Fate and effects of soluble silicate (waterglass) emissions to surface waters. Executive summary

In line with the principles of Responsible Care, CEES is interested in the fate and (potential) effects of soluble silicates that enter water ecosystems through the water route. In August 2000, CEES has commissioned TNO to carry out a desk study to assess the fate and effects of soluble silicates. This report is the result of this study.

The production of waterglass by CEES members in Western Europe is ca. 700 kton SiO_2 per year. This study is focussed on four applications areas where emissions to water systems might occur. The production volume of waterglass used in these applications is estimated by CEES at 145 kton/year, or ca. 21% of the total waterglass production. The application areas are:

- Household detergents (78 kton SiO_2/year);
- Pulp- and paper production (53 kton SiO_2/year);
- (waste-)Water treatment (3 kton SiO_2/year);
- Soil stabilisation (12 kton SiO_2/year)

Silicon is known to be present in all living organisms. This element occurs in the form of hydrated amorphous silica, referred to as opal, and is required for the production of structural materials in single-celled organisms through to higher plants and animals. For many live forms, silicon can even be considered to be an essential element. The assessment of the effects of soluble silicate emissions must be reviewed in this context.

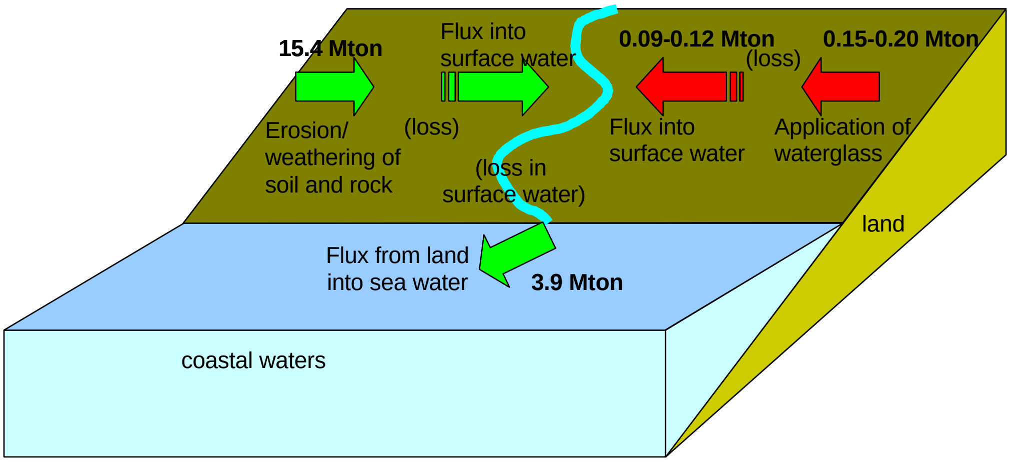
The volume of waterglass used in these application areas was checked by a top-down emission assessment, where the consumption figures of the final product are taken as a starting point instead of the production figures. This assessment was only possible for the first two application areas. The results are somewhat higher than the production data: 91 kton SiO_2/year for waterglass in household (laundry, dishwashing) detergents and 107 kton SiO_2/year for waterglass used in pulp- and paper production.

Not all the soluble silicates used in these application areas enter the water system, because part is retained in the process or product (e.g., paper) and part is removed in the sewer system or sewage treatment plant. The emission pathways were studied, and quantified as much as possible. The resulting emission factors (fraction that enters the surface water) are:

- Household detergents: ca. 85%
- Pulp- and paper production: ca. 40%
- (waste-)Water treatment: unknown; ca. 90%
- Soil stabilisation: unknown; no significant emission assumed.

The main uncertainties in the assessment is the retention of silicates in sewer systems.

The resulting amount of soluble silicate entering the surface water (88 to 121 kton SiO_2/year) must be seen in the context of the natural silica cycle, and natural loading of water systems with silicates due to weathering of soil and rocks, weathering of the sea floor and atmospheric deposition. The natural fluxes can be quantified with (rough) estimations. In the figure on the following page, the natural and anthropogenic fluxes of silicate are visualised. The amount of silicate from waterglass from the four most relevant application areas that finally enters the coastal waters is ca. 0.6 to 3% of the natural silicate flux.



In representative local exposure scenario's, the increase of silicate concentration in the near proximity of discharge points from municipal sewage treatment plants or water treatment facilities of paper plants was estimated at 0.15 to 1.1 mg/L (expressed as SiO_2). This must be compared to an average (but strongly fluctuating) background concentration of ca. 2.2 to 6.4 mg/L (as SiO_2).

Chemical (speciation) modelling has shown that the predominant form of silica from waterglass in wastewater, fresh surface water and sea water is orthosilicic acid, the biologically active form. Therefore, waterglass emissions must be regarded as additions to the natural silicate pool.

To understand the effects of increased silicate concentrations, one must understand the biological function of silicate in water ecosystems, which is complex. In water systems, algae (and aquatic plants) are responsible for primary production: the transformation of inorganic nutrients and carbon dioxide into organic biomass. The algae biomass (density) is determined by several, potentially limiting, factors, such as temperature, light intensity and nutrient concentrations. All algae, such as green and bluegreen algae, require phosphorus and nitrogen as nutrients, but only diatoms (a type of algae) also require silicate for growth. The ratio between Si and P, and the ratio between Si and N, determines which algae is (dominantly) present in the water. In natural waters, diatoms are often dominant in the spring (March-May). Their dominance is usually ended when all silicate is used and stored in the diatoms. When the diatom "bloom" collapses, it is often followed by dominance of other (non-diatom) algae.

The effects of an increased silicate concentration can be:

- Shifts in algae species composition. Additional silicate will increase the Si:P and Si:N ratio in the water, thus creating conditions more favourable for diatoms;
- Increased algae biomass. As mentioned, the development of diatoms in the spring is usually ended when silicate is depleted. Additional silicate will enable the algae to continue their (exponential) growth for a longer period of time; the biomass increase is directly related to the increase of silicate concentration;
- Increased production in "trophic levels" of the food chain: increased primary production can result in an increased zooplankton biomass (grazing on the algae) and increased fish biomass (feeding on zooplankton).

There are, however, complicating factors when assessing the effects of waterglass emissions:

- The effluent of municipal sewage treatment plants, where silicates from household detergents enter the water system, contains not only silicate but also phosphorus and nitrogen. This will affect the Si:P and Si:N ratio's, and therefore the algae species composition.
- The cycling of silicon, phosphorus and nitrogen in water systems are interlinked. Examples are (i) that a diatom bloom, resulting from increased silicate concentration, will remove phosphorus and nitrogen from the water column, and (ii) increased concentrations of biogenic silicate in the sediment (from dead diatoms) is reported to increase phosphorus desorption from the sediment, due to competition for sorption sites. The interactions make a direct and conclusive assessment of the ecological effects impossible.

It is clear that increased silicate concentrations will affect the water ecosystem, but the effects and their intensity depend on the local situation, e.g., season, phosphorus, nitrogen and silicon concentration of the receiving water, and composition of the effluent (silicate or silicate in combination with phosphorus and nitrogen).

Changes in ecosystems are generally regarded as undesirable. However, silicate will not only affect the ecosystem processes, but also the possibilities for the use of the water system by humans. Depending on the use functions of the water system, these effects can be positive as well as negative. A qualitative assessment of the effects of waterglass emissions on the human use of water systems is presented in the table at the following page.

Use functions	**Shifts in phytoplankton community**	**increase of phytoplankton production**	(Possible) increased benthos and fish production	Desorption of P from sediment
Transport/shipping	**0**	**0**	0	0
Preparation of drinking water	**+**	**-**	0	- (indirect)
Recreation (swimming, sailing)	**+**	**-**	0	- (indirect)
Fisheries (professional and sports)	**+**	**+**	+	+ (indirect)

Shifts in plankton communities to diatoms are regarded as positive, as some species of non-diatom algae (bluegreen algae) may produce toxins or surface scums. The increase of primary production can be regarded as positive because of the increased fish production that might result from it, but as negative from the recreation point-of-view (increased turbidity of the water).

Due to the complexity of interacting processes there remain some uncertainties regarding the effects of silicates on water ecosystems. Based on thorough review of literature and on our own investigations and modelling calculation, no significant adverse effects to ecosystems are to be assumed