HERA

Human & Environmental Risk Assessment on ingredients of
European household cleaning products

February 2005

Soluble Silicates
-draft-

(CAS No.: 1344-09-8, 6834-92-0, 10213-79-3, 13517-24-3, 1312-76-1)

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1 EXECUTIVE SUMMARY

The use of soluble silicates is manifold. Approximately 50 % of produced soluble silicates are further processed to derivatives; the remaining 50 % are used directly with detergents and pulp and paper as the predominate application areas.

Soluble silicates are solid inorganic compounds used in a large variety of household cleaning products. Soluble silicates are widely used in regular and compact laundry detergents (powder, tablets), automatic dishwashing detergents (powder, liquid, gel, tablets), toilet cleaners, and surface cleaners. Thus, soluble silicates provide a number of functions including sequestration of “water hardness” enabling surfactants to function effectively, bleaching, pH buffering and corrosion prevention. In Europe, in the year 2000, the total use of soluble silicates in these applications were estimated to be approximately 188 000 tonnes.

Environmental risk assessment

Due to the physico-chemical properties of soluble silicates a release into the atmosphere during its use as household product is not to be expected. Direct emissions from soluble silicates used as detergents to the terrestrial compartment are considered negligible. Consequently, no environmental risk assessment related to the use of soluble silicates in detergents for the compartments soil and air has been performed.

As ingredients of household cleaning products, soluble silicates present in domestic waste waters are mainly discharged to the aquatic compartment, directly, via waste water treatment plants, via septic tanks, infiltration or other autonomous waste water systems.

As soluble silicates are inorganic substances, biodegradation studies are not applicable. However, the removal of silica in several sewage treatment plants was measured and an average removal of 10 % was determined. In addition, it was found that silica is continuously removed from water by biochemical processes: diatoms, radiolarians, silicoflagellates, and certain sponges serve as a sink for silica by incorporating it into their shells and skeletons as amorphous biogenic silica, frequently referred to as opal ($SiO_2 \cdot nH_2O$).

The primary hazard of commercially used soluble silicates is their moderate-to-strong alkalinity. Soluble silicates with a low molar ratio (SiO_2:M_2O < 2; M = Na or K) like sodium metasilicate and its hydrates with a molar ratio (MR) of 1.0 exhibit a higher alkalinity than the soluble silicates of higher molar ratio. However, most of natural aquatic ecosystems are slightly acid or alkaline and usually their pH values fall within the range of 6 – 9, and due to the high buffer capacity of these ecosystems pH effects of released soluble silicates to aquatic organisms are very unlikely. Consequently, the PNEC derived from artificial laboratory test systems overestimate the effects of soluble silicates to aquatic organisms in realistic natural ecosystems. Therefore, the PNEC was derived from the ubiquitous SiO_2 background concentration in the environment (mean of 7.5 mg SiO_2/L in European rivers). This conservative PNEC of 7.5 mg SiO_2/L was used for the final risk characterisation. Based on the EUSES HERA detergent scenario the PECregional.added and PEClocal.added of SiO_2 were calculated to be 0.536 and 1.75 mg/L, respectively. The resulting PEC/PNEC ratio was found to be 0.07 and 0.23 for the regional and local compartment, respectively. These ratios are far below 1, indicating that there is no risk to aquatic organisms after an input of silicates due to the use in detergent household products.

In addition, the amount of soluble silicates introduced into the environment must be seen in the context of the background level due to geochemical weathering processes of silicate minerals. The overall anthropogenic contribution to this total flux is only about 4 % and even lower for the use of soluble silicates in household detergents indicating that the natural background concentration/fluctuation is of much higher significance for the silica content of aquatic ecosystems than the use of silicates in detergents. For this reason it can be concluded that the SiO_2, which originates from the use of soluble silicates in household cleaning products has a negligible effect on the aquatic ecosystems.

The measured concentrations in the influent of domestic sewage treatment plants as well as the calculated PECs with the EUSES HERA detergent scenario showed that the expected concentrations of silica in sewage treatment plants will not have adverse effects on the functions of the sewage treatment plants, i.e. the degradation or the reduction of organic carbon (COD/BOD), phosphorus and nitrogen.

An eutrophication of surface waters due to nutrient enrichment as a result of the use of silica in household detergent products is not expected. The growth of diatoms and their seasonal fluctuation (blooms) is not influenced significantly by the additional anthropogenic silica input, taking into account that the input of silica from the use of commercial silicates is negligible as compared to geochemical weathering processes. Such effects are dependent on many factors varying spatially and temporally (temperature, light, concentrations of phosphates and of other nutrients, activity of grazer population, etc.).

Based on the available data, the use of soluble silicates in household cleaning products is not expected to have adverse effects on the aquatic ecosystem.

Human Health risk assessment

Consumers can be exposed to silicates from household cleaning products by the routes, skin contact, eye contact, oral ingestion or by inhalation. Using exposure scenarios relevant for consumer uses, the total potential exposure was estimated to be 12.4 µg SiO_2/kg/day.

Experimental data showed that soluble silicates have a low acute toxicity by the oral route. No data are available on dermal toxicity of soluble silicates. However, due to moderate to high water solubility, very low lipophilicity and the molecule size of soluble silicates, the dermal bioavailability for such ionic substances is assumed to be rather limited. Soluble silicates can be irritating to corrosive to the skin and eyes, depending on their molar ratio and concentration. Skin sensitising properties of soluble silicates are highly unlikely. In several repeated dose studies the NOAELs of soluble silicates ranged from 159 mg/kg bw/d (180 days) to 284 mg/kg bw/d (90 days). Because of severe limitations in a poorly conducted 4-generation study, no firm conclusions could be drawn on potential reproductive effects. The noted effects in the daughter generations cannot be evaluated from the limited data given in the study and due to the generally low surveillance rate noted in all groups including the controls. No teratogenic effects were observed in a mouse developmental toxicity study. No genotoxic effects are reported in in vitro or in vivo studies for silicates or very similar compounds like magnesium silicates. Consequently, there is no risk for developmental or reproductive toxicity or genotoxicity. The only critical endpoint for soluble silicates seems to be local irritation or even corrosive properties on skin or eye.

It should be noted that the primary hazard of commercially used soluble silicates is their moderate-to-strong alkalinity causing the observed local irritations/corrosive properties. Soluble silicates with a low molar ratio like sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the soluble silicates of higher molar ratio.

Consumers may be exposed to soluble silicates due to direct skin contact with solutions containing silica. These can be laundry hand washing or the use of products containing soluble silicates for surface and toilet cleaning. However, the estimated concentrations of soluble silicates (0.22 to 2.5 mg/mL) and contact time in these solutions are generally too low to cause local skin irritation.

Accidental acute overexposure to soluble silicates may occur via the oral route, via exposure of the eyes (e.g. due to splashing) or via inhalation. Due to the particle size, formulation and bad taste of the products an accidental overexposure to soluble silicates is rather unlikely to occur. In addition, the available data do not indicate severe adverse effects when accidental overexposure to soluble silicates occurs.

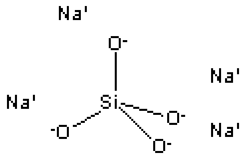
Comparison of the total estimated systemic exposure to silica through the use of detergents (5.1 µg SiO_2/kg/day) to the No Effect Level estimated in animals (159 mg SiO_2/kg/day, 180d) results in a margin of safety of approximately 31 000. Consequently, soluble silicates are of low concern for the consumer use in household detergents.

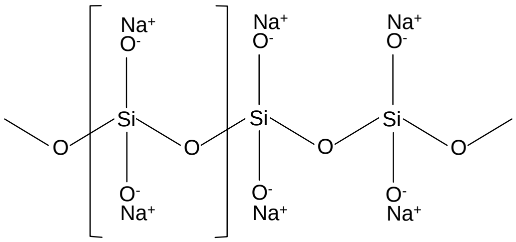
In addition, the average daily intake of silica background exposure via drinking water and diet is in the range of 43 - 107 mg SiO_2/d and therefore, an exposure of silica due the use of household products is negligible in comparison of the average daily intake via drinking water and diet.

2 SUBSTANCE CHARACTERISATION

2.1 CAS No and grouping information

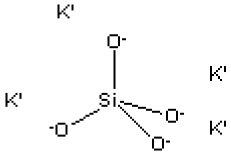
Table 1 Substance identification

Sodium silicates	
Name:	Silicic acid, sodium salt
CAS number:	1344-09-8
EINECS number:	215-687-4
Molecular formula:	$Na_2O \cdot nO_2Si$
Molecular weight:	184.04 (tetrasodium orthosilicate); soluble silicates are generally not distinct stoichiometric chemical substances (with a specific chemical formula and molecular weight), but rather glasses or aqueous solutions of glasses.
Molar ratio:	0.5 for tetrasodium orthosilicate. Commercial sodium silicates have molar ratios between 1.5 and 4.0
Synonyms:	Water glass; soluble glass; silicate of soda; sodium orthosilicate; sodium silicate glass.
Structural formula:	 The formula describes tetrasodium orthosilicate (monomer). For common silicates structural formulae are complex: monomer, linear and planar cyclic oligo-, and three-dimensional polysilicate anions with sodium cations as counterions.

Sodium metasilicates	
Name:	Silicic acid, disodium salt (anhydrous)
CAS number:	6834-92-0
EINECS number:	229-912-9
Molecular formula:	Na_2O_3Si
Molecular weight:	Not applicable, sodium metasilicate is comprised of infinite chains of Na_2SiO_3 units of variable length.
Molar ratio:	1.0
Synonyms:	Sodium metasilicate; disodium monosilicate; silicic acid (H_2SiO_3), disodium salt.
Structural formula:	

Name:	Silicic acid, disodium salt (crystalline pentahydrate)
CAS number:	10213-79-3
EINECS number:	229-912-9
Molecular formula:	$Na_2O_3Si \cdot 5H_2O$
Molecular weight:	Not applicable, see anhydrous metasilicate
Molar ratio:	1.0

Name:	Silicic acid, disodium salt (crystalline nonahydrate)
CAS number:	13517-24-3
EINECS number:	229-912-9
Molecular formula:	$Na_2O_3Si \cdot 9H_2O$
Molecular weight:	Not applicable, see anhydrous metasilicate

Molar ratio:	1.0
Potassium silicates	
Name:	Silicic acid, potassium salt
CAS number:	1312-76-1
EINECS number:	215-199-1
Molecular formula:	$K_2O \cdot nO_2Si$
Molecular weight:	248.44 (tetrapotassium orthosilicate); soluble silicates are generally not distinct stoichiometric chemical substances (with a specific chemical formula and molecular weight), but rather glasses or aqueous solutions of glasses.
Molar ratio:	0.5 for tetrapotassium orthosilicate. Commercial potassium silicates have molar ratios between 1.5 and 5.0
Synonyms:	Potassium silicate; potassium waterglass.
Structural formula:	 The formula describes tetrapotassium orthosilicate (monomer). For common silicates structural formulae are complex: monomer, linear or planar cyclic oligo-, and three-dimensional polysilicate anions with potassium cations as counterions.

2.2 Identity and Chemical structure

2.2.1 General description and characterisation of category members

Soluble silicates are produced by fusing high purity quartz sand (SiO_2) and soluble carbonate (soda, Na_2CO_3 or potash, K_2CO_3) at temperatures of 1300-1500 °C. The resulting product is an amorphous glass that can be dissolved in water to produce silicate solutions. The fusion reaction follows the equation

$$M_2CO_3 + n\ SiO_2 \rightarrow M_2O \cdot nSiO_2 + CO_2 \qquad M = Na \text{ or } K$$

The various products are obtained by varying the mixing ratio of the two components. They are therefore characterised primarily by the weight ratio (WR) or molar ratio (MR), SiO_2 to Na_2O or K_2O, respectively. Soluble silicates are generally not distinct stoichiometric chemical substances (with a specific chemical formula and molecular weight), but rather glasses or aqueous solutions of glasses.

Soluble silicates used in industry are divided into two groups:

Amorphous silicates are solidified as a glass from the melt (solid or lump glasses). These amorphous glasses are essentially anhydrous and differ from ordinary glasses in that they are soluble in water at elevated temperature and pressure leading to silicate solutions (liquid glasses). Both solid and liquid glasses are often referred to as waterglass. Silicate solutions are defined by their density and viscosity, which together with the silica to metal-oxide ratio defines a unique composition for the silicate solution. By evaporation of silicate solutions, normally in the sodium form, fine powders or granules are obtained that have a residual water content of ca. 20 %. Unlike ground lump glass, these materials dissolve readily in water to give silicate solutions.

Crystalline silicates occur exclusively in the sodium form. They are formed by controlled crystallisation of silicate solutions. Commercial products of this type are sodium orthosilicate (MR 0.5) or sodium metasilicate (MR 1.0). Sodium metasilicate can be prepared in anhydrous form, or with water of crystallisation as the penta- or nonahydrate. It is readily soluble in water.

2.2.2 Physico-chemical data

The most important physico-chemical data for the soluble silicates are given in Table 2.

Melting point: Solid crystalline silicates have discrete melting points which depend on the content of crystallisation water: anhydrous sodium metasilicate melts at 1089 °C (Kracek 1930), while sodium penta- and nonahydrate melt at 72 °C and 48 °C, respectively (Baker et al. 1933). Due to their glass nature, solid amorphous silicates do not have discrete melting points but rather flow points. They reversibly solidify and soften within a broad temperature range depending on their molar ratio. Sodium silicate lumps start to soften at 550 - 670 °C and reach the flow point at 730 - 870°C, potassium silicate lumps start to soften at 700 °C and reach the flow point at 900°C (Engler 1974). Aqueous silicate solutions have a melting point only slightly lower than that of water.

Vapour pressure: The vapour pressures that have been measured for three solid sodium silicates are extremely low: 0.0103 hPa at 1175 °C (MR 1.0, metasilicate), 0.0031 hPa at 1165 °C (MR 2.0) and 0.0016 hPa at 1172°C (MR 3.0). This indicates that the respective pressures at ambient temperature will be unmeasurably small. The penta- and nonahydrates of sodium metasilicate contain significant amounts of hydration water (pentahydrate: 43 %; nonahydrate: 57 %). In commercial silicate solutions the water content is still higher and can reach up to 70 %. Therefore, the vapour pressures of the solid hydrates and the solutions are expected to be significantly higher. However, this would be governed by the high water content and reflect rather the vapour pressure of water than that of the respective silicates. The vapour pressures of potassium silicates have not been determined, but they are not expected to vary significantly from those determined for the respective sodium silicates.

Solubility and stability in water: Crystalline silicates like sodium metasilicate are readily soluble in water. For example, the solubilities for anhydrous sodium metasilicate and the pentahydrate are 210 g/l at 20 °C and 610 g/l at 30 °C, respectively. Amorphous silicate glasses are only slightly attacked by water at ambient temperatures. They can be solubilised only at elevated temperature and pressure (ca. 150 °C and $\geq$ 5 bar). The solutions are infinitely dilutable with water. Silicate powders obtained by water evaporation from silicate solutions are readily soluble in water. Amorphous silica which precipitates when silicate solutions are neutralised has a water solubility of 115 mg/L at 25 °C and neutral pH (Morey et al. 1964).

Upon dissolution, the soluble silicates give rise to molecular speciation (Figure 1). Depending on both pH and concentration the respective solutions contain varying proportions of monomeric tetrahedral ions, oligomeric linear or cyclic silicate ions (for example di- or trisilicate ions) and polysilicate ions of three-dimensional structure (Fig. 2) which are in a dynamic equilibrium. The degree of polymerisation of the silicate anions increases with increasing concentration and increasing SiO_2/M_2O ratio of the solution. On the other hand, pH is also strongly influencing the polymerisation-depolymerisation equilibrium: above a pH of 11 - 12 stable solutions of monomeric and polymeric silicate ions exist and no insoluble amorphous silica is present. Acidification below pH 11 - 12 leads to increasing precipitation of amorphous silica which is characterised by the loss of interstitial alkali ions from the three-dimensional network (cf. Fig. 2 c). The soluble content rapidly decreases when the pH is lowered to 9. At pH values below 9 only a low but constant amount remains in solution as monomeric silicate ions.

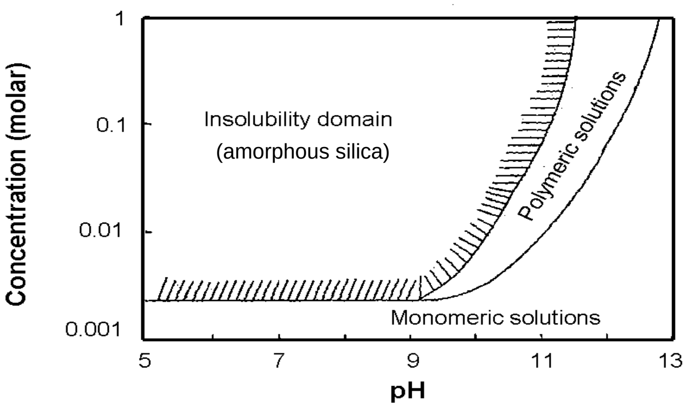


Figure 1 **Soluble silicate speciation. Derived from Schleyer and Blumberg (1982)**

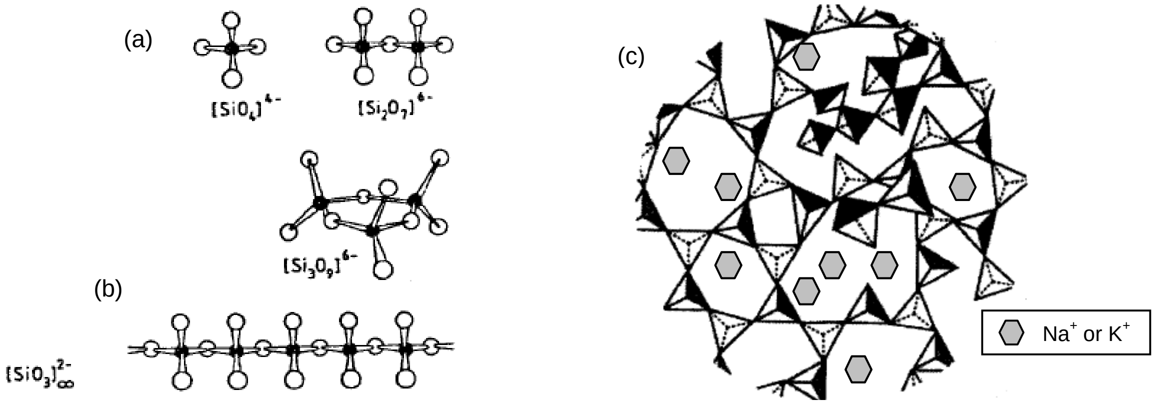


Figure 2 Silicate anion structures (a), metasilicate chain (b) and amorphous silicate glass (c). Derived from Christophliemk (1985) and Fine (1991).

Alkalinity: The pH of silicate solutions is inversely correlated with the silica to alkali ratio (SiO_2:M_2O; M = Na or K) and ranges from pH 10 - 13 (CEES, 2003). Soluble silicates with a low molar ratio (MR < 2) like sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the soluble silicates of higher molar ratio. Dilution reduces the pH, but less than might be expected due to the buffering action of the silicate: the pH of a 1 wt % solution is lowered by only about 1 unit compared to the concentrated solution (Minihan and Lovell 2000).

Octanol solubility and partition coefficient: Soluble silicates are insoluble in n-octanol. The octanol/water partition coefficient is therefore not applicable or relevant (CEES 2003).

Specific gravity: The specific gravity or density of silicate solutions depends on the concentration (solids content), the temperature, and the silica to alkali ratio (SiO_2:M_2O; M = Na or K). At a given solids content the density will increase with decreasing ratio. Commercial silicate solutions have densities ranging from ca. 1.2 – 1.7 g/cm^3 at 20 °C (Falcone 1997; Henkel, undated; Minihan and Lovell 2000).

Viscosity: Among the many factors that influence the viscosity of sodium silicate solutions the molar ratio, concentration, and temperature are the most important. The viscosity increases with rising concentration and ratio. It decreases with rising temperatures. For a given molar ratio there is a limiting concentration above which the solution becomes too viscous for handling (Crosfield undated).

Impurities: Soluble silicates are very pure substances with impurities less than 1 %: The impurities stem from the quartz sand used rather than from the potash or soda components of the fusion mixture. Therefore, impurities of potassium silicates are similar to sodium silicates of comparable molar ratios.

Table 2 Physico-chemical data

Physicochemical Properties					
	Silicic acid				
Test	**sodium salt** **CAS-No. 1344-09-8**	**disodium salt** **CAS-No. 6834-92-0**	**disodium salt, 5-hydrate** **CAS-No. 10213-79-3**	**disodium salt, 9-hydrate** **CAS-No. 13517-24-3**	**potassium salt** **CAS-No. 1312-76-1**
Physical State	Amorphous glass melt (lumps), aqueous solution or spray-dried powder with ca. 20 % of residual water	Crystalline anhydrous powder	Crystalline powder with water of crystallisation	Crystalline powder with water of crystallisation	Amorphous glass melt; aqueous solution or spray-dried powder with ca. 20 % of residual water
Melting Point	730 - 870 °C (flow point); aqueous solutions have a melting point only slightly lower than that of water	1089 °C	72.2 °C	47.9 °C	905 °C (flow point); aqueous solutions have a melting point only slightly lower than that of water
Density	1.26 - 1.71 g/cm^3 (solutions); 700 - 800 kg/m^3 (bulk density;spray-dried powders)	2.61 g/cm^3 1200 kg/m^3 (bulk density)	1.75 g/cm^3 1000 kg/m^3 (bulk density)	1.65 g/cm^3 800 kg/m^3 (bulk density)	1.25 - 1.6 g/cm^3 (solutions); 750 kg/m^3 (bulk density; spray-dried powders)
Vapour Pressure	0.0031 hPa at 1165 °C (solid, MR 2.0). 0.0016 hPa at 1172 °C (solid; MR 3.0) Negligible at ambient temperature.	0.0103 hPa at 1175 °C Negligible at ambient temperature.	Negligible at ambient temperature.	Negligible at ambient temperature.	Negligible at ambient temperature.
Partition Coeff.	The oil/water partition coefficient is not relevant, as soluble silicates are ionisable inorganic compounds.				
Water Solubility	Anhydrous solid dissolves extremely slow at ambient conditions; solutions are infinitely miscible with water; spray-dried solutions readily dissolve in water	210 g/L at 20°C	610 g/L at 30°C	-	Anhydrous solid dissolves extremely slow at ambient conditions; solutions are infinitely miscible with water; spray-dried solutions readily dissolve in water
General Comments on	Determination of quantitative water solubilities is difficult. Aqueous solutions are characterised by a dynamic polymerisation/hydrolysis equilibrium of monomeric SiO_2 (aq.), oligomeric silicate ions and polysilicate ions which is strongly pH-dependant. At pH below 9 silicates				

Physicochemical Properties					
Test	**Silicic acid**				
	sodium salt **CAS-No. 1344-09-8**	**disodium salt** **CAS-No. 6834-92-0**	**disodium salt, 5-hydrate** **CAS-No. 10213-79-3**	**disodium salt, 9-hydrate** **CAS-No. 13517-24-3**	**potassium salt** **CAS-No. 1312-76-1**
Water Solubility	are present as amorphous silica (SiO_2) whose water solubility is 115 mg/L at 25°C. At pH values above 9 undissolved amorphous silica rapidly diminishes, soluble polysilicate ions aggregate and solubility of monomeric silica increases to up to 300 mg/L.				

2.3 Manufacturing route and Production/Volume statistics

The worldwide production volume is approximately 3-4 million metric tons per year (Kuhr 1998). Production of sodium silicates and disodium metasilicates (calculated as SiO_2) in Western Europe was estimated to be 770,000 metric tons in 2000 (Lauriente and Sakuma 2002). The European consumption (including imports and excluding exports) was ca. 890,000 metric tons SiO_2. Potassium silicates were produced at approximately 22,000 metric tons (Lauriente and Sakuma 2002). Sodium silicates are produced at 34 locations in Western Europe; 11 plants are reported for potassium silicates (Briggs 2001).

Typically, solid glasses are produced in tank furnaces or rotary kilns by fusion of quartz sand and soda or potash at temperatures of 1100 - 1300 °C. The vast majority of soluble silicates produced is in the form of sodium silicates. The resulting lump glass is almost exclusively converted to aqueous solutions either at 100 °C and normal pressure or at 150 °C in the autoclave. Concentration or dilution with water and addition of soluble hydroxide is used to adjust the silicate solutions to the desired properties for the wide variety of their applications. The hydrothermal production process is less common: here silicate solutions are directly obtained from fusion of sand and sodium or potassium hydroxide at temperatures around 200 °C and under high autoclave pressure (20 bar). Readily soluble silicate powders are usually produced by spray- or drum-drying processes from solutions (Kuhr 1998).

The uses of soluble metal silicates are manifold and can only be illustrated by selected important examples (Minihan and Lovell 2000; Kuhr 1998):

Raw materials for industrial products (colloidal silica, silica gel, precipitated silica, zeolites, aluminosilicates, magnesium silicates, synthetic clays, ceramics, and catalysts).

Detergents (fabric washing powders, dishwasher detergents, industrial cleansing agents).

Adhesives and binders (paperboard and cardboard, coal dust briquettes, roofing tiles, bricks and ceramics, refractory cements, plasters and mortars, foundry molds and cores, welding rods).

Surface Coatings (TiO_2 production, concrete, paints for masonry and glass surfaces, fire-proof glass and surface coatings, spray-coating in tunnel construction and mining).

Pulp and paper manufacture (deinking and bleaching).

Water Treatment (corrosion protection).

Civil Engineering (soil sealing and stabilisation in drilling, tunnelling, and mining, sealing of landfills, building pits, and coastline stabilisation).

Enhanced Oil Recovery (oil flow improvers).

Textile processing (bleach and dye stabiliser).

Ceramic products (liquefying agent in porcelain slips).

Approximately 50 % of soluble silicates are further processed to derivatives; the remaining 50 % are used directly, with detergents and pulp and paper as the predominant application areas. Table 3 gives a more detailed breakdown of the various applications.

Table 3 Soluble silicate usage by industry application in Western Europe for 2000 (derived from Lauriente and Sakuma 2002)

	Applications	SiO_2 in metric kilotons	% of total usage	
Direct uses:	Detergents, soaps and cleaners	188	21	ca. 40
	Pulp and paper	136	15	
	Soil stabilizers	32	3.5	
	TiO_2	29	3	ca. 10
	Refractories	20	2	
	Ceramic binders	19	2	
	Miscellaneous (incl. water treatment)	15	2	
	Building industry	10	1	
	Welding rods	4	0.5	
Derivatives:	Precipitated silica, silica gel, colloidal silica, detergent zeolites, alumino silicates, potassium silicates, molecular sieves	460	50	50

Based on the data from Lauriente and Sakuma (2002) for Western Europe, the soluble silicates and their emissions into the environment can be broken down into the different application areas. About 50 % of the combined sodium and potassium silicates production (460 ktons SiO_2/year) is further processed to derivatives. Emissions to the environment may take place during production and processing, but no quantitative information is available for those scenarios. Another 10 % of total silicate production (ca. 80 ktons SiO_2/year) go into direct uses which result in inclusion into or onto a matrix (e.g. refractories, TiO_2, ceramic binders, welding rods, building industry). There is potential for release to the aqueous and terrestrial environment during production, processing and use, but no emission data are available. The remaining soluble silicates (ca. 40 % of total silicate production or 360 ktons SiO_2/year) are used in applications with likely emissions into the hydro- and/or geosphere (e.g. detergents, pulp and paper, water/wastewater treatment and soil stabilization). Detergents (188 ktons SiO_2/year) and pulp and paper (136 ktons SiO_2/year) are by far the most important water-relevant applications with soil stabilizers and water/wastewater treatment being of minor relevance for emissions into the hydro- and/or geosphere.

An amount of 188 000 t soluble silicates per year corresponding to 21 % of the total production volume are used in formulations for laundry detergents, dishwashing agents or surface and toilet cleaners. This volume will be used as input in the EUSES HERA detergent scenario for the calculations of the predicted environmental concentrations. For the content of soluble silicates in different product types see chapter 5.1 (Table 8).

3 ENVIRONMENTAL ASSESSMENT

3.1 Environmental Exposure Assessment

General discussion

Due to the physico-chemical properties of soluble silicates (i.e. very low vapour pressure) a release into the atmosphere during use is not to be expected. Direct emissions from soluble silicates used in detergents to the terrestrial compartment are considered negligible in Western Europe, as the used detergents will be completely released into the public waste water system.

Based on the moderate to high water solubility of soluble silicates and based on their use as detergents, the most important environmental compartment is water. Therefore, the following assessment will mainly address this compartment.

Due to a strong dependence on pH and concentration which leads to a dynamic polymerisation-depolymerisation equilibrium with speciation into a variety of mono-, oligo-, and polymeric anions and amorphous silica, calculations on the distribution in various environmental compartments are not feasible. However, the amount of soluble silicates introduced into the environment must be seen in the context of the background input due to geochemical weathering processes of silicate minerals. For example, the total flux of dissolved silicate transported by rivers to the sea in Western Europe is estimated to be 5 Mtons SiO_2/year (van Dokkum et al. 2004). The anthropogenic contribution to this total flux represents 4 % and the input via household detergents is even lower. Therefore, the contribution of the anthropogenic input via household detergents to the occurrence in the various compartments is negligible compared to the background concentrations due to the natural silica flux.

Background concentrations of silica

Dissolved silica from commercial soluble silicates is indistinguishable from natural dissolved silica. Of the elemental composition of the earth's crust, SiO_2 represents about 59 %. Similar percentages are obtained for many sediments and soils (Jackson 1964). Thus, silica is the second most abundant element on earth.

Compounds of silicon and oxygen are ubiquitous in the environment; they are present in inorganic matter, like minerals and soils as well as in organic matter, like plants, animals and man. By weathering of soil, rocks and sediments and by atmospheric deposition, silica is released into surface and ground waters from where it may be removed by precipitation and sedimentation or taken up by living organisms, especially diatoms. Dead sedimenting diatoms also contribute significantly to sediment silica (diatomaceous earth).

Silica is found in all natural waters and the median values in the US were reported to be 17 mg SiO_2/L for ground waters and 14 mg SiO_2/L for streams (Davis 1964). The worldwide mean concentration in rivers is 13 mg SiO_2/L (Edwards and Liss 1973). The surface layers of seawater and lakes are very low in silica (commonly <1 mg/L) apparently due to incorporation of Si into the skeletons of diatoms (Hem, 1985). The biomass, including protozoans, sponges, animals and plants, also contains soluble silica, which is an essential constituent of many biochemical processes. Diatoms and lower plants, such as grasses, are particularly rich in silica (Schleyer and Blumberg 1982). Large deposits of diatoms sedimented over geological times (diatomaceous earth or kieselguhr) are found on every continent.

3.1.1 Environmental fate

Biotic and abiotic degradability

Soluble silicates are inorganic substances and therefore not amenable to biodegradation. In view of their chemical structure and inorganic nature, they are also not photodegradable. The substances have no COD or BOD impact on effluents (CEES 2003). In a simulation test following the OECD confirmatory test procedure, the effect of sodium silicate with a molar ratio of 2.1 (MR) on the biological activity of a model sewage treatment plant was determined (see chapter 4.2.2). Elimination of sodium silicate was only marginal; 90 - 100 % was detected in the effluent (Richterich 1994).

The removal of silica was also measured in several sewage treatment plants and an average removal of 10 % was determined (van Dokkum et al. 2004). The authors assume another 10 % removal from losses through sedimentation and adsorption in the sewer system before the sewage plant.

Once soluble silicates reach the hydrosphere, they are diluted and depolymerize rapidly to give molecular species indistinguishable from natural dissolved silica (H_4SiO_4 or SiO_2 [aq.]) in the hydrosphere.

Silica is continuously removed from water by biochemical processes: diatoms, radiolarians, silicoflagellates, and certain sponges serve as a sink for silica by incorporating it into their shells and skeletons as amorphous biogenic silica, frequently referred to as opal ($SiO_2 \cdot nH_2O$). They can deplete dissolved silica in surface waters to less than 1 mg/L during blooms (Edwards 1973).

3.1.2 EUSES Calculations

Scenario description

The HERA environmental risk assessment of soluble silicates is based on the Technical Guidance Document for new and existing substances (TGD, 2003). At lower tier level it makes use of the EUSES program to calculate the local and regional exposure levels. In the European Union the model EUSES has been used to calculate the PEC of organic compounds. In some cases it can also be used for inorganic compounds to get an idea about the order of magnitude of the PEC. Within HERA the EUSES model has been adapted to develop a specific scenario for detergents (HERA, 2002). The total soluble silicate tonnage produced for and used in detergency was used for the calculation of the PEC of soluble silicates in the environment.

The production and formulation releases, at local level, were not considered because this release scenario falls outside the scope of HERA. The tonnage was calculated as SiO_2 equivalents. For the calculation, the HERA exposure scenario (to assign 7 % of the EU tonnage to the standard EU region, instead of the TGD default 10 %, and to increase the emissions at local level by a factor of 1.5, instead of the TGD default factor of 4) was adopted. These changes introduced by HERA more realistically represent the regional emissions and the local input of substances used in household detergents, as experimentally demonstrated (Fox, 2001).

More details and justification of this modification can be found in chapter 2.6 of the HERA methodology document (HERA, 2002).

Table 4 HERA exposure scenario

Total yearly use in household products (HERA scope), kton	188 000
Continental usage going to standard EU region, %	7
Increase factor for local usage	1.5

Substance data used for the exposure calculations

Data used for the exposure calculations following the TGD guidelines and EUSES model are summarised in Table 5. The data were taken from the OECD SIDS Initial Assessment Report on the Soluble Silicates Category (Anonymous, 2004). Due to the fact that soluble silicates consist of amorphous and crystalline silicates, the worst-case parameters were chosen for the EUSES model calculation.

Table 5 Data for exposure calculations with EUSES

Name of field	Value	Remark
Molecular weight (g/mol)	248.4	highest value derived from potassium salt
Octanol-Water partition coefficient (log Pow)	-1	minimum value in EUSES
Water solubility (mg/L)	1×10^5	maximum value in EUSES
Biodegradation rate constants in STP and surface water	0	-
STP removal %	10	measured removal by van Dokkum et al., 2004
Fraction to air by STP	0	-
Fraction to water by STP	1	-
Fraction to sludge by STP	0	-

3.1.3 PEC Calculations

PEC-calculations using the EUSES model

The relevant values that were obtained using the input parameters outlined above are summarised in Table 6.

Table 6 Relevant PEC values from EUSES calculations

Parameter	Value
Local concentration STP influent	13.5 mg/L
Local concentration in the STP effluent	12.2 mg/L
Local concentration in sludge	0
Local PEC in STP	12.2 mg/L
Local PEC surface water	1.75 mg/L
Regional PEC surface water	0.536 mg/L

PEC Soil/ PEC Sediment

Direct emission of silica to the terrestrial compartment during the use of detergents is considered to be negligible, as the used detergents will completely released into the public waste water system.

PEC STP

In general, the silicate content in raw domestic sewage is derived from the use of silicates in household detergent products. The removal of soluble silicates in several sewage treatment plants was measured and an average removal of 10 % was determined (van Dokkum et al. 2004). No difference between sewage treatment plants with or without P (Phosphorus) removal was found with respect to the silica removal. According to the EUSES calculations a **PEC STP** of **12.2 mg SiO_2/L** was estimated.

PEC STP calculated from monitoring data:

Measurements of silica in the influent and effluent of 6 representative sewage treatment plants in the Netherlands are published (van Dokkum et al. 2004). Three sewage treatment plants were chosen with chemical phosphorus removal facilities and three without P removal. The influent concentrations varied between 5 and 12 mg Si/L (corresponding to 10.8 and 25.9 mg SiO_2/L), with an average of 7.3 mg/L (corresponding to 15.8 mg SiO_2/L). The measured average effluent concentration is comparable to the influent figure but slightly smaller with 6.7 mg Si/L (corresponding to 14.5 mg SiO_2/L). However, waste water contains significant quantities of rainwater and runoff water next to tap water, and therefore, input of silica to waste water can therefore not simply be attributed to the use of soluble silicates in household products. It should be noted that sodium silicates may be added to drinking water as a corrosion inhibitor and sequestering agent. According to European Standard EN 1209, the maximum permissible concentration is 15 mg/L (European Committee for Standardization 1997). In the US public water supply, a median SiO_2 content of 7.1 mg/L was reported (Schleyer and Blumberg 1982). By taking into account the input of silicates to waste water via drinking water of ca. 7 mg SiO_2/L plus the input via rainwater and run off (no data available) the measured release due to the use of household cleaning products (< 7.5 mg SiO_2/L) is far below the result of the EUSES calculation (12.2 mg SiO_2/L) which is based on worst-case assumptions.

3.1.4 Indirect exposure via the environment

Background exposure via the environment can be expected, as compounds of silicon and oxygen are the primary constituents of earth's landmasses, and an important compound in the biomass. Dissolved silica is also a minor but widespread solute in the earth's surface waters. Furthermore, silica compounds are present in plants and animal or human organs, tissues, blood and serum (Carlisle 1986).

3.2 Environmental Effects Assessment

3.2.1 Ecotoxicity – Aquatic: acute test results

The biological properties of soluble silicates are mainly governed by their intrinsic alkalinity. At a given concentration the alkalinity of silicate solutions is inversely correlated with the ratio SiO_2/M_2O: the lower the ratio, the higher the alkalinity. As a result of the low molar ratio, sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the silicates of higher molar ratios. Results of toxicity tests with sodium silicates and metasilicates are summarised in Table 7.

3.2.1.1 Toxicity to fish

Sodium silicates and metasilicates

Two guideline studies with the freshwater Zebra-fish *Danio rerio* were performed. In the first study, sodium metasilicate (MR 1.0) had a 96 h LC_{50} of 210 mg/L at pH 9.1 - 9.8 (Richterich and Mühlberg 2001d). The study was performed following guideline ISO 7346/2, but not according to GLP. The second study, following OECD guideline 203 was performed under GLP: for a sodium silicate solution (MR 3.46, 34.8 wt %) the 96 h LC_{50} was 1108 mg active matter/L. The NOEC values for mortality and swimming behaviour were 348 and 1114 mg active matter/L, respectively (Adema 1988). The pH varied depending on the test substance concentration from 7.9 to 10.3.

In two non-guideline studies offering limited information on the test conditions, the following results were observed. The 96 h LC_{50} of sodium silicate (MR and concentration not indicated) to the freshwater mosquito-fish *Gambusia affinis* was established by Wallen *et al.* (1957) as 2320 mg/l at pH 8.9-10.1. Maruyama et al. (1989) examined the toxicity of a neutralised sodium silicate solution (MR 3.1, concentration not indicated) to rainbow trout (*Oncorhynchus mykiss*). In four replicates the 96 h LC_{50} varied from 260 mg/L (pH 6.8 - 7.5,) to 310 mg/L (pH 7.2 - 8.0). Necrosis of gill filaments as a result of the formation of colloidal silica was observed. However, this is considered a physical rather than toxic effect.

No studies are available for sodium metasilicate, penta- and nonahydrate.

Potassium silicates

A 48-hour toxicity test was performed with freshwater golden orfes (*Leuciscus idus*) according to DIN 38412/15, a German standard method that corresponds to OECD guideline 203. When exposed to 500 mg/L of a potassium silicate solution (MR 3.9 – 4.1, 29.1 wt %) at unknown pH no mortality or signs of toxicity were observed (Richterich and Mühlberg 2001b). The 24 h LC_{50} is therefore >146 mg active matter/L.

3.2.1.2 Toxicity to aquatic invertebrates

Sodium silicates and metasilicates

In a GLP study following EU Guideline 92/69/EWG, which corresponds to OECD guideline 202, part 1, exposure of the freshwater cladoceran *Daphnia magna* to sodium silicate solutions (MR 3.2, 35 wt %) at pH 9 - 11 and a pH adjusted to 7.8 - 8.0 resulted in a 48 h EC_{50} of 1700 mg active matter/L in both cases (Kirch 1997).

Potassium silicates

In a 24-hr toxicity test performed essentially according to OECD guideline 202, part 1, *Daphnia magna* were exposed to 500 mg/L (= 146 mg active matter/L) of a potassium silicate solution (MR 3.9 – 4.1, 29.1 % active matter) at unknown pH: no mortality or signs of toxicity were observed (Richterich and Mühlberg 2001a). The 48 h LC_{50} is therefore >146 mg active matter/L.

No studies are available for sodium metasilicate (anhydrous, penta- and nonahydrate).

3.2.1.3 Toxicity to aquatic plants

Sodium silicates and metasilicates

Sodium silicate (MR 3.0, 34.54 wt %) was tested on the algae *Scenedesmus subspicatus*, in a guideline, GLP study according to German standard method DIN 38412, part 9, which corresponds to OECD guideline 201 (Rieche 1995). The 72 h EC_{50} based on biomass was 207 mg active matter/L at pH 8.2 - 9.5. The EC50 for growth rate was determined as >345.4 mg active matter/L, the highest concentration tested.

No studies are available for sodium metasilicate (anhydrous, penta- and nonahydrate).

Si is the primary constituent of the frustules of diatoms (Vymazal 1995). Silicates may therefore promote the growth of diatoms in cases were other factors like phosphorus or nitrogen are not limiting.

Potassium silicates

No studies are available for potassium silicates.

3.2.2 Toxicity to micro-organisms

Sodium silicates and metasilicates

The toxicity of a sodium silicate solution (MR 3.46, 34.8 wt %) has been determined with a growth inhibition test in compliance with German standards and GLP using the bacterium *Pseudomonas putida* (Hanstveit 1989). The 18 h toxicity threshold (EC_{10}, 10 % inhibition) of a neutralised silicate solution of pH 7.6 - 7.8 was >3480 mg active matter/L, the highest concentration tested, while for the unneutralised solution (pH 7.9 - 10.4) effects were found at concentrations above 348 mg active matter/L. In two GLP guideline studies complying with German standards corresponding to OECD 209, the toxicity to *Pseudomonas putida* was tested in oxygen consumption inhibition tests. Concentrations of a sodium silicate solution (MR 3.0, 34.54 wt %) of up to 3454 mg active matter/L at pH 8.0 - 11.1 and a sodium metasilicate solution of 1000 mg active matter/L at unknown pH did not cause toxic effects (Kirch 1993; Richterich and Mühlberg 2001c).

No significant inhibition of respiration was registered at exposure concentrations up to 100 mg/L sodium metasilicate (MR 1.0, 100 % active matter) for microorganisms from active sludge (Calmels 1994). The 3 h EC_{50} was > 100 mg active matter/L. The pH of the test media at the start and at the end of the study was 6.56 - 8.95 and 5.96 - 8.07, respectively. The study was carried out in compliance with GLP, OECD Guideline 209 and EEC Directive 88/302.

No studies are available for sodium metasilicate, penta- and nonahydrate.

In a simulation test following the OECD confirmatory test procedure, the elimination and influence of spray-dried sodium silicate (MR 2.1) on the biological activity of a model sewage treatment plant was determined. At doses of 25 mg/L, sodium silicate had no adverse effect on the biodegradation of easily degradable nutrients fed simultaneously: DOC (Dissolved Organic Carbon), pH and dry weight of activated sludge was comparable to the untreated control model plants. Visual inspection of colour and settling behaviour of activated sludge also did not reveal any differences between treated and untreated test runs. Elimination of sodium silicate in the model sewage treatment plant was only marginal; 90 - 100 % was detected in the effluent. The study was carried out in compliance with GLP and EU guidelines 82/242/EEC and 82/243/EEC (Richterich 1994).

Potassium silicates

No studies are available for potassium silicates.

Summary of aquatic effects

Table 7 Aquatic toxicity of soluble silicates

Species	Test type	Exposure period	Test substance Ion	MR	Effects [mg/L]	Reference
Fish						
Danio rerio	semistatic	96 h	Na	3.46	LC_{50} = 1108	Adema 1988[1]
Danio rerio	semistatic	96 h	Na	1.0	LC_{50} = 210	Richterich and Mühlberg 2001d[2]
Gambusia affinis	unknown	96 h	Na	1.0	LC_{50} = 2320	Wallen et al. 1957[2]
Oncorhynchus mykiss	unknown	96 h	Na	3.1	LC_{50} = 260 - 310^n	Maruyama et al. 1989[2]
Lepomis macrochirus	unknown	96 h	Na	not known	LC_{50} = 301 - 478	UK Department of the Environment 1991[4]
Leuciscus idus	static	48 h	K	3.9 - 4.1	LC_{50} = >146 (highest tested conc.)	Richterich and Mühlberg 2001b[2]
Invertebrates						
Daphnia magna	static	48 h	Na	3.2	EC_{50} = 1700	Kirch 1997[2]
Daphnia magna	unknown	96 h	Na	not known	EC_{50} = 216 - 247	Dowden and Bennett 1965[4]
Daphnia magna	unknown	100 h	Na	not known	EC_{50} = 247	Freeman and Fowler 1953[4]
Daphnia magna	static	24 h	K	3.9 - 4.1	EC_{50} = >146 (highest tested conc.)	Richterich and Mühlberg 2001a[2]
Amphipoda (probably *Hyallela sp.*)	unknown	96 h	Na	not known	EC_{50} = 160	Dowden and Bennett 1965[4]
Lymnea sp. Eggs	unknown	96 h	Na	Not known	EC_{50} = 632	Dowden and Bennett 1965[4]
Algae						
Scenedesmus subspicatus	static	72 h	Na	3.0	ErC_{50} = >345 (highest tested conc.) EbC_{50} = 207	Rieche 1995[2]
Microorganisms						
Pseudomonas putida	static	18 h	Na	3.46	EC_0 = 348 EC_0 = 3480^n	Hanstveit 1989[1]
Pseudomonas putida	static	30 min	Na	3.0	EC_0 = 3454^n	Kirch 1993[2]
Pseudomonas putida	static	30 min	Na	1.0	EC_0 = 1000	Richterich and Mühlberg 2001c[2]
Activated sludge	static	3 h	Na	1.0	EC_{50} = >100	Calmels 1994[2]

MR Molar ratio
^{n} neutralised test solutions
$^{1,2 \text{ or } 4}$ reliability rating according to Klimisch et al. 1997.

3.2.3 Conclusion of aquatic effects

The primary hazard of commercial soluble silicates is their moderate-to-strong alkalinity, which can be harmful to aquatic life. However, most of natural and artificial aquatic ecosystems (e.g. sewage treatment plants) are slightly acid or alkaline and usually their pH values fall within the range of 6 – 9, and due to the high buffer capacity of these ecosystems pH effects of released soluble silicates to aquatic organisms are very unlikely. Therefore, the effects described in the following are relevant only in artificial laboratory test systems and not in aquatic ecosystems.

All available aquatic ecotoxicity tests with silicates of varying molar ratios and cation species revealed toxicity only at concentrations well above 100 mg/L. As a result of the low molar ratio, sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the silicates of higher molar ratio. With the assumption that the primary hazard of soluble silicates is their alkalinity, it is expected that sodium metasilicates generally exhibit a higher toxicity than silicates of molar ratios 3 - 4. This is confirmed by toxicity data available for fish (LC_{50} = 210 mg/L at MR = 1.0 and up to 1108 mg/L at MR = 3.46). Concerning invertebrate and algae toxicity, studies are available only for silicates of molar ratios 3 - 4 or of unknown ratios. Because of their higher alkalinity, sodium metasilicates also expected to exhibit a higher toxicity towards daphnia and algae. The extent of the potential increase in toxicity is expected to be similar to that observed for fish toxicity in *Danio rerio* (cf. metasilicate versus silicates with a MR of 3.46). Based on this extrapolation toxicity towards algae and daphnia for metasilicates is expected to be in the same range as observed for fish and bacteria, i.e. well above 100 mg/L.

Sodium silicate (MR 2.1) at 25 mg/L did not affect the biological activity of a model sewage treatment plant. This indicates, that no adverse effects of silicates on the micro-organisms in sewage treatment plants are expected. However, a sodium silicate tested in a bacterial toxicity test as such and after neutralization shows a ten-fold lower toxicity in the neutralized state. Whenever the pH is lowered –in laboratory studies or under environmental conditions- two effects of neutralization superimpose each other and in combination result in reduced toxicity: i) reduced alkalinity and ii) reduced bioavailability due to increasing precipitation (amorphous silica) at pH values below 11.

A wide variation regarding toxicity towards fish is observed depending on species and molar ratio of silicates tested. This can be explained by the lower alkalinity of MR 3-4 silicates (see above) and by interspecies variation in sensitivity. Penta- and nonahydrate of sodium metasilicate are not expected to reveal a higher toxicity than anhydrous metasilicates, since they differ from the anhydrous form only by their content of water due to hydration. Thus, this toxicity can be deduced from the anhydrous forms.

The few existing data on potassium silicates fit well into the toxicity pattern of the sodium silicates. Consequently, the aquatic effects for both, potassium and sodium soluble silicates can be assessed from the available data.

3.2.4 PNEC calculations

Aquatic compartment

The primary hazard of commercial soluble silicates is their moderate-to-strong alkalinity, which can be harmful to aquatic life. However, most of natural aquatic ecosystems are slightly acid or alkaline and usually their pH values fall within the range of 6 – 9, and due to the high buffer capacity of these ecosystems pH effects of released soluble silicates to aquatic organisms are very unlikely. Consequently, the PNEC derived from artificial laboratory test systems overestimate the effects of soluble silicates to aquatic organisms in ecosystems. Therefore, the PNEC was derived from the ubiquitous SiO_2 background concentration in the environment. The median values in the US were reported to be 17 mg SiO_2/L for ground waters and 14 mg SiO_2/L for streams (Davis 1964). The world-wide mean concentration in rivers is 13 mg SiO_2/L (Edwards and Liss 1973) and in Europe is 7.5 mg SiO_2/L (Jorgensen et al. 1991). Therefore, the conservative PNEC for aquatic organisms is 7.5 mg SiO_2/L and was used for the final risk characterisation.

PNEC STP (sewage treatment plant)

In contrast to the PNEC for surface waters which is determined by the most sensitive species, for STP it is important to maintain the function, i.e. the degradation or the reduction of organic carbon (COD/BOD), phosphorous and nitrogen. Therefore the most important value for STP is the concentration of a substance which does not damage the function of the STP.

According to the TGD, the PNEC of the STP is the No Observed Effect Concentration (NOEC), determined from a chronic test with bacteria. The NOEC obtained with *Pseudomonas putida in a* growth inhibition test was 348 mg Na silicates/L resulting in a PNEC = 254 mg SiO_2/L.

On the other hand, there was no influence of sodium silicates on either the biocenosis or the functional performance of a model STP up to at least 25 mg sodium silicates/L (corresponding to 18.2 mg SiO_2/L). An assessment factor of 1 is appropriate as the figure reflects the situation in the STP itself. Therefore, a PNEC of the STP was calculated to be 18.2 mg SiO_2/L. This value will be used in the risk assessment.

3.3 Environmental Risk Characterisation

3.3.1 Aquatic compartment

The amount of soluble silicates which is used in the EU in household cleaning products was estimated to be 188,000 tonnes per year. Based on the EUSES HERA detergent scenario the PECregional.added and PEClocal.added of SiO_2 were calculated to be 0.536 and 1.75 mg/L, respectively. A conservative PNEC of 7.5 mg/L was derived (mean SiO_2 concentration in European rivers). The resulting PEC/PNEC ratio was found to be 0.07 and 0.23, respectively. These ratios are far below 1, indicating that the use of silicates in detergent household products poses no risk to aquatic organisms.

In addition, the amount of soluble silicates introduced into the environment must be seen in the context of the background level due to geochemical weathering processes of silicate minerals. The total anthropogenic contribution to this total flux is only 4 % and even lower for the use of household detergents (Dokkum 2004). According to the requirements of the HERA guidance

document (2002), further considerations regarding the environmental risk assessment are not necessary if the detergent-based contribution of the chemical of interest to the environmental background concentration is insignificant (< 10 % of total concentration).
Furthermore, since only a small proportion of the total amount of anthropogenic silicates is used in detergent household products, other anthropogenic releases and the natural background concentration/fluctuation are of much higher relevance for silica content of aquatic ecosystems than the use of silicates in detergents. For this reason it can be concluded that the SiO_2, which originates from the use of soluble silicates in household cleaning products has a negligible effect on aquatic ecosystems.

3.3.2 Eutrophication of the aquatic compartment

Silica is continuously removed from water by biochemical processes: diatoms, radiolarians, silicoflagellates, and certain sponges serve as a sink for silica by incorporating it into their shells and skeletons as amorphous biogenic silica, frequently referred to as opal ($SiO_2 \cdot nH_2O$). They can deplete dissolved silica in surface waters to less than 1 mg/L during blooms (Edwards 1973).

It is not expected that the growth of diatoms and their seasonal fluctuation (blooms) is significantly influenced by the additional anthropogenic silica input, taking into account that the input of silica from the use of commercial silicates is negligible as compared to geochemical weathering processes. The possible effects of anthropogenic silica on diatomaceous growth are discussed in detail by van Dokkum et al. (2004). They predict i) an extension of the spring (and fall) blooms of diatoms (which often ends when the dissolved silicate pool is depleted) and (ii) a possible reduction in summer green or bluegreen algae blooms (because a larger amount of phosphorus is used up in the spring bloom). This in turn could lead to (iii) a shift in biomass production from summer to spring and fall, and, possibly, (iv) an overall increase of phytoplankton biomass over the year (when the increase in summer and fall bloom is larger than the decrease in summer density). However, these speculations are not corroborated by experimental evidence.

3.3.3 Sewage treatment plant

With the EUSES model, the PEC in sewage treatment plant effluent was calculated to be 12.2 mg SiO_2/L. In the effluent of 6 representative sewage treatment plants located in the Netherlands the average concentration was determined to be 6.7 mg Si/L (corresponding to 14.5 mg SiO_2/L). The most conservative PNEC was 25 mg sodium silicates/L (corresponding to 18.2 mg SiO_2/L). The resulting PEC/PNEC ratio was found to be 0.67 and 0.80 based on the PEC calculated with EUSES and the monitoring PEC, respectively. These ratios are below 1 and indicate that there is no risk for the function of a STP after an input of silicates due to the use in detergent household products.

3.4 Discussion and conclusions

The most important applications with respect to the emissions of silicates into the hydro- and/or geosphere are detergents, pulp and paper production, (waste-) water treatment and soil stabilisation. Detergents (188 ktons SiO_2/year) and pulp and paper production (136 ktons SiO_2/year) together represent about 90 % of the soluble silicates used in these application areas, relevant for emissions into the hydro- and/or geosphere.

Emissions of soluble silicates into the atmosphere and to the terrestrial compartment during its use are not to be expected and therefore, the environmental risk assessment can be focussed on the aquatic compartment.

The primary hazard of commercially used soluble silicates is their moderate-to-strong alkalinity. Soluble silicates with a low molar ratio, like sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the soluble silicates of higher molar ratio. However, most of natural aquatic ecosystems are slightly acid or alkaline and usually their pH values fall within the range of 6 – 9, and due to the high buffer capacity of these ecosystems pH effects of released soluble silicates to aquatic organisms are very unlikely. Consequently, the PNEC derived from artificial laboratory test systems overestimate the effects of soluble silicates to aquatic organisms in realistic natural ecosystems. Therefore, the PNEC was derived from the always present SiO_2 background concentration in the environment. The mean concentration in European rivers is 7.5 mg SiO_2/L (Edwards and Liss 1973). This conservative PNEC for aquatic organisms of 7.5 mg SiO_2/L was used for the risk characterisation. Based on the EUSES HERA detergent scenario the PECregional.added and PEClocal.added of SiO_2 were calculated to be 0.536 and 1.75 mg/L, respectively. The resulting PEC/PNEC ratio was found to be 0.07 and 0.23 for the regional and local compartment, respectively. These ratios are far below 1, indicating that input of silicates through the use in detergent household products poses no risk to aquatic organisms.

In addition, the amount of soluble silicates introduced into the environment must be seen in the context of the background level due to geochemical weathering processes of silicate minerals. The total anthropogenic contribution to this total flux is only 4 % and even lower for the use of household detergents indicating that the natural background concentration/fluctuation is of much higher relevance for silica content of aquatic ecosystems than the use of silicates in detergents. For this reason it can be concluded that SiO_2 originating from the use of soluble silicates in household cleaning products has a negligible effect on the aquatic ecosystems.

The measured concentrations in the influent of domestic sewage treatment plants as well as the calculated PECs with the EUSES HERA detergent scenario showed that the expected concentrations of silica in sewage treatments plants will not have adverse effects on the functions of sewage treatment plants, i.e. the degradation or the reduction of organic carbon (COD/BOD), phosphorous and nitrogen.

A eutrophication of surface waters due to nutrient enrichment as a result of the use of silicate in household detergent products is not expected. The growth of diatoms and their seasonal fluctuation (blooms) is not influenced significantly by the additional anthropogenic silica input, taking into account that the input of silica from the use of commercial silicates is negligible as compared to geochemical weathering processes. Such effects are dependent on many factors varying spatially and temporally (temperature, light, concentrations of phosphates and of other nutrients, activity of grazer population, etc.).

Based on the available data, the use of soluble silicates in household cleaning products is not expected to have adverse effects on the aquatic ecosystem.

4 HUMAN HEALTH ASSESSMENT

In line with the objectives of the HERA initiative, this human health assessment focuses on the use of soluble silicates as an ingredient in household cleaning products. This report covers only exposures resulting from its use in household products.

Exposure to silicate solutions means exposure to silica in the form of its various silicate anions on the one hand and alkalinity on the other hand. Both distribution of the various silicate anion species and alkalinity depend on the silica to alkali ratio and the concentration of a given solution. It is not possible to distinguish if the observed toxicity of a silicate solution is resulting from silicate itself, the alkalinity or a combination of both. However, the observed toxicological symptoms are indicative of effects due to high alkalinity. Toxicity tests executed with the dissolved pentahydrate or nonahydrate forms of the disodium salt of silicic acid (CAS no. 10213-79-3 and 13517-24-3, respectively) are directly applicable to the anhydrous form (CAS no. 6834-92-0) and vice versa, as they all have the same molar ratio. Furthermore, results obtained with sodium silicate can be extrapolated to potassium silicates of the same molar ratio as the nature of the soluble ion has no effect on the biological properties (Schleyer and Blumberg 1982; Falcone 1997; Kuhr 1998).

4.1 Consumer Exposure

Consumer exposure may occur primarily by contact with laundry or automatic dishwashing detergents that contain soluble silicates in maximum concentrations of ca. 25 % or ca. 45 %, respectively. Short-term exposure to dust may occur by the use of products in powder form only, other application forms, like tablets or liquids are of no concern with respect to inhalative exposure. Generally, the average particle size in powder detergents is far in excess of respirability, since the silicates in powder form used in consumer products are sieved to retain only non-respirable particles. In addition consumer detergents are specifically formulated to form non-dusting powders: in a process called agglomeration the various dry ingredients are combined into single granular particles through the binding power of liquid silicate leading to particle sizes from 230 to 1500 microns or higher (PQ Corp., undated). Alternatively, they are provided in the form of tablets sealed by individual package allowing only limited short-term exposure. Consequently, an inhalation of silicates via detergent household products is very unlikely to occur.

The silicate content in the different products has been provided by AISE, 2004 and is summarised in Table 8.

The calculated exposure concentrations expressed in soluble silicates/kg bw/day were transferred to SiO_2/kg bw/day. In household cleaning products, soluble silicates with molar ratios ranging from 1 to 3.2 are used, with the majority belonging to the higher molar ratios of 2 to 3.2 (except automatic dischwashing agents where MR 1 is used). In order to cover all soluble silicates used in household detergents the transformation was based on soluble silicates with a MR of 1 as a worst case assumption.

For this transformation, the molecular weight ratio between silica and sodium silicate of molar ratio 1 was taken into account: SiO_2 has a molecular weight of 60.08 and Na_2O x SiO_2 has a molecular weight of 122.05 resulting in a conversion factor of 0.5. The formula below was used for the transformation:

Calculated silicate concentration x 0.5 = **SiO_2 concentration**

Table 8 Soluble silicates content in different detergent products

Product	Typical range (%)	Maximum (%)
LAUNDRY REGULAR powder	0.12 - 4	15
LAUNDRY COMPACT		
powder	0.2 – 4.5	7
tablet	2 - 10	25
Laundry additive		
powder bleach tabs	0.3 – 7	15
liquid bleach	0 – 0.12	1
Machine dishwashing		
Powder	2.9 – 20	45
liquid & gel	18 – 23	25
tablet	1.9 – 4.4	8.7
Surface cleaners		
Liquid	0.06 – 1	1
Concentrate	0.92	0.92
Powder	0.07	0.07
Gel	0.4	0.4
Spray	0.2 – 0.7	0.7
Toilet cleaners		
Liquid	0.03	0.03

4.1.1 Consumer exposure via skin contact

4.1.1.1 Laundry handwashing

Consumers may be exposed to soluble silicates via solutions if machine-laundering detergents are used for handwashing or by using surface and toilet cleaners containing soluble silicates.

AISE, 2002 has issued an overview of habits and practices for consumer products in Western Europe that will be used to calculate the possible consumer exposure.

The highest concentration of laundry detergent used in the handwashing solution is approximately 1 % (10 g/L), a typical amount is 5 g/L. For the exposure calculations the maximum concentrations in the different types of products are used. The highest concentration of soluble silicates in the laundry detergent is 25 % (tablets). The resulting maximum concentration of soluble silicates is 2.5 g/L. As those products are used alternatively, no cumulative exposure is calculated.

Worst case estimates for the hand-washing scenario were:

- Contact time is 10 minutes (AISE, 2002)
- Frequency of tasks per week typically 4 (AISE, 2002). In the same document a maximum of 10 tasks per week is mentioned. The latter scenario is more related to machine washing and seems to represent an extreme worst case assumption hardly being applicable to the hand-washing scenario.
- Direct contact of hands and forearms into the wash water solution results in an exposed skin surface of maximal 1980 cm^2 (TGD, 2003).

The amount of silicates absorbed via the skin is calculated from the silicate concentration applied, surface area of hands exposed, film thickness, and fraction absorbed using the exposure model of the HERA guidance document (HERA, 2002) by using the following assumptions:

- A film thickness of 100 µm (0.1 mm or 0.01 cm) on the hands (Vermeire et al., 1993; TGD, 2003);
- A percutaneous absorption of 1 % within 24 hour exposure time because ionic substances are considered to be less easily absorbed through the skin than non-ionic compounds (Schaefer and Redelmeier, 1996);

Using the equations of the HERA guidance document (2002) the following exposure can be derived:

$C_{\text{soluble Silicates}}$ = maximum product concentration, in mg/cm^3:	2.5 mg/mL = 2.5 mg/cm^3
T_{der} = the thickness of product layer in contact with skin, in cm:	100 µm = 0.01 cm
S_{der} = surface area of exposed hands, in cm^2:	1980 cm^2
F = % weight fraction absorbed via skin in a 24 hour period :	1 % = 0.01

$$EXP_{sys} = C_{\text{soluble Silicates}} \times T_{der} \times S_{der} \times F$$

EXP_{sys} = 2.5 mg/mL (mg/cm^3) x 0.01 cm x 1980 cm^2 x 0.01 = 0.5 mg soluble Silicates absorbed in 24 hours

Assuming 10 min contact time per task and a very conservative maximum task frequency of 10 washes per week (AISE, 2002) the total daily contact time adds to ca. 14 min. Assuming such very conservative daily duration of exposure the amount of absorbed silicates per day can be calculated as [(0.5 mg/day) x (14/60 hr) x (1/24 day/hr)] = 0.005 mg. Assuming a body weight of 60 kg, the resulting estimated systemic dose is:

$EXP_{sys\ (\text{direct skin contact})}$ = **0.08 µg soluble Silicates /kg bw/day (= 0.04 µg SiO_2/kg bw/day)**

A more realistic worst case estimate is based on the typical use frequency of 4 times per week for 10 min. This would result in an exposure of (0.5 mg/day) x (4/7) x (10/60) x (1/24)= 0.002 mg of Soluble Silicates /day and for a 60 kg individual of 3.3 x 10^{-5} mg/kg bw/day, which can be regarded as negligible.

4.1.1.2 Contact from pre-treatment of clothes with products containing soluble silicates

Skin contact can occur during spot-treatment with a detergent paste (60 % paste, or 600 mg powder/mL), liquid, gel, or liquid bleach used undiluted (AISE, 2002). Tablets are not used for spot-treatment.

The highest concentration of soluble silicates in powder laundry detergents (regular) and powder bleach (undiluted) is 15 % (150 mg/kg) and for liquid bleach 1 % (10 mg/mL).
In case liquid bleach is used undiluted as laundry pre-treatment, the resulting estimated hand exposure is 10 mg/mL. The highest concentration of soluble silicates in the hand washing paste prepared from powder at approximately 60 % (AISE, 2002) is approximately 90 mg/mL.
Since the hand exposure by using powder is higher than using liquid bleach and powder is used more frequently than liquids or tablets (21 tasks per week for powder, and 10 tasks a week for liquid or tablets) (AISE, 2002) the use of powder detergents is taken as worst case scenario in the following calculations.
The amount of soluble silicates absorbed via the skin is calculated from the silicate concentration applied, surface area of hands exposed, film thickness, and fraction absorbed, using the exposure model of the HERA guidance document (HERA, 2002). The following assumptions were made:

- Direct contact of hands results in an exposure of maximal 840 cm^2 of the skin surface (TGD, 2003).
- A film thickness of 100 µm (0.1 mm or 0.01 cm) on the hands (Vermeire et al., 1993; TGD, 2003);
- A percutaneous absorption of 1 % within 24 hour exposure time (Schaefer and Redelmeier, 1996)

$C_{\text{Soluble Silicates}}$= maximum product concentration, in mg/cm^3: 90 mg/mL = 90 mg/cm^3
T_{der} = the thickness of product layer in contact with skin, in cm: 100 µm = 0.01 cm
S_{der} = surface area of exposed hands, in cm^2: 840 cm^2
F = % weight fraction absorbed via skin in a 24 hour period : 1 % = 0.01

$$EXP_{sys} = C_{\text{Soluble Silicates}} \times T_{der} \times S_{der} \times F$$

EXP_{sys} = 90 mg/cm^3 x 0.01 cm x 840 cm^2 x 0.01 = 7.6 mg Soluble Silicates absorbed in 24 hours

With the very conservative assumptions of a 10-min contact time per task and a task frequency of 21 tasks pre-treatment wash per week using powder (AISE, 2002), the total daily contact time is 30 minutes.

Therefore, the daily exposure can be calculated as [(7.6 mg/day) x (30/60) x (1/24)] yielding an assumed absorption of 0.16 mg per day.

Based on a body weight of 60 kg, the estimated systemic dose of silicates resulting from laundry pre-treatment would be equal to 0.16 / 60 = 2.6 10^{-3} mg/kg body weight/day, or **2.6 µg soluble Silicates/kg bw/day** (= **1.3 µg SiO_2/kg bw/day).**

4.1.1.3 Contact from laundry or automatic dishwashing products (powder, tablets)

Soluble silicates are present in laundry detergents (machine or hand-washing products) and in products for automatic dishwashers, but not in hand dishwashing formulations (AISE, 2004).

Direct contact with powder or tablets may occur when handling the solid product to place it into the laundry washer, preparing hand wash solution for clothes, or when loading dishwashing detergent in the automatic dishwasher. Contact time is usually very short (less than 1 minute) (AISE, 2002), and the skin area in contact is limited. The resulting uptake of silicates is assumed to be negligible under these conditions, and it is not expected to impact the overall exposure.

4.1.1.4 Contact from surface cleaning with detergent products containing soluble silicates

Skin contact can occur during surface cleaning with a detergent solution containing soluble silicates.
The highest concentration of liquid surface cleaners used in a volume of wash water of 5 litres is 110 g per task, resulting in a maximum concentration of 22 g/L of detergent in water (AISE, 2002). The highest concentration of silicates in liquid surface cleaners is estimated to be 1 % (AISE, 2004). Therefore, the amount of soluble silicates in the wash water used for surface cleaning is 0.22 g/L (0.22 mg/mL). Due to the fact that the concentration of silicates in the other formulation types is lower, this figure is taken as worst case scenario for the exposure assessment.
The amount of silicates absorbed via the skin is calculated from the silicate concentration applied, surface area of hands exposed, film thickness, and fraction absorbed, using the exposure model of the HERA guidance document (HERA, 2002), and using the following assumptions:

- Direct contact of hands into the wash water solution would expose a maximum of 840 cm^2 (TGD, 2003) of the skin surface.
- A film thickness of 100 µm (0.1 mm or 0.01 cm) on the hands (Vermeire et al., 1993; TGD, 2003)
- A percutaneous absorption of 1 % within 24 hour exposure time (Schaefer and Redelmeier, 1996)
- 100 % of the product remaining on the skin (no wiping or rinsing) as a worst case scenario.

$C_{\text{soluble Silicates}}$ = maximum substance concentration, in mg/cm^3:	0.22 mg/mL = 0.22 mg/cm^3
T_{der} = the thickness of product layer in contact with skin, in cm:	100 µm = 0.01 cm.
S_{der} = surface area of exposed hands and forearms, in cm^2:	840 cm^2
F_1 = percentage (%) weight fraction remaining on skin	100 % (worst case)
F_2 = % weight fraction absorbed via skin in a 24 hour period:	1 % = 0.01

$$EXP_{sys} = C_{\text{soluble Silicates}} \times T_{der} \times S_{der} \times F_1 \times F_2$$

EXP_{sys} = 0.22 mg/cm^3 x 0.01 cm x 840 cm^2 x 0.01 = 0.02 mg Soluble Silicates absorbed in 24 hours

Under the very conservative assumptions of 20 min contact time per task and a task frequency of 7 tasks per week (AISE, 2002) (1 task a day), the total daily contact time is 20 minutes.

Therefore, the daily contact can be calculated as [(0.02 mg/day) x (20/60) x (1/24)], yielding an assumed absorption of 0.0003 mg per day.

Based on an average adult body weight of 60 kg the systemic dose of soluble silicates during the task of surface cleaning would be equal to 0.3 / 60 = **0.005 µg soluble Silicates/kg bw/day (= 0.0025 µg SiO_2/kg bw/day).**

4.1.1.5 Contact from toilet cleaning with product containing soluble silicates

Skin contact can occur during the cleaning of the lavatory pan with a detergent containing soluble silicates. This is commonly a liquid cleaner, containing a maximum of 0.03 % silicates (AISE, 2004).

Investigations on uses and consumer in-home observations have shown that most people pour the toilet cleaner directly into the lavatory pan (Weegels and van Veen, 2001). Contact time is estimated to be very short (less than 1 minute) (AISE, 2002), and the skin area in contact is expected to be limited. The resulting uptake of soluble silicates for this application is assumed to be negligible.

4.1.1.6 Indirect skin contact via wearing clothes

Residues of components of laundry detergents may remain on textiles after washing and can transfer from the textile to the skin. There are no data available showing how much silicates are deposited on the fabric following a wash process. However, the conservative assumption was made that 5 % of the silicates might be deposited on the fabrics (HERA guidance document, 2002).

The following algorithm is recommended in the HERA guidance document (2002) to estimate the dermal exposure to detergent residues in the fabric:

$$Exp_{sys} = F_1 \times C' \times S_{der} \times n \times F_2 \times F_3 \times F_4 / bw$$

For the silicate exposure estimate, the terms are defined with the following values for the calculation:

F_1 = percentage (%) weight fraction of substance in product
C' = product load in (mg/cm²)
S_{der} = surface area of exposed skin in (cm²)
n = product use frequency in number (events/day)
F_2 = percentage (%) weight fraction transferred from medium to skin
F_3 = percentage (%) weight fraction remaining on skin
F_4 = percentage (%) weight fraction absorbed via skin
bw = body weight in kg

Determination of C'("Product applied to skin via fabric wash (hand, machine) and wear"):

$$C' = M \times F` \times FD / wl \ (mg/cm^2)$$

M = amount of undiluted product used in (mg)
F` = percentage (%) weight fraction of substances deposited on fabric
FD = fabric density in (mg/cm²)
wl = total weight (of fabric) in (mg)

According to these algorithms cited above the following calculations were done:

1.) Determination of C':

M 135000 mg (135 g tablets/cup as the maximum amount used)
F` 5 % = 0.05 (conservative assumption)
FD 10 mg/cm² (HERA, 2002)
wl 1000000 mg (HERA, 2002)

C' = 0.0675 mg/cm²

2.) Calculation of systemic exposure:

F1 = 0.25 (is equivalent to the maximum amount of 25 % soluble Silicates in tables)
C' = 0.0675 mg/cm²
S_{der} = 17600 cm^2 (TGD, 2003)
n = 1 (event/day)
F2 = 10 % = 0.1 (worst case assumption !)
F3 = 100 % = 1 (worst case assumption !)
F4 = 1 % bioavailability = 0.01 (Schaefer and Redelmeier, 1996)
bw = 60 kg (TGD, 2003)

$EXP_{sys \ (indirect \ skin \ contact)}$ = 0.005 mg/kg bw/day = **5.0 µg soluble Silicates/kg bw/day (= 2.5 µg SiO_2/kg bw/day)**

4.1.2 Consumer exposure via the oral route

4.1.2.1. Indirect oral exposure via residues on dinnerware

The daily exposure to silicates from eating with utensils and from dishware that have been washed in dishwashing detergents can be estimated according to the following algorithm from the HERA guidance document:

$$Exp_{sys} = F_1 \times C' \times Ta \times Sa / bw$$

For this exposure estimate, the terms are defined with following values for the calculation considering a worst-case scenario:

F_1 = percentage weight fraction of substance in product:	45 % (0.45); (AISE, 2004)
C' = concentration of product in dish wash solution:	1 mg/cm³ (HERA Table of H&P, 2002)
Ta = amount of water left on dishes after rinsing:	5.5 x 10^{-5} mL/cm^2 (Schmitz, 1973)
Sa = area of dishes in daily contact with food:	5400cm² (Jorf, 1990)

bw = body weight: 60 kg (TGD, 1996)

Exp_{sys} (oral dish deposition) = [0.45 x (1 mg/mL) x (5.5 x 10^{-5} mL/cm²) x (5400 cm²)]/60 kg = 0.0022 mg/kg bw/day = **2.2 µg soluble Silicates/kg bw/day (= 1.1 µg SiO_2/kg bw/day)**

4.1.2.2. Indirect oral exposure via other sources

Oral exposures can be assumed to originate from drinking water and food. Sodium silicate may be added to drinking water as a corrosion inhibitor and sequestering agent. According to European Standard EN 1209, the maximum permissible concentration is 15 mg/L (European Committee for Standardization 1997). Assuming 2 L of daily water consumption (TGD,2003), 100% oral bioavailability of soluble silicates in humans (worst case) and 60 kg of body weight, the daily human exposure to soluble silicates from drinking water can be estimated as:

$Exp_{(drinking\ water)}$ = [15 (µg/l) x 2 (l)]/60 (kg) = **0.5 µg soluble Silicates/kg bw/day (= 0.25 µg SiO_2/kg bw/day)**

Silica is an ubiquitous constituent of foods. While the highest concentrations of total silica are found in seafood, eggs and dairy products, the main dietary sources are cereals and beverages. The average daily intake of silica is in the range of 43 - 107 mg SiO_2/day. According to Pennington 1991, the estimated silica intake via diets in the United States is:

$Exp_{(diet)}$ = **0.68 mg SiO_2/kg bw/day in females and 1.13 mg SiO_2/kg bw/day in males**

These figures can be considered as representative for the intake in the Western world, too.

4.1.3 Consumer exposure via the inhalation route

4.1.3.1 Direct exposure via the inhalation route

Short-term exposure to dust may occur by the use of products in powder form only, other application forms, like tablets or liquids being of no concern regarding inhalation exposure. Generally, the average particle size in powder detergents is far in excess of respirability. In a process called agglomeration the various dry ingredients are combined into single granular particles through the binding power of liquid silicate leading to particle sizes from 230 to 1500 microns or higher (PQ Corp., undated).

According to van de Plassche et al. (1998) studies indicate an average exposure of about 0.27 µg dust per cup of product used for machine laundering, of which up to 25 % or 0.07 µg/use are silicates. For the worst case assumptions that all the dust is inhaled during machine loading and that this task is performed up to 3 times a day, the exposure to silicates of an adult with an average body weight of 60 kg is estimated to be:

$EXP_{sys\ (dust\ inhalation)}$ = [0.07 µg/use x 3] / 60 kg = **0.0035 µg soluble Silicates /kg bw/day (= 0.0018 µg SiO_2 /kg bw/day)**

Based on an uptake of 0.27 µg dust per cup for machine dishwashing powder containing up to 45 % soluble silicates (AISE, 2004) a maximum uptake of 0.12 µg/use of soluble silicates is obtained. For the worst case assumptions that all the dust is inhaled during machine loading and that this task is performed up to once a day, the exposure to silicates of an adult with an average body weight of 60 kg is estimated to be:

$$EXP_{sys\ (dust\ inhalation)} = [0.12\ \mu g/use \times 1] / 60\ kg = \mathbf{0.002\ \mu g\ soluble\ Silicates\ /kg\ bw/day}$$
$$\mathbf{(= 0.001\ \mu g\ SiO_2\ /kg\ bw/day)}$$

Even if the whole amount of dust is inhaled during machine loading the amount does not contribute significantly to the total exposure of silicates. The dust formation from products which are either granulated or in tablet form is so small that it can be considered negligible.

4.1.3.2 Direct exposure via the Inhalation of aerosols from cleaning sprays

Soluble silicates are also present in surface cleaning sprays. The HERA guidance document specifies the algorithm to be used for calculation of consumers' worst-case exposure to soluble silicates containing aerosols generated by the spray cleaner:

$$Exp_{sys} = F_1 \times C` \times Q_{inh} \times t \times n \times F_7 \times F_8 / BW$$

F_1 = percentage weight fraction of substance in product:	0.7% = 0.07
C` = product concentration in air:	0.35 mg/m^3 *(Procter &Gamble, 2001)
Q_{inh} = ventilation rate:	0.8 m^3/h (TGD, 2003)
t duration of exposure:	10 min = 0.17h (AISE/HERA, 2002)
n = product use frequency (tasks per day):	1 (AISE/HERA, 2002)
F_7 = weight fraction of respirable particles:	100%
F_8 = weight fraction absorbed or bioavailable:	75%; 075 (TGD, 2003)
BW = body weight:	60 kg (TGD, 2003)

$$Exp_{sys\ (inhalation\ of\ aerosols)} = [0.07 \times (0.35\ mg/m^3) \times (0.8\ m^3/h) \times (0.17\ h) \times 0.75]/60\ kg$$
$$= \mathbf{4.2 \times 10^{-5}\ mg/kg\ bw/day\ = 4.2 \times 10^{-2}\ \mu g/kg\ bw/day\ (= 2.1 \times 10^{-2}\ \mu g\ SiO_2/kg\ bw/day)}$$

* This value was obtained by experimental measurements of the concentration of aerosol particles smaller than 6.4 microns in size which are generated upon spraying with typical surface cleaning spray products.

5.1.3 Total Consumer exposure of SiO_2 (all routes) from household cleaning products

1. Dermal

Hand washing laundry:	0.04 µg/kg/day
Fabric pre-treatment:	1.3 µg/kg/day
Pouring product:	negligible
Surface cleaning:	0.0025 µg/kg/day
Wearing laundered fabric:	2.5 µg/kg/day

Total dermal: **3.9 µg/kg/day**

2. Oral

Residues on dishes: 1.1 µg/kg/day

Total oral exposure: **1.1 µg/kg/day**

3. Inhalation

Pouring laundry detergent: 0.0018 µg/kg/day
Pouring dishwashing detergent: 0.001 µg/kg/day
Aerosols from cleaning sprays: 0.021 mg/kg/day

Total inhalation: **< 0.01 µg/kg/day**

Total exposure via all routes due to the use of detergent household products:

5.1 µg SiO_2/kg bw/day

5.1.4 Accidental overexposure

Accidental overexposure to soluble silicates may potentially occur via household detergents and by various routes. Two main routes of accidental exposure should be considered.

Eye exposure

Accidental eye exposure to soluble silicates may occur through splashing of a detergent solution while handwashing clothes, dishwashing, brushing the lavatory pan, or from handling powder. Therefore, the eye irritation potential should be considered in the context of accidental exposure.

Oral exposure

Oral exposure can occur following ingestion of detergent products containing soluble silicates, or solutions of these products in water. Detergent products usually contain bitter agents to discourage children from uptake. Therefore, most accidental ingestions of laundry or dishwashing products by young children involve small amounts of products (1 teaspoon or less) (Petersen, 1989). However, in some cases, adults may overcome the bitter taste and consume toxic quantities.

No fatal cases arising from oral uptake have been reported. The accidental overexposure of silicates directly is not considered a likely possibility for consumers, but it may occur via laundry or dishwashing detergents and surface cleaners. Furthermore, case reports related to high exposure to silicates (solutions) have not been reported in the medical literature. The German Federal Institute for Health Protection of Consumers and Veterinary Medicine (BgVV, 1999) published recently a report on products involved in poisoning cases. No fatal case of poisoning with detergents was reported. Detergent products were not mentioned as dangerous products with a high incidence of poisoning. Equally, in the UK, the Department of Trade and Industry

(DTI) produces an annual report of the home accident surveillance system (HASS). The data in this report summarizes the information recorded at accident and emergency (A&E) units at a sample of hospitals across the UK. It also includes death statistics produced by the Office for National Statistics for England and Wales. The figures for 1998 show that for the representative sample of hospitals surveyed, there were 33 reported accidents involving detergent washing powder (the national estimate being 644) with none of these resulting in fatalities (DTI,1998). In 1996 and 1997, despite their being 43 and 50 reported cases, respectively, no fatalities were reported either.

5.2 Hazard assessment

5.2.1 Toxicokinetics, metabolism and mechanism of action

Silica is an essential trace element participating in the normal metabolism of higher animals. It is required in bone, cartilage and connective tissue formation as well as participating in other important metabolic processes. The silica is present almost entirely as free soluble monosilicic acid (Carlisle 1986). No reliable toxicokinetic, metabolic or mechanistic studies are available for soluble silicates. Since concentrated silicate solutions are only stable at pH values above 11.5 and lowering the pH below 11.5 leads to the formation of an insoluble silica gel, it can be reasonably assumed that after ingestion gel formation will be induced by the hydrochloric acid of the stomach. The degree of gel formation will depend on the amount of ingested silicate solution and the neutralising and buffering capacity of the gastrointestinal tract. Thus, a sodium silicate solution of molar ratio 3 would lead to precipitation of silica according to the following equation:

$$3\ SiO_2 \cdot Na_2O + 2\ HCl \rightarrow 3\ SiO_2 + 2\ NaCl + H_2O$$

Gastrointestinal absorption of insoluble silica will be insignificant. Uptake of soluble silicates are excreted via urine and to a lesser extent via the faeces. Markedly increased and rapid urinary excretion of silica was observed when soluble sodium silicates were administered by various routes to rats (oral, Benke and Osborn 1979), dogs (oral and intravenous, King et al. 1933), cats (oral, intraperitoneal and inhalative, King and McGeorge 1938) and guinea pigs (oral and intraperitoneal, Sauer et al. 1959). The urinary silica excretion half-life after administration of sodium silicate to rats via stomach tube was 24 h (Benke and Osborn 1979). The excretion rate was independent of the doses applied indicating that the limiting factor is the rate of production of soluble or absorbable silica in the gastrointestinal tract. The same observation was made with sodium metasilicate, pentahydrate in guinea pigs (Sauer et al. 1959).

5.2.2 Acute toxicity

5.2.2.1 Acute Oral Toxicity

Animal data

The results of the most relevant acute oral toxicity studies are summarised in Table 9. Only the studies by Spanjers and Til are performed under conditions comparable to OECD guidelines.

Sodium silicates and metasilicates

Sodium silicates of varying molar ratios from 0.5 to 3.38 have been tested in rats. Toxicity decreased with increasing molar ratio (MR): from LD_{50} of 500 mg/kg bw for molar ratio 0.5 to 8650 mg/kg bw for 3.38. This shows the inverse correlation between MR and toxicity. The majority of the test results are cited as secondary literature only (Schleyer and Blumberg 1982), but several study reports are available, albeit in limited detail (Potokar 1982; Gloxhuber and Potokar 1971a and b; Gloxhuber et al. 1973; Saiwai 1980; Spanjers and Til 1981a, b). Clinical symptoms observed near to or exceeding the LD_{50} values (Saiwai 1980) consisted of apathy, staggering gait, dyspnoea, piloerection, abdominal discomfort, and unconsciousness. The results of autopsy revealed acute gastro-enteritis, vascular congestion, mottled livers, changes in pH of body fluids, shock, chemical irritation and/or corrosion of the viscera. All symptoms are indicative of effects due to high alkalinity and explain the lower LD_{50} figures for lower molar ratios (high alkaline) silicates.

Potassium silicates

One study with rats assesses the acute oral toxicity of a potassium silicate (molar ratio 2.25) (Spanjers and Til 1981c). The LD_{50}-value was 5700 mg/kg bw. All clinical effects: sedation, signs of abdominal discomfort, sluggishness and unconsciousness, were reversible. No treatment-related gross alterations were found at autopsy.

Table 9 Results of acute oral toxicity studies

Silicate (molar ratio SiO_2/M_2O)	Na/K	Concentration (wt. %)	LD_{50} (mg/kg bw)	Species	Reference
2.25[e]	K	-	5700	Rat	Spanjers and Til 1981c
3.38[c]	Na	35[c]	8650	Rat	Gloxhuber and Potokar 1971b
3.35[a]	Na	-	6600	Mouse	Gloxhuber 1973
3.3	Na	36	3200	Rat	Schleyer and Blumberg 1982
3.3	Na	-	>2000	Rat	Potokar 1982
3.27[d]	Na	-	5150	Rat	Spanjers and Til 1981a
3.1	Na	-	1600, 8600	Rat	Schleyer and Blumberg 1982
2.1	Na	-	1300, 2100	Rat	Schleyer and Blumberg, 1982
2.1	Na	81	1500 - 2200	Rat	Schleyer and Blumberg 1982
2.0[f]	Na	-	3400	Rat	Spanjers and Til 1981b
1.7	Na	51	2000, 2500	Rat	Schleyer and Blumberg 1982
1.0[b]	Na	98[b]	1750	Rat	Gloxhuber and Potokar 1971a
1.0	Na	99	600	Rat	Schleyer and Blumberg 1982
1.0	Na	50	800	Rat	Schleyer and Blumberg 1982
1.0	Na	20	1152 - 1349	Rat	Saiwai 1980
1.0	Na	10	770 - 820	Mouse	Saiwai 1980
0.7	Na	61	1000, 1500	Rat	Schleyer and Blumberg 1982
0.5	Na	90	500	Rat	Schleyer and Blumberg 1982

- not specified
a not specified in report whether it concerns a weight or molar ratio
b calculated on the basis of 51 % Na_2O and 47 % SiO_2
c calculated on the basis of 8 % Na_2O and 27 % SiO_2
d natron waterglass 38/40 (3.27), no further specification in study (density 1.37)
e kali waterglass 35.5/36.5 (2.25), no further specification in study (density 1.32)
f natron wasserglas 40/42 (2.0), no further specification in study (density 1.39)

Acute Inhalation Toxicity

No data are available on acute inhalation of soluble silicates. It should be noted that no effects are known from respirable crystaline silica have to be expected for soluble silicates due to their physico-chemical properties.

Acute Dermal Toxicity

No data are available on dermal toxicity of soluble silicates. Due to the skin irritating/corrosive properties of soluble silicates, acute dermal toxicity, if noted at all will predominately be a result of the local tissue damage and not due to systemic toxic effects. This evaluation is supported by a low skin penetration rate resulting in a low bioavailability after dermal contact and a low acute oral toxicity for soluble silicates not causing tissue damage after oral application.

Conclusion

The acute oral toxicity of soluble silicates is generally inversely correlated to the molar ratio SiO_2/Na_2O. Toxicity decreases in rats with increasing molar ratio from LD_{50} of 500 mg/kg bw for molar ratio 0.5 to 8650 mg/kg bw for 3.38. The one solitary study on potassium silicate fits well into the toxicity pattern of the sodium silicates. The LD_{50} of silicates which are used in household detergents ranged from 1152 to 5700 mg/kg bw.

5.2.3 Corrosiveness/irritation

Skin Irritation

Animal data

Several primary skin irritation studies have been performed in rabbits (presented in Table 11), including studies by Cuthbert and Carr (1985), ECETOC (1995), Heisler (1990a, b), Heisler (1993a, b), Karlsson and Loden (1984) and Mercier (1990a, b) performed in compliance with or under similar conditions as the relevant OECD guidelines.

Sodium silicates and metasilicates

The degree of irritation caused in the studies, indicate that the irritation response is inversely correlated with the molar ratio of the silicates; a lower molar ratio $SiO_2 : Na_2O$ leads to a higher irritation score and vice versa. This correlation is superimposed by the concentration effect: lower concentrations will exhibit lower irritancy as compared to higher concentrations of the same molar ratio. The inverse correlation with molar ratio is demonstrated by the studies of Cuthbert and Carr (1985) where sodium silicates of comparable concentrations (38 - 41 %) but different molar ratios were tested. Whereas ratios of 2.0 and 2.4 exhibited irritating properties, ratios of 2.8 and 3.3 were not irritating. The concentration effect becomes evident when the irritancy of identical molar ratios but different concentrations are compared. A sodium silicate of MR 2.4 is irritating at 40 % and corrosive at 82 % (Cuthbert and Carr 1985; Karlsson and Loden 1984); sodium metasilicate is irritating at 10 % and corrosive at 50 % (ECETOC 1995). Sodium silicates of molar ratios 1.6 and below and concentrations greater than 50 % are corrosive. Sodium metasilicate, when tested as an anhydrous powder was not irritating to the skin; when moistened with water it was found to be corrosive (Mercier 1990a, b).

Potassium silicates

The limited studies available for potassium silicates are in line with the inverse correlation of skin effects and molar ratio that is observed for sodium silicates. Likewise, higher concentrations of the same molar ratio are expected to exhibit higher irritating potential. As observed with sodium silicates, potassium silicates of comparable concentrations and different molar ratios show the same inverse correlation to irritancy. Molar ratios of 2.0 and 3.0 and 33 - 36 % concentrations were irritating to the skin (Cuthbert and Carr 1985), whereas MR 3.4 and 3.9

(29 - 35 %) showed no irritation (Heisler 1990a, b; Heisler 1993a, b). The results indicate that the counterions of soluble silicates have no influence on skin irritation.

Human data
In an open epicutaneous test performed according to COLIPA, volunteers were exposed to 5, 10 or 50 % aqueous solutions or undiluted sodium silicate solution (MR 3.45) for 30 minutes (Kremer, 1997a). The light redness experienced by 2 - 3 of the 20 volunteers in each group tested with an aqueous solution disappeared within 20 minutes. The wax-like undiluted solution did not cause adverse effects. Under semi-occlusive (but otherwise identical) conditions, both a 50 % aqueous solution and undiluted solution resulted in peeling of the skin in a third of the subjects after 4 hrs exposure (Kremer 1997b). The study corresponded to OECD 404, with adjustments for human subjects. Both studies were performed under Good Clinical Practice.

Table 10 Results of acute skin irritation studies

Silicate (MR SiO_2 / M_2O)	Na / K	Concentration (wt. %)	Result / PII ^{1}	Conclusion	Method	Reference
3.3	Na	38.3	0.33	-	OECD 404, 1981	Cuthbert and Carr 1985
2.8	Na	39	0	-		
2.4	Na	39.9	3	I		
2.0	Na	40.9	3	I		
1.0	Na	NR^2	8	C		
1.0 (5 aq)	Na	NR^2	8	C		
1.0 (9 aq)	Na	NR^2	8	C		
3.4	Na	34.5	0.4	-	OECD 404, 1981	Karlsson and Loden 1984
2.4	Na	82^3	4.6	C		
1.6	Na	53.5	8	C		
1.0 (5 aq)	Na	57.5^3	7.8	C		
1.0	Na	97^3	5.1	C		
1.0	Na	83^4	4.67	C	OECD 404, 1981	Mercier 1990a
1.0	Na	100^3	0.17	-		Mercier 1990b
1.0	Na	50	3.67	I-C	OECD 404	ECETOC 1995
1.0		10	1.22	I		
3.0	K	33	3	I	OECD 404, 1981	Cuthbert and Carr 1985
2.0		36	1	I		
3.9	K	29	0.25	-	OECD 404	Heisler 1990b
3.9		7	0	-		Heisler 1990a
3.4		35	0.17	-		Heisler 1993b
3.4		8.8	0	-		Heisler 1993a

-	Not irritating
C	Corrosive
I	Irritating
NR	Not reported
1	Primary Irritation Index
2	Sodium silicate powder, moistened before application to the skin. Application of dry powder did not cause irritation.
	Sodium metasilicate powder was applied dry to the skin.
	Sodium silicate powder, applied as an 83 % aqueous paste

Conclusion

Sodium and potassium silicates can be irritating to corrosive to the skin of rabbits, depending on their molar ratio and concentration. The nature of the counterion (Na$^+$ or K$^+$) has no influence as sodium and potassium silicates behave similarly with respect to skin irritation. Any effects on the skin decrease with increasing the molar ratio, superimposed by increasing irritancy with increasing concentrations.

Eye Irritation

Several *in vivo* and *in vitro* eye irritation studies have been performed in rabbits, of which only the studies by Heisler (1990c, d; 1993c, d) with potassium silicates were performed according to OECD guidelines. The results are presented in Table 10.

Sodium silicates and metasilicates

A series of non-validated *in vitro* studies indicate the same inverse correlation between molar ratio and irritation that has been observed for skin irritation (York et al. 1994; Wilson and Hartop 1993; Wilson and Lea 1994). The powders of varying molar ratios exhibited effects in enucleated rabbit eyes ranging from corrosive (MR 1.0) to severely irritating (MR 2.0, 2.4 and 2.6) to slightly irritating (MR 2.8, 3.0 and 3.3). As these results originate from non-validated test systems, their reliability is uncertain.

Potassium silicates

Potassium silicates have been tested on the rabbit eye at molar ratios of 3.4 and 3.9. At concentrations of 35 % or lower they are not or only slightly irritating (Heisler 1990c, d; Heisler 1993c, d).

Table 11 Results of acute eye irritation studies

Silicate (MR SiO_2 / M_2O)	Na / K	Concentration (wt. %)	Result	Method	Reference
3.3[1]	Na	Powder[3]	Slightly irritating	*In vitro* enucleated rabbit eye irritation study[2] (non-validated test system)	York et al. 1994; Wilson and Hartop 1993; Wilson and Lea 1994
3.0[1]			Slightly irritating		
2.8[1]			Moderately irritating		
2.6[1]			Moderately/ severely irritating		
2.4[1]			Severely irritating		
2.0[1]			Severely irritating		
1.0			corrosive		
3.9	K	29	Not irritating	OECD 405	Heisler, 1990d
3.9		7	Not irritating		Heisler, 1990c
3.4		35	Slightly irritating		Heisler, 1993d
3.4		8.8	Not irritating		Heisler,1993c

- not reported

[1] not specified in report whether it is a molar or weight ratio

[2] 1 minute exposure to the test substance, except for MR 1.0 where exposure was only for 10 sec.

[3] 50 mg water-soluble powder of dried silicate solution applied. Dried silicate solutions usually contain about 20 % residual water.

Conclusion

At concentrations of 35 % and 29 % (highest tested concentrations) potassium silicates with molar ratios of 3.4 and 3.9 were only slightly, and not irritating to the eyes of rabbits, respectively. Results from non-validated *in vitro* assays indicate that the severity of eye effects is inversely correlated with the molar ratio, with corrosive effects found in the enucleated rabbit eye test after exposure to disodium silicate powder with a molar ratio of 1.0.

5.2.4 Sensitisation

Skin

Sodium silicates and metasilicates

Karrow et al. (2002) tested the sensitisation potential in the local lymph node assay. Sodium metasilicate solutions (aqueous formulation containing 15 % ethanol) were first tested with regard to their irritation potential. At 6 % significant dermal irritation was noted. This concentration was therefore chosen as the maximum concentration in the local lymph node assay. Sodium metasilicate did not exhibit a significant effect on cell proliferation in the auricular lymph nodes of mice after sensitisation with 2, 4, and 6 % metasilicate for 3 consecutive days. The respective mean stimulation indices were 1.0, 1.4 and 1.3 for the test doses. The positive control demonstrated the sensitivity and validity of the test.

Human data

Tanaka et al. (1982) describe a 57-year-old worker, who had suffered recurrent ulcerative lesions on his left hand for two years, after repeated occupational exposure to 20 % aqueous sodium silicate. In a 24-hour patch test with 20 % sodium silicate (MR unspecified) ulcer formation could be elicited in the patient, but not in 30 healthy volunteers. An immediate wheal formation was observed in the patient 15 minutes after a scratch test was performed with 20 % metasilicate, whereas 30 control subjects did not show wheal formation.

Potassium silicates

No data available.

Respiratory Tract

No data available. For more details see point 5.2.4, Inhalation and Dermal application.

Conclusion

Sodium metasilicate was not sensitising in the local lymph node assay. In a human case study, contact urticaria induced by sodium silicate was observed in a single individual.

5.2.5 Repeated Dose Toxicity

Oral administration

Sodium silicates and metasilicates

Newberne and Wilson (1970) fed 2400 mg sodium silicate/kg bw/day of unspecified molar ratio, to Beagle dogs (8/sex) and rats (15/sex) via the diet for a period of four weeks. The study design was similar to OECD guideline 407. Significant clinical observations were polydipsia, polyuria and soft stools in an unspecified number of dogs and rats. Body weight, food intake, and urinary and blood measurements were essentially normal in all animals. All chemical clinical tests were within normal limits. Gross cortical lesions of the kidney were observed in all male and 7/8 female dogs fed sodium silicate, but not in rats. Histopathological examination revealed irritation of the renal tubular epithelium followed by degenerative and regenerative changes and inflammatory cell infiltration into the interstitium.

Smith et al. (1973) exposed male and female rats (6/sex/group) to sodium silicate (MR 3.2) in drinking water for a period of 180 days. The animals were administered the equivalent of 600 and 1200 mg SiO_2/L, corresponding to 78.9 and 158.7 mg sodium silicate/kg bw/d with a diet containing 0.1 to 1.0 % of SiO_2 (based on dry weight). Body weight and mortality were the only parameters monitored. Statistically significant differences in body weight between experimental groups and controls were registered, but these were small (6 % or less), not consistent and not dose related. No mortalities were observed. After 180 days exposure, the male rats were used in a nitrogen and phosphorous retention study during a total of 17 days. Phosphorus retention was somewhat increased in the high dose group (approximately 12 %), while in the low dose group no effect of treatment was seen. Nitrogen retention was 50 % of controls in the lower dose group only.

Ito et al. (1975) conducted a 3-month toxicity study in rats (5/sex/group) with sodium metasilicate, administered via drinking water in concentrations of 200, 600 and 1800 mg/L (corresponding to approximately 26.4, 76.2 and 227.1 mg/kg bw/d for males and approximately 32.1, 97.6 and 237.2 mg/kg bw/d for females.). The study conditions were similar to OECD guideline 408. No clearly treatment related effects were found.

In a 3-month feeding study reported by Saiwai *et al.* (1980), 10 mice/sex/dose were exposed to sodium metasilicate in the drinking water at concentrations of 300, 900 and 2700 ppm (males) and 333, 1000 and 3000 (females). This corresponds to 96 - 100, 264 - 280 and 776 - 832 mg/kg bw/d for males and 88 - 104, 260 - 284 and 716 - 892 mg/kg bw/d for females. Parameters examined were body weight, urinalysis, clinical chemistry, haematology, organ weights, and histopathology. No fatalities occurred. In females a significant decrease in pituitary glands weight was observed in the highest dose group. Other effects occasionally observed were single incidences and not dose-related.

Kayongo-Male and Jia (1999) studied the effect of various silica sources added to diets of rats and turkeys. Rats were exposed for 8 weeks to sodium metasilicate, pentahydrate at 500 ppm Si (corresponding to 1259 mg metasilicate/kg bw/d). Parameters examined were body weight, organ weight (liver and heart), hemoglobin, hematocrit, and mineral concentrations in blood plasma and organ tissues (liver and heart). No effects on body and organ weights were observed, whereas plasma Ca and Mg and liver Zn were reduced significantly. Turkeys exposed to 270 ppm Si (corresponding to 2039 ppm sodium metasilicate, pentahydrate,) for 4 weeks in a similar experiment did not exhibit significant effects on body and organ weights. Plasma P was increased and Cu was decreased. Minerals in heart and liver tissue were unaffected.

Potassium silicates

No studies are available for potassium silicates.

Table 12 Repeated dose toxicity of soluble silicates

Species	Exposure Period	Test Substance / Dosage	Effects	Reference
Rat	4 weeks	Sodium silicate (MR unspecified) 2400 mg/kg bw/d via diet	Polydipsia, polyuria and soft stools in an unspecified number of animals.	Newberne and Wilson (1970)
Rat	180 days	Sodium silicate (MR 3.2) 79 and 159 mg/kg bw/d via drinking water	No treatment-related effects[1].	Smith et al. (1973)
Rat	3 months	Sodium metasilicate 26.4, 76.2 and 227.1 mg/kg bw/d (males) and 32.1; 97.6 and 237.2 mg/kg bw/d (females) via drinking water	No treatment-related effects.	Ito et al. (1975)
Rat	8 weeks	Sodium metasilicate, pentahydrate 1259 mg/kg bw/d via the diet	Reduction of blood plasma Ca and Mg and liver Zn concentrations. No other effects[2].	Kayongo-Male and Jia (1999)
Mouse	3 months	Sodium metasilicate 96-100, 264 - 280 and 776 - 832 mg/kg bw/d (males) and 88 - 104, 260 - 284 and 716 - 892 mg/kg bw/d (females) via drinking water	Females showed reduced pituitary glands weight at 716 - 892 mg/kg bw/d. No other dose-related effects.	Saiwai et al. (1980)
Dog	4 weeks	Sodium silicate (MR unspecified) 2400 mg/kg bw/d via diet	Gross cortical lesions of kidneys in all males and 7/8 females. Polydipsia, polyuria and soft discoloured feces in an unspecified number of animals.	Newberne and Wilson (1970)
Turkey	4 weeks	Sodium metasilicate, pentahydrate 2039 ppm in the diet	Increased blood plasma P and decreased Cu. No other effects[2].	Kayongo-Male and Jia (1999)

[1] body weight , mortality and nitrogen/phosphorus excretion were the only parameters monitored.

[2] a limited number of parameters was monitored: body, liver and heart weight, hemoglobin, hematocrit and mineral concentrations in blood plasma and livers and hearts.

Conclusion

Repeated dose toxicity studies with sodium silicate or sodium metasilicate ranging from 4 weeks to 180 days have been conducted with rats, mice, dogs and turkeys. The only treatment-related effects observed in rats were:

- polydipsia, polyuria and soft stools at 2400 mg/kg bw/d (sodium silicate of unspecified MR; 4 weeks exposure).

- Reduction of blood plasma Ca and Mg and liver Zn concentrations at 1259 mg/kg bw/d (sodium metasilicate, pentahydrate; 8 weeks exposure).

In female mice, a reduced pituitary gland weight was observed at 716 - 892 mg/kg bw/d (sodium metasilicate; 3 months exposure). Dogs exhibited gross cortical lesions of the kidneys, polydipsia, polyuria and soft feces at 2400 mg/kg bw/d (sodium silicate of unspecified MR; 4 weeks exposure). In turkeys, blood plasma phosphate was increased and Cu decreased at 2039 mg/kg diet (sodium metasilicate, pentahydrate; 8 weeks exposure).

From these studies a NOAEL (90 d) of 227 - 237 mg/kg bw/d and of 260-284 mg/kg bw/d can be deduced for rats and mice, respectively. The NOAEL (180 d) for rats was 159 mg/kg bw/d.

Inhalation and Dermal application

No repeated dose animal studies on the inhalation and dermal toxicity of silicates are available. Sodium metasilicate has been nominated to the National Toxicology Program (NTP) for Toxicological Studies in the United States. A subchronic inhalation study was recommended by the National Institute for Occupational Safety and Health (Federal Register 2002). At present, the technical feasibility and practical relevance of such a study is under discussion with the following points to consider:

- Commercial sodium metasilicates are sieved to contain only large non-respirable particles of >200 µm in granular products, or >50 µm in powders (Minihan and Lovell 2000; Rhodia 2003 and 2001; Cognis 2003), i.e. the commercial products are non-respirable. For the inhalation assay grinding to a fine and respirable powder would be required, representing a test substance which is not existing under real life conditions.

- Due to the hygroscopic properties and the ready solubility in water, the majority of particles, if inhaled, will be retained and dissolved by mucus in the upper respiratory tract. Thus, effects would be restricted to local corrosive/irritant effects, due to the intrinsic alkalinity of sodium metasilicate. However local effects are not the target of a subchronic inhalation study, in which systemic toxicity is investigated. In addition, due to the expected local irritation effects such a study is not in line with animal welfare regulations.

- Acidification to pH below 11 or 12 leads to precipitation of sodium metasilicate and transformation into amorphous silica. Amorphous silica has already been investigated and toxicological properties, including inhalation toxicity, are available on this compound.

- Due to its hygroscopic properties, anhydrous sodium metasilicate tends to aggregate in the presence of moisture, and this limits further the technical realisation of such a study without specific conditions to maintain a dry atmosphere.

5.2.6 Genetic Toxicity

In vitro

Sodium silicates and metasilicates

Sodium metasilicate was tested for DNA-damaging capacity and mutagenicity in the *Bacillus subtilis* strains H17 (Rec-, arg-, try-) and M45 (Rec+, arg-, try-). The result was negative for concentrations 0.005 - 0.5 M, however the test did not comply with an approved guideline (Kanematsu et al. 1980). An Ames test with sodium metasilicate, performed according to current guidelines using *Salmonella typhimurium* TA98, TA100, TA1535 and TA1537 with and without metabolic activation did not reveal a mutagenic activity for concentrations 0.1-10 mg/plate (Saiwai et al. 1980; Ito et al. 1986).

Sodium silicate of unspecified MR and concentration was investigated in the streptomycin-dependent strains *Escherichia coli* B/Sd-4/1,3,4,5 and B/Sd-4/3,4 in a non-guideline study. No evidence of mutagenicity was observed at concentrations of 0.025 - 0.3 % (Demerec et al. 1951). Of the 31 chemicals tested in this study, 19 were found to be mutagenic, indicating in the absence of positive control data that the test was sensitive and could detect a mutagenic activity.

Potassium silicates

No studies are available for potassium silicates.

Conclusion

The available *in vitro* genotoxicity tests with bacteria were all negative.

In vivo

Sodium silicates and metasilicates

Sodium metasilicate was tested in a cytogenetic test for chromosome aberrations in bone marrow cells of male mice in a study similar to OECD TG 475 with the restriction that no information on the use of positive controls was available. Groups of 4 - 6 animals were administered single oral doses of sodium metasilicate at dose levels between 740 and 1340 mg/kg bw (in total, seven dose levels were used in this study). Animals were sacrificed 24 hours after the last administration of the test substance; 2 hours before sacrifice a metaphase arresting agent (colchicine; 4 mg/kg bw) was injected intraperitoneally. Slides from femur bone marrow cells were prepared according to standard methods, and 100 metaphases per animal analyzed for chromosomal aberrations (including gaps, breaks, deletions, and exchanges). No indication of chromosomal aberrations was detected. In a range-finding study, no mortality occurred within 4 days after administration in animals dosed up to 940 mg/kg bw. Mortality occurred at higher doses (Saiwai et al. 1980).

Potassium silicates

No studies are available for potassium silicates.

Conclusion

Sodium metasilicate was not mutagenic in an *in vivo* chromosomal aberration study performed similar to OECD TG 475, with the restriction that no information on the use of positive controls was available for this study. Although the reliability of this study can therefore not be fully evaluated, the negative result is corroborated by the fact that the chemical structure does not contain elements that rise concern for a genotoxic activity, and by the negative results of genotoxicity tests with similar silicates. For instance, magnesium silicate (CAS No. 14807-96-6) did not induce dominant lethal mutations or chromosomal aberrations in bone marrow cells of rats treated *in vivo* or chromosomal aberrations in human cells *in vitro* (IARC 1987).

This finding corroborates the negative results in the *in vitro* studies.

5.2.7 Carcinogenicity

No valid data are available for sodium or potassium silicates.

5.2.8 Toxicity to reproduction

5.2.8.1 Fertility

Sodium silicates and metasilicates

In a limited 4-generation study, Smith et al. (1973) assessed the effect of sodium silicate (MR 3.2) administered via drinking water to rats. The exposure concentration was 600 and 1200 mg SiO_2/L, corresponding to 79 and 159 mg sodium silicate/kg bw/d from weaning until mating. Control groups received no sodium silicate in their drinking water. For 4 consecutive generations, the rats were mated and the total number of offspring analysed. No dose-related effect on litter number up to and including 159 mg/kg bw/d was observed. Survival of offspring until weaning was poor, even in the controls (35, 24, and 11 % at 0, 79, 159 mg/kg bw/d, respectively). The total number of offspring born was reduced to 67 % of the controls at 79 mg/kg bw/d and to 80 % at 159 mg/kg bw/d. Litters born to females receiving silicate were frequently stillborn or small and weak, with survival limited to only a few days. In addition, cannibalism was prevalent and necrosis of the tail and occasionally the feet was observed in offspring of silicate-treated animals. Severe limitations of the study and inter-current deaths, including controls make it however difficult to draw any firm conclusions from this study.

Potassium silicates

No data are available.

5.2.8.2 Developmental effects

Sodium silicates and metasilicates

In a developmental toxicity study by Saiwai *et al*. (1980), pregnant mice were administered 12.5, 50 or 200 mg/kg bw/d sodium metasilicate in aqueous solution from day 0 until 17/18 of gestation by daily gavage. Among the mother animals 2 fatalities occurred both in the 50 and 200 mg/kg group (total number of animals: 33 and 27, respectively); body and organ weights and dissection findings were not affected. On day 18 of gestation fetuses were delivered by hysterectomy and examined. No differences to controls were observed for the following parameters: number of pregnancies and living or dead fetuses, body weight and malformations of inner organs and the skeleton. 10 mother animals were allowed to deliver their young naturally. The neonates were observed for 30 days. Litter size and fertility index were not significantly affected up to and including 200 mg/kg bw/d. Body weight gain, organ weights and behavioral development did not reveal any differences to the control. Skeletal malformations did not exhibit a correlation with dosage.

Potassium silicates

No data are available.

5.2.9 Other studies

In a study by Kamboj and Kar (1964), male rats were injected subcutaneously and intratesticularly with doses of 0.08 mmole/kg sodium silicate (MR not specified). When the testes were examined 7 d after injection, no morphological or histological effects were seen in either application route nor was there any effect on residual spermatozoa in the ductus deferens. Testicular weight was slightly reduced as compared to controls injected with sterile water.

Some of the available subchronic/chronic repeat dose studies (cf. 5.2.4) shed also light on the effects of sodium silicates on the reproductive organs:

In the 3-month study performed by Sawai et al. (1980) with mice, exposure via drinking water to metasilicate concentrations up to and including 832 and 892 mg/kg bw/d for males and females, respectively, did not show treatment-related effects on the pathohistology of testes and ovaries. The mean wet weight of these organs was also not affected (testes: 0.13 - 0.14 g for control; 0.12 - 0.14 g for dosage groups; ovaries: 7.3 - 8.4 g for control; 7.4 - 9.7 g for dosage groups).

No effects on the male and female reproductive organs were observed upon macroscopic and microscopic examination when rats were exposed to 200, 600 and 1800 ppm in drinking water (26, 76 and 227 mg/kg bw/d for males; 32, 98 and 237 mg/kg bw/d for females) for 3 months (Ito et al. 1975).

Rats and beagle dogs were exposed to sodium silicate of unknown molar ratio for 4 weeks at a single concentration of 2400 mg/kg bw/d via the diet. According to the authors, a complete necropsy and histopathological study was performed and no treatment-related effects except in the kidneys observed (Newberne and Wilson 1970).

Conclusion

The available data on toxicity to reproduction are limited. In a 4-generation study, the total number of offspring born at 79 mg/kg bw/d was reduced to 67 % of offspring weaned to 46 % of the control, respectively. Severe limitations of the study and inter-current deaths, including controls make it however difficult to draw any firm conclusions from this study. In mice, litter size and fertility index were unaffected at sodium metasilicate concentrations up to and including 200 mg/kg bw/d. No developmental effects were observed in this study up to and including 200 mg/kg bw/d. In repeat dose toxicity studies with rats, mice and dogs the macroscopic and microscopic examination of reproductive organs did not reveal treatment-related effects.

5.2.10 Identification of critical endpoints

Overview on Hazard identification

Soluble silicates are of moderately acute toxicity via the oral route in experimental animals. The acute oral toxicity of soluble silicates are generally inversely correlated to the molar ratio SiO_2/Na_2O. Toxicity decreases in rats with increasing molar ratio from LD_{50} of 500 mg/kg bw for molar ratio 0.5 to 8650 mg/kg bw for 3.38. Silicates which are used in household detergents have a higher molar ratio ranging from 1.0 to 5.0 (see table 1) and oral LD_{50} doses ranging from 1152 to 5700 mg/kg bw.

Sodium and potassium silicates can cause eye irritation and may have an irritant to corrosive effect on skin. These effects decrease by increasing molar ratio of the silicates. Based on the available data of soluble silicates skin sensitising properties are highly unlikely.

There is no danger of serious damage of health by prolonged exposure of soluble silicates. The NOAELs (90d) of sodium metasilicates ranged from 227 to 284 mg/kg bw/d in rats and mice, and the NOAEL (180d) of sodium silicate in rats was 159 mg/kg bw/d.

Because of severe limitations in a poorly conducted 4-generation study, no firm conclusions could be drawn on potential reproductive effects. The noted effects in the daughter generations cannot be evaluated from the limited data given in the study and due to the generally low surveillance rate noted in all groups including the controls. No teratogenic effects were observed in a mouse developmental toxicity study. No genotoxic effects are reported in *in vitro* or *in vivo* studies for silicates or very similar compounds like magnesium silicates. Consequently, based on the available data the class of soluble silicates is not expected to present a risk for developmental or reproductive toxicity or genotoxic effects.

Rationale for identification of critical endpoints

There is a background exposure of silicates due to its natural occurrence in the environment and in food . In addition, silicates have been used widely and for a long time e.g. for drinking water treatment. However, until today, no adverse effects have been noted with regard to systemic toxicity, sensitisation or carcinogenicity.

The most important potential effects with regard to possible consumer exposure are local irritating effects in particular on the eyes and skin.

5.3 Risk Assessment

5.3.8 Margins of exposure

The Margin of Exposure (MOE) is the ratio of the No Observed (Adverse) Effect Level and the predicted exposure level or systemic estimated dose (SED) as calculated above in section 5.1.3. From the available prolonged exposure animal studies, the lowest NOEL (180 days) was determined to be 159 mg SiO_2/kg/d.

Because ionic substances are considered to be less easily absorbed through the skin than non-ionic compounds (Schaefer and Redelmeier, 1996), as a worst case assumption a percutaneous absorption of 1 % in 24 hour exposure time was used in the assessment of the systemic exposure by dermal route. The systemic (bioavailable) dose based on this assumption is compared with the NOEL value obtained in a repeated oral dose study.

Contact from hand washing laundry with solutions containing soluble silicates

$MOE_{\text{direct skin}}$ = systemic oral NOEL/estimated systemic dose
$MOE_{\text{direct skin}}$ = (159 000 µg/kg/d) / (0.04 µg SiO_2/kg/d) = **3 975 000**

The systemic dose was estimated from the worst case scenario, using the highest use concentration and use frequency.

Contact from pre-treatment of clothes with product containing soluble silicates

$MOE_{\text{direct skin}}$ = systemic oral NOEL/estimated systemic dose
$MOE_{\text{direct skin}}$ = (159 000 µg/kg/d) / (1.3 µg SiO_2/kg/d) = **120 000**

The systemic dose was estimated from the worst case scenario, using the highest use concentration and use frequency. The other products would result in a lower exposure, and therefore in a larger margin of exposure.

Contact from surface cleaning with product containing soluble silicates

$MOE_{\text{direct skin}}$ = systemic oral NOEL/estimated systemic dose
$MOE_{\text{direct skin}}$ (159 000 µg/kg/d) / (0.0025 µg SiO_2/kg/d) = **636 000 000**

Indirect skin contact via wearing clothes

$MOE_{\text{indirect skin}}$ = systemic oral NOEL/estimated systemic dose
$MOE_{\text{indirect skin}}$ = (159 000 µg/kg/d) / (2.5 µg SiO_2/kg/d) = **63 000**

Indirect oral exposure via residues on dinner ware

The total estimated exposure to silica from residues left on eating utensils and dishware was 1.1 µg/kg/d.
$MOE_{\text{indirect oral}}$ = systemic oral NOEL/estimated systemic dose
$MOE_{\text{indirect oral}}$ = (159 000 µg/kg/d) / (1.1 µg SiO_2/kg/d) = **140 000**

Indirect oral exposure via other sources

The estimated exposure to silica in drinking water was 0.25 µg/kg/d.
MOE $_{\text{indirect oral}}$ = systemic oral NOEL/estimated systemic dose
MOE $_{\text{indirect oral}}$ = (159 000 µg/kg/d) / (0.25 µg SiO_2/kg/d) = **636 000**

The estimated exposure to silica via diet was 1.13 mg/kg/d (worst-case for males).
MOE $_{\text{indirect oral}}$ = systemic oral NOEL/estimated systemic dose
MOE $_{\text{indirect oral}}$ = (159 mg/kg/d) / (1.13 mg SiO_2/kg/d) = **140**

Inhalation

The total estimated exposure to silica by inhalation while pouring detergent powder into a machine and inhalation of aerosols by using cleaning sprays was below 0.05 µg SiO_2/kg/d.
MOE $_{\text{inhalation}}$ = systemic oral NOEL/estimated systemic dose

MOE $_{\text{inhalation}}$ = (159 000 µg/kg/d) / (0.05 µg SiO_2/kg/d) = **3 180 000**

Total consumer exposure

The integrated consumer exposure to soluble silicates via all routes due to the use of detergent household products results in an estimated total body burden of 3.9 + 1.1 + 0.1 µg/kg/d = 5.1 µg SiO_2/kg bw/day.
Comparison of the total predicted consumer exposure to SiO_2 with the systemic NOEL (159 mg/kg/d) results in an estimated Margin of Exposure of approximately **31 000.**
Given the very low exposures from its use in household cleaning products and the resulting very high Margin Of Safety, soluble silicates present no significant risk from the normal use or from accidental misuse of these products. The determined MOS is certainly large enough to account for the inherent uncertainty and variability of the hazard data on which it is based. The MOS is based on worst-case exposure assumptions and a well-defined systemic NOAEL. The true consumer exposure is with a very high likelihood significantly lower than the one presented here.
The comparison of the MOE of 31 000 for the exposure of SiO_2 via household cleaning products and the MOE of 140 for the daily exposure via diet indicate that the exposure to SiO_2 via the use in household detergents is negligible.

From the available data skin irritating effects in humans cannot completely be excluded especially when highly concentrated detergents with high contents of soluble silicates and a low molar ratio are not handled properly, e. g. in accordance with the handling recommendations provided on the product label. However, if skin contact does occur by using household detergents, the contact is confined to a fraction of the skin of the hands (palms or fingers), is of very short duration (typically a few minutes at most) and the initial high soluble silicate concentration is usually diluted out rapidly in the course of the pre-treatment task. Failing to rinse hands in water after contact with the laundry pre-treatment paste or liquid may result in transient skin irritation in the hands, which is expected to be mild in nature and effectively avoided by prompt washing with water.

Accidental (over)exposure

a) Oral

The experimental acute oral toxicity studies for soluble silicates used in household detergents showed that the LD_{50} ranged from 1152 to 5700 mg/kg bw in rats depending on the molar ratio of silicate species. Clinical signs included apathy, staggering gait, tonic cramps, dyspnoea, cyanosis, piloerection and signs of abdominal discomfort. All symptoms are indicative of effects due to high alkalinity. The uptake of soluble silicates must be high to reach acute lethal effects. In the available studies, lethal effects were reported at concentrations above 2500 mg/kg in rats. The assumption is made that no lethal effects in humans at doses of 1000 mg/kg bw (lowest LD_{50} 1152 mg/kg bw in rats) will occur. This would correspond to the ingestion of 60 g silicates by an adult of 60 kg, or 10 g by a 10-kg child, and an even higher amount of the detergent containing up to 45 % soluble silicates. Ingestion of a 200 mL solution containing 5 to 36 % sodium silicate (10 – 72 g sodium silicate) caused severe symptoms, but was not fatal. However, ingestion of 500 mL of a solution containing sodium silicates in suicidal intention led to the death of a 68 year old woman by suffocation. However, an ingestion of high amounts of detergents is an unlikely case in young infants because the amount ingested accidentally by children is generally limited by the taste of the detergent. It seems that child poisoning cases are usually not severe, except in case of massive ingestion or bronchial aspiration of foam (Petersen, 1989; Repetto, 1996; Herrington et al., 1998). Published data indicate that most cases of accidental ingestion of laundry or dishwashing products by young children involve small amounts of product (1 teaspoon or less) (Petersen, 1989).

b) Skin

Experimental data show that soluble silicates are irritating or even corrosive to the skin and eyes. Any effects on skin and eyes depend on the molar ratio of silicate species and concentration. The symptoms are indicative of effects due to high alkalinity. Undiluted, dry soluble silicates were not or only slightly irritating to eye and skin in contrast to highly concentrated solutions. Therefore, contact with solid products should not lead to local irritation.

With up to 25 %, liquid machine dishwashing detergents have the highest concentration within the group of liquid detergents. However, an exposure of liquid machine dishwashing detergents to the skin is very unlikely to occur. In surface cleaners and in toilet cleaners the maximum concentration is 1 % and 0.03 % soluble silicates, respectively. Experimental data show that these concentrations should not lead to skin irritation.

c) Eye

If 0.1 g of a solid detergent were brought into the eye, this would correspond to 0.045 g of silicates. If this would be diluted in 0.5 mL of tear liquid this would result in a solution of around 9 %, which would be expected to be irritant, but would not cause irreversible damage to the eye. This is in accordance with the reports of poison centres that report rather slight irritation effects from detergent spills into the eyes (DTI, 1998).

Accidental splashes into the eye may occur through the use of products containing soluble silicates. As stated in Section 5.2.2, tests in rabbit eyes show that potassium silicate solutions of varying molar ratios at concentrations of 29 % and 35 % were not or only slightly irritating to eyes of rabbits in the latter case. The same behaviour is expected for sodium silicates of comparable molar ratio and concentration. Therefore, the maximum concentrations used in liquid laundry bleach, surface cleaners, and toilet cleaners (0.03 – 1 %) are not expected to cause eye irritation. However, the severity of eye effects is inversely correlated with the molar ratio. Thus, for silicates with a low molar ratio, like sodium metasilicate used in liquid machine dishwashing detergents, eye irritating effects cannot be excluded.

d) Inhalation

Short-term exposure to dust may occur by the use of products in powder form only, other application forms, like tablets or liquids being of no concern for inhalation exposure. Generally, the average particle size in powder detergents is far in excess of respirability. In addition, for sheer consumer acceptance reasons detergents are formulated in such a way that pestering dust formation does not occur. Therefore, since the dust inhalation is very low and occurs infrequently as a typical acute exposure situation there is no concern with regard to possible effects after inhalation.

5.3.9 Consumer Risk characterisation

Skin contact, inhalation and oral ingestion scenarios were assessed for human exposure to soluble silicates in detergents, comprising laundry and automatic dishwashing detergents, as well as hard-surface and toilet cleaners.

The Margin of exposure for the combined estimated systemic exposures is 31 000. This margin takes into account uncertainties and variability associated with the hazards database, such as inter- and intra-species variability, as well as extrapolation.

A number of worst case assumptions were made for the estimation of exposure. Maximal use frequency and use quantities were used in the calculations, and in the absence of specific data, default values representing worst case assumptions were used in the estimation of exposure.

The margin of exposure obtained with such worst case assumptions does not raise any particular safety concerns with regard to systemic or local effects of soluble silicates for use in consumer detergent products. The true consumer exposure is with a very high likelihood significantly lower than figures presented here.

5.3.10 Indirect exposure via the environment

Background exposure of soluble silicates via the environment can be expected, as compounds of silicon and oxygen are the primary constituents of earth’s landmasses, and an important compound in the biomass. Dissolved silica is also a minor but widespread solute in the earth’s surface waters. Silicon compounds are present in plants and animal or human organs, tissues, blood and serum (Carlisle 1986).

Silicon is an ubiquitous constituent of foods. The average daily intake of silicon is in the range of 20 - 50 mg total Si/d (corresponding to 43 - 107 mg SiO_2/d). The estimated adult silicon intake via diets in the United States of 0.32 mg Si/kg bw/d (corresponding to 0.68 mg SiO_2/kg bw/d) in females and 0.53 mg Si/kg bw/d (corresponding to 1.13 mg SiO_2/kg bw/d) in males can be considered as representative for the intake in the Western world, too (Pennington 1991). While the highest concentrations of total silicon are found in seafood, eggs and dairy products; the main dietary sources are cereals and beverages.
Another route of exposure is ingestion of drinking water and the intake via diet. Sodium silicate may be added to drinking water as a corrosion inhibitor and sequestering agent. According to European Standard EN 1209, the maximum permissible concentration is 15 mg/L (European Committee for Standardization 1997).
The total estimated systemic exposure to silica through the use of detergents (5.1 µg SiO_2/kg/day) is very low compared to the average daily intake of silica background exposure via drinking water and diet (43 - 107 mg SiO_2/d). Therefore, an exposure of silica due the use of

household products is negligible in comparison of the average daily intake via drinking water and diet.

5.3.11 Discussion and conclusions

Experimental data showed that soluble silicates have a low acute toxicity by the oral route. For silicates used in household detergents the LD_{50} ranged from 1152 to 5700 mg/kg bodyweight depending on the molar ratio of silicate species. No data are available on dermal toxicity of soluble silicates. However, due to moderate to high water solubility, very low lipophilicity and the molecule size of soluble silicates, the dermal bioavailability for such ionic substances is assumed to be rather limited. Soluble silicates can be irritating to corrosive to the skin and eyes, depending on their molar ratio and concentration. Skin sensitising properties of soluble silicates are highly unlikely. In several repeated dose studies the NOAELs of soluble silicates ranged from 159 mg/kg bw/d (180 days) to 284 mg/kg bw/d (90 days). Because of severe limitations in a poorly conducted 4-generation study, no firm conclusions could be drawn on potential reproductive effects. The noted effects in the daughter generations cannot be evaluated from the limited data given in the study and due to the generally low surveillance rate noted in all groups including the controls. No teratogenic effects were observed in a mouse developmental toxicity study. No genotoxic effects are reported in *in vitro* or *in vivo* studies for silicates or very similar compounds like magnesium silicates. Consequently, there is no risk for developmental or reproductive toxicity or genotoxicity. The only critical endpoint for soluble silicates seems to be local irritation or even corrosive properties on skin or eye.
It should be noted that the primary hazard of commercially used soluble silicates is their moderate-to-strong alkalinity causing the observed local irritations/corrosive properties. Soluble silicates with a low molar ratio, like sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the soluble silicates of higher molar ratio.

Consumers may be exposed to soluble silicates via direct skin contact during laundry hand washing or the use of surface and toilet cleaning products containing soluble silicates. However, the estimated concentrations of soluble silicates (0.22 to 2.5 mg/mL) and contact time in these solutions are generally too low to cause local skin irritation.

Accidental acute overexposure to soluble silicates may occur via the oral route, via exposure of the eyes (e.g. due to splashing) or via inhalation. Due to the particle size, formulation and bad taste of the products an accidental overexposure to soluble silicates is rather unlikely to occur. In addition, the available data do not indicate severe adverse effects when accidental overexposure to soluble silicates occurs.

Comparison of the total estimated systemic exposure to silica through the use of detergents (5.1 µg/kg/day) to the No Effect Level estimated in animals (159 mg/kg/day, 180d) results in a margin of safety of approximately 31 000. Consequently, soluble silicates are of low concern for the consumer use in household detergents.
In addition, the average daily intake of silica background exposure via drinking water and diet is in the range of 43 - 107 mg SiO_2/d and therefore, an exposure of silica due the use of household products is negligible in comparison of the average daily intake via drinking water and diet.

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7 CONTRIBUTORS TO THE REPORT

This report has been prepared by SCC GmbH, Wendelsheim (Germany), on behalf of CEES, a sector group of Cefic. It has been reviewed by experts of CEES and the members of the HERA Environmental and Human Health Task Forces.