**SIDS INITIAL ASSESSMENT PROFILE**

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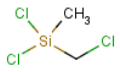
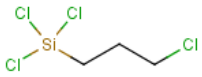
| **Category Name** | Chloroalkyl chlorosilanes Category |
| **CAS No(s). and Chemical Name(s)** | 1558-33-4 Silane, dichloro (chloromethyl) methyl<br>2550-06-3 Silane, trichloro (3-chloropropyl)- |
| **Structural Formula(s)** |  <br><br>CAS No. 1558-33-4<br>  <br><br>CAS No. 2550-06-3 |

**SUMMARY CONCLUSIONS OF THE SIAR**

**Analogue/Category Rationale**

Chloroalkyl chlorosilanes are Si containing materials containing a single chloride terminated alkyl side chain of various length. Chlorosilanes, including the chloroalkyl chlorosilanes, react rapidly when exposed to moisture or polar reagents, producing hydrogen chloride (HCl; CAS No. 7647-01-0) and the corresponding silanols (in general, siloxane oligomers and polymers). The half-lives of the chloroalkyl chlorosilanes are expected to be <1 minute based on data from an analogous substance, trichloro(methyl)silane (CAS No. 75-79-6). Specifically, the silanol produced following chloroalkyl chlorosilane hydrolysis is silanediol, (chloromethyl)methyl (CAS No. 3959-16-8) for silane, dichloro (chloromethyl) methyl and silanetriol, (3-chloropropyl)- (CAS No. 64426-41-1) for silane, trichloro (3-chloropropyl). Data are available for HCl (previously assessed in the OECD HPV Chemicals Programme: http://www.chem.unep.ch/irptc/sids/OECDSIDS/7647010.pdf).

For mammalian toxicity and acute aquatic toxicity endpoints, data are provided for a structurally similar analogue and two hydrolysis products as follows:

- The sponsored substances are structurally analogous to 3-chloropropyl trimethoxysilane (CPTMO, CAS No. 2530-87-2). Silane, dichloro (chloromethyl) methyl rapidly hydrolyzes to form 1 mole of silanediol, (chloromethyl)methyl (CAS No. 3959-16-8) and two moles of HCl. Silane, trichloro (3-chloropropyl) and CPTMO hydrolyze to form 1 mole of silanetriol, (3-chloropropyl)- (CAS No 64426-41-1). Silane, trichloro (3-chloropropyl) forms 3 moles of HCl per mole of silanetriol; CPTMO forms 3 moles of methanol per mole of silanetriol. CPTMO has previously been assessed in the OECD HPV Chemicals Programme (http://www.chem.unep.ch/irptc/sids/OECDSIDS/2530872.pdf). Though not as highly unstable as the chlorosilane, CPTMO has a short hydrolysis half-life of 1 hour or less at 25 °C. Endpoints are filled in part through the use of analogues (CPTMO, DMSD) and hydrolysis products (HCl) which have similar structures or rapid hydrolysis to the same or structurally analogous silanols. The hydrolysis product, HCl, but not analogues CPTMO or DMSD, provides information on acute toxicity (e.g. site of contact and pH changes). The levels of the chloroalkyl chlorosilanes required to generate significantly toxic concentrations of silanols would result in severely corrosive HCl concentrations. It is not expected that silanetriol, (3-chloropropyl)- and silanediol, (chloromethyl)methyl can be isolated for testing as they are not stable; these silanols will condense to form highly cross-linked, high molecular weight polymers as concentration increases.

- Data for a well-studied, isolatable (stable) silanol hydrolysis product, dimethylsilanediol (DMSD; CAS No. 1066-42-8) is included to further characterize the toxicity of the sponsored substance silanol hydrolysis product.

- Although methanol is a hydrolysis product associated with the analogue substance, CPTMO, the primary human health hazard for the chloroalkyl chlorosilanes is considered to be exposure to the hydrolysis product, HCl. Human health and aquatic toxicity data for HCl are provided.

**Physical-chemical Properties**

Silane, dichloro (chloromethyl) methyl is a liquid with a melting point of -63.3 °C (calculated using MPBPVP v1.43 in EPI Suite v4.10), a boiling point of 121.5 °C (measured) and a vapour pressure of 54.4 hPa at 25°C (measured). The calculated octanol-water partition coefficient (log $K_{ow}$) is 2.5, and the calculated water solubility is 484.8 mg/L, both at 25 °C. Silane, trichloro (3-chloropropyl-) is a liquid with a melting point of -48.85 °C (calculated), a boiling point of 182.3°C (measured) and a vapour pressure of 1.54 hPa at 25°C (extrapolated). The calculated octanol-water partition coefficient (log $K_{ow}$) is 3.24, and the calculated water solubility is 64.44 mg/L, both at 25°C. The calculated water solubility and log Kow values may not be relevant because the substances are hydrolytically unstable.

**Human Health**

No data are available on the toxicokinetics, metabolism and distribution of the chloroalkyl chlorosilanes.

However, these substances rapidly hydrolyze to their corresponding silanol, and HCl on contact with moisture. Data from the silanol, DMSD, shows penetration through human skin *in vitro*. HCl will rapidly dissociate and its effects are thought to be a result of pH change.

The acute inhalation toxicity of the chloroalkyl chlorosilanes is well characterized by the effects of HCl exposure, rather than systemic effects of silanol hydrolysis products. The 4-hour acute inhalation $LC_{50}$ for silane, dichloro (chloromethyl) methyl is 6.8 mg/L (OECD TG 403); the estimated $LC_{50}$ for a 1-hour exposure is 8.39-11.04 mg/L (calculated; similar to OECD TG 403). The estimated 1-hour $LC_{50}$ for silane, trichloro (3-chloropropyl-) is 8.41-10.64 mg/L. The acute inhalation hazard posed by a chlorosilane, as defined by an $LC_{50}$ value, is directly proportional to its chlorine content and subsequently to the HCl that is liberated during hydrolysis. The principal clinical signs are expected to be indicative of respiratory and ocular effects resulting from HCl exposure. Inhalation 1-hour $LC_{50}$ values for HCl were determined to be 4.2-4.7 mg/L in rats. The approximate lethal dose (oral) for silane, dichloro (chloromethyl) methyl in corn oil was 2200 mg/kg bw (method not specified); the $LD_{50}$ for silane, trichloro (3-chloropropyl-) in corn oil was 200-2000 mg/kg bw (OECD TG 423). The oral $LD_{50}$ of CPTMO in rats was > 2000 mg/kg bw (OECD TG 401). The oral $LD_{50}$ of DMSD, was > 2000 mg/kg bw in rats; there was a general effect on condition, but no remarkable findings at necropsy (OECD TG 425). The acute oral $LD_{50}$ values of HCl were determined to be 238-277 mg/kg bw for female rats.

The chloroalkyl chlorosilanes rapidly hydrolyze to HCl and either silanetriol, (3-chloropropyl)- or silanediol, (chloromethyl)methyl. Silane, dichloro (chloromethyl) methyl was corrosive to the skin (Department of Transportation Skin Corrosion Test in Rabbits Regulation 49 CFR 173.240(9)(1)) and respiratory tract (OECD TG 403). Irritation data were not located for silane, trichloro (3-chloropropyl). HCl is corrosive and highly irritating to the skin, eyes and respiratory tract with no data reported to suggest as a sensitizer. Based on HCl formation, chloroalkyl chlorosilanes possesses properties indicating possible hazards for acute inhalation toxicity, skin, eye, and respiratory tract irritation.

No skin sensitization data were available for the chloroalkyl chlorosilanes or the appropriate analogue substance.

Repeated dose toxicity data for the chloroalkyl chlorosilanes were not available. Data from an analogous substance, CPTMO, a silanol, DMSD, and hydrolysis product, HCl, were used to fill the repeated-dose toxicity endpoint for the chloroalkyl chlorosilanes. The toxicity of the chloroalkyl chlorosilanes is well characterized by the effects of HCl inhalation exposure, the prevalent route of the chloroalkyl chlorosilanes exposure. Systemic effects following inhalation of an analogous substance (likely as a mixture with silanol hydrolysis products) are also well characterized. Although the effect of CPTMO on the urinary bladder and kidney was not observed in all repeated inhalation exposure studies, the NOAEC for this effect across all studies was considered to be 0.041 mg/L. The NOAEL for DMSD following repeated oral exposure was 250 mg/kg bw/day based on liver porphyria in male rats and liver vacuolation in female rats (OECD TG 422). By the inhalation route, during repeated dose toxicity studies, the local effects of irritation of HCl were observed in the groups of 0.015 mg/L and above in the 90-day inhalation study. The NOAEC for systemic toxicity for HCl, excluding the local effects of irritation, has been determined to be 0.030 mg/L for rats and mice. Similar effects are expected following the hydrolysis of the chloroalkyl chlorosilanes to HCl.

The sponsored substances did not induce gene mutations in bacterial cells *in vitro* (OECD TG 471). The analogous substance, CPTMO, did induce gene mutations in bacterial or mammalian cells *in vitro* but did not induce micronuclei *in vivo*. DMSD (OECD TG 471), and the hydrolysis product, HCl, did not induce gene mutations in bacterial cells. DMSD did not induce chromosomal aberrations *in vitro* in mammalian cells (OECD TG 473); positive results in the *in vitro* chromosome aberration test with HCl were considered to be the effect of low pH. Based on the available data, the chloroalkyl chlorosilanes are not expected to be genotoxic.

No data were available for the carcinogenicity of the chloroalkyl chlorosilanes.

Toxicity for reproduction data for the chloroalkyl chlorosilanes were not available. However; data were available for the analogous substance, CPTMO, the silanol, DMSD and the hydrolysis product, HCl.

In an OECD TG 422 repeated dose inhalation study in rats, exposure to CPTMO up to and including the high concentration of 0.814 mg/L did not result in any signs of developmental toxicity. Based on these results the NOEL for general or reproductive toxicity was established at 0.814 mg/L. No test substance-related effects were

observed in any of the developmental parameters evaluated following repeated oral exposure to DMSD (OECD TG 422). The NOAEL for maternal and developmental toxicity of DMSD in rats was 500 mg/kg bw/day (highest dose tested). No reliable studies have been reported regarding toxicity to reproduction and development in animals after oral, dermal or inhalation exposure to HCl. No reliable studies have been reported regarding toxicity to reproduction and development in animals after oral, dermal or inhalation exposure to hydrogen chloride/hydrochloric acid. Because protons and chloride ions are normal constituents in the body fluid of animal species, low concentrations of hydrogen chloride gas/mist or solution do not seem to cause adverse effects to animals. In fact, the cells of gastric glands secrete hydrochloric acid into the cavity of the stomach and orally administered sulfuric acid, which results in pH change as well, did not cause developmental toxicity to laboratory animals. These facts indicate that hydrogen chloride/hydrochloric acid is not expected to have developmental toxicity. In addition, no effects on the gonads were observed in a 90-day repeated-dose inhalation study up to 50 ppm. Based on data for the analogous substance and the hydrolysis product, the chloroalkyl chlorosilanes are not expected to be a reproductive or developmental toxicant.

**The chloroalkyl chlorosilanes possess properties indicating a hazard for human health (lethality from acute inhalation, corrosive and highly irritating to the skin, eyes and respiratory tract. repeated dose toxicity). Adequate screening-level data are available to characterize the human health hazard for the purposes of the OECD Cooperative Chemicals Assessment Programme.**

**Environment**

Not all programs within EPI Suite have been validated for chemicals that contain the element Si, but recent upgrades to the Kow module, found in the current version of EPI Suite (v4.10), may improve estimates for silanes and siloxanes for this endpoint. However, there is still uncertainty associated with the calculated values and they should be used with caution whenever they are reported. The chlorine group is the most active functional group on these molecules and determines many aspects of the behaviour of the category members. The chloroalkyl chlorosilanes are expected undergo rapid hydrolysis in the presence of water to form one to three moles of HCl and one mole of di- or tri- silanol, depending on the parent substance. Hydrolysis is the primary reaction in aqueous systems. Hydrolysis studies were not conducted on the chloroalkyl chlorosilanes. Using an analogous substance, trichloro(methyl)silane (CAS No. 75-79-6), the chloroalkyl chlorosilanes are expected to hydrolyze to HCl and the corresponding silanols in less than 1 minute at pH 4, 7, and 9 and 1.5 ºC. This is further supported by the data for two additional chlorosilane materials (Alkyl Chlorosilanes Category: SIAM 31: http://www.oecd.org/env/hazard/data), which were less similar structurally, but that all had half-lives of less than 1 min at 1.5 ºC. Observed rates of hydrolysis were so rapid in all cases that it was not possible to distinguish among the different pH conditions.

The overall rate constants for reaction with OH radicals in the atmosphere for the chloroalkyl chlorosilanes and resulting half-lives due to indirect photolysis are 0.54 E-12 $cm^3$/molecule-sec and 19.8 days for silane, dichloro (chloromethyl) methyl and 2.11 E-12 $cm^3$/molecule-sec and 5.1 days for silane, trichloro (3-chloropropyl) (12-h day; 1.5 E+6 OH/$cm^3$). Any potential for photodegradation might be superseded by hydrolysis of the parent compound depending on the concentration of water vapour in the air. The biodegradation of the chloroalkyl chlorosilanes was not determined due to rapid hydrolysis; any potential for biodegradation is likely to be of the hydrolysis products. Consequently, the only biodegradable materials in the test system will be silanols, and condensed silanol materials (high molecular weight polymers). No measured data are available for the hydrolysis products. At high concentrations, the silanols will condense to form highly cross linked, high molecular weight polymers that are water insoluble and effectively non biodegradable. Based on studies of DMSD in soil at 25 ºC, the substance was not readily biodegradable. HCl is an inorganic compound and biodegradation tests are not applicable.

A level III fugacity model calculation with equal and continuous distributions to air, water and soil compartments suggests that the chloroalkyl chlorosilanes will distribute mainly to the air (ca. 48 % for both substances) and soil (ca. 48% for both substances) compartments, with minor distribution to water (ca. 5%) and negligible distribution to sediments (<0.1). Since the parent materials are not expected to be released to soil or water based on its uses and handling, a scenario of 100% emission to air is more realistic. When the chloroalkyl chlorosilanes are released to air exclusively, the fugacity model predicts that 99.8% is reacted. The unreacted 0.2% remains in air (100%). The modeling results showed that the environmental fate of the chloroalkyl chlorosilanes is controlled by

its high reactivity with water in all compartments. Level III fugacity modeling using equal loading rates of 1000 kg/h each for air, soil and water predicts that the hydrolysis product silanediol, (chloromethyl)methyl-, will distribute mainly to soil (81.6%), with a smaller fraction to water (18.2%) and negligible amounts to sediment and air (0.11 and < 0.1%). Based on the more realistic scenario of 100% release to air, the model predicts that silanediol, (chloromethyl)methyl- will be distributed mainly in soil (91.6%) and water (8.3%). In the case of the other hydrolysis product, silanetriol, (3-chloropropyl)-, the results are similar; Level III fugacity modeling using equal loading rates of 1000 kg/h each for air, soil and water predicts that the hydrolysis product distributes mainly to soil (86.2%), with a smaller fraction to water (13.5%) and negligible amounts to sediment and air (0.22 and < 0.1%). Based on the more realistic scenario of 100% release to air, the model predicts that silanetriol, (3-chloropropyl)- will be distributed mainly in soil (95.5%) and water (4.4%). Fugacity modelling of HCl is not applicable.

The bioaccumulation potential of the chloroalkyl chlorosilanes was not measured due to rapid hydrolysis. An estimated BCF using the BCFBAF Program (v3.01) in is 20.7 L/kg wet-wt for silane, dichloro (chloromethyl) methyl and 64.1 L/kg wet-wt for silane, trichloro (3-chloropropyl), indicating the chloroalkyl chlorosilanes are not expected to bioaccumulate. For the hydrolysis products, silanediol, (chloromethyl) methyl, and silanetriol, (3-chloropropyl)-, the estimated BCFis 3.162 L/kg wet-wt.

Acute aquatic toxicity data are not available for the chloroalkyl chlorosilanes with the exception of an acute toxicity to daphnia study for silane, dichloro (chloromethyl) methyl. The chloroalkyl chlorosilanes undergo rapid hydrolysis, which occurs during testing; exposure to parent chlorosilane is likely to be transient and observed toxicity is likely due its hydrolysis products, HCl and the respective silanol hydrolysis products. Acute toxicity test results for analogous substance CPTMO and hydrolysis products DMSD and HCl have been determined for aquatic species:

**Fish**

CPTMO [*Brachydanio rerio*] 96 h $LC_{50}$ >100 mg/L (nominal; TOC) [semi-static]
DMSD [*Oncorhynchus mykiss*] 96 h $LC_{50}$ >126 mg/L (measured) [static]
HCl [*Cyprinus carpio*] 96 h $LC_{50}$ = pH 4.3 (= 4.92 mg/L) (measured; pH) [semi-static]

**Invertebrate**

CPTMO [*Daphnia magna*] 48 h $EC_{50}$ = 869 mg/L (nominal) [static]
DMSD [*Daphnia magna*] 48 h $EC_{50}$ >117 mg/L (measured) [static]
HCl [*Daphnia magna*] 48 h $EC_{50}$ = pH 5.3 (=0.492 mg/L) (measured; pH) [semi-static]

**Algae**

CPTMO [*Scenedesmus subspicatus*] 72 h $ErC_{50,}$ $EbC_{50}$ > 883 mg/L (nominal)
DMSD [*Pseudokirchneriella subcapitata*] 72 h $E_rC_{50}$, $E_bC_{50}$ > 118 mg/L (measured) [static]-
HCl [*Selenastrum capricornutum*] 72 h $E_rC_{50}$ = pH 5.3 (=0.492 mg/L) [static](measured; pH)

Hydrogen Chloride (HCl)

The hazard of hydrochloric acid for the environment is caused by the proton (pH effect). For this reason the effect of hydrogen chloride on the organisms depends on the buffer capacity of the aquatic ecosystem. Also the variation in acute toxicity for aquatic organisms can be explained for a significant extent by the variation in buffer capacity of the test medium. For example, $LC_{50}$ values of acute fish toxicity tests varied from 4.92 to 282 mg/L. The toxicity values to *Selenastrum capricornutum* 72h-$EC_{50}$ is 0.780 mg/L at pH 5.1 for biomass, 0.492 mg/L at pH 5.3 for growth rate and the 72h-NOEC is 0.097 mg/L at pH 6.0 for biomass and growth rate. The 48h-$EC_{50}$ for *Daphnia magna* is 0.492 mg/L at pH 5.3 based on immobilization.

**Based on the properties of the hydrolysis products, the chloroalkyl chlorosilanes possess properties indicating a hazard for the environment (acute toxicity to fish between 1 and 100 mg/L acute toxicity to aquatic invertebrates and toxicity to algae <1 mg/L). Toxic effects are expected primarily from the hydrolysis products (in particular hydrogen chloride, and depend on the buffering capacity of a particular aquatic environment. Therefore, the stated effect levels pertain to unbuffered systems and can be viewed**

**as conservative). The chloroalkyl chlorosilanes and their hydrolysis products are not expected to be readily biodegradable or to bioaccumulate. Adequate screening-level data are available to characterize the hazard for the environment for the purposes of the OECD Cooperative Chemicals Assessment Programme.**

**Exposure**

Dichloro (chloromethyl) methylsilane is not produced in the United States (the sponsor country). Trichloro (3-chloropropyl)silane is commercially produced with an annual production volume (year 2010) of 4536-11340 tonnes in the United States. The European production volume (year 2010) for silane, dichloro (chloromethyl) methyl was 454-2268 tonnes; trichloro (3-chloropropyl)silane is not produced in Europe. All (100%) of dichloro(chloromethyl)methylsilane and trichloro(3-chloropropyl)silane by volume are used as intermediates in the manufacture of organosilanes. The chloroalkyl chlorosilanes are reacted during use and lose their chemical identities.

The chloroalkyl chlorosilanes are produced and processed in closed systems. There are no intentional releases to the environment from the manufacturing processes among the companies that are sponsoring this case. Many engineering controls are in place at all the companies sponsoring this case to prevent occupational exposure and include air monitoring, process control systems, collection of off-gasses through a vent system and central incineration, on-site incineration of waste, local and general ventilation, ventilation system tied into scrubbers, nitrogen pad on system, and DCS control of process with instrumentation. Employees involved in chlorosilane production and application are required to use personal protective equipment such as chemical resistant suits, gas masks or respirators, rubber boots, protective gloves and goggles/face shields. For any situation (e.g. equipment maintenance and repair) where potential exposure to chlorosilanes is expected, the use of acid resistant protective equipment, respiratory equipment and face shield is recommended because of their irritating or corrosive properties. Environmental exposure is not expected.

There are no consumer uses of the chloroalkyl chlorosilanes.