if the use of these chelators would stop, the negative environmental impacts would dominate, mostly as a consequence of increased use of resources.

12 Conclusions and recommendations for continued use of chelators in the production of pulp and paper

12.1 Conclusions

There are, neither from earlier studies nor this one, no indications that neither EDTA nor DTPA can be considered as a risk to a person, the unborn child nor the environment in the amounts that are used today with the external water treatment processes installed at the pulp and paper mills.

The human exposure through recipient water or via food and beverage packaging is, according to the analyses and calculations performed on worst case scenarios, by a factor of 1000 lower than those which have shown to be potentially harmful.

EDTA and DTPA are essential to the production of important and high quality pulp and paper products that contribute substantially to the economy of the Swedish forest industry.

A small amount of added EDTA and DTPA are found in the final product from the pulp and paper mill. Both EDTA and DTPA are partly removed/degraded in the process system and in a biological water treatment plant to up to 95%. The chelators are also degraded in the recipient.

The use of EDTA and DTPA is regulated through each mill's permissions from the Environmental Court, most commonly allowing approximately 1-2 kg/tonne pulp, calculated as free acid. The use is also regulated in the now published BAT Conclusions (The Commission's Implementing Decision of September 26th, 2014). In the BAT Conclusions (BAT3) it is stated, regarding the use of chelators, that the mills must strive to limit the use of these and to evaluate alternatives if they can be expected to have better properties and also to monitor use and emissions.

12.2 Recommendations for continued use of chelators in the production of pulp and paper

Considering the assessments presented in this report concerning the environmental and health related risks associated with the use of EDTA and DTPA, the significant economic importance of their use and that their use is regulated through both the permissions granted by the Environmental Courts and the BAT Conclusions, the recommendation is that the exceptions for EDTA and DTPA in the chemical criteria of the Nordic Swan Ecolabel for pulp and paper products described in K2, classification of production chemicals in the chemical module (version 2.2) should be permanent.

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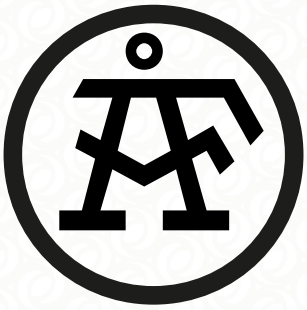

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