SILICONE RESEARCH

AN INDUSTRY COMMITMENT

An initiative of
the Global Silicones Council

GSC
GLOBAL SILICONES COUNCIL

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CES - SILICONES EUROPE

American Chemistry Council | SEHSC Silicones Environmental, Health, and Safety Center

SIAJ Silicone Industry Association of Japan

CONTENTS

GLOSSARY

BENTHIC (ZONE)
The benthic zone is the ecological region at the lowest level of a body of water such as an ocean or a lake, including the sediment surface and some sub-surface layers.

BIOACCUMULATION
The relative increase in concentration of a substance from the environment (food uptake, respiration, contact) to an organism in a food chain. The bioaccumulation factor (BAF), the ratio of a chemical concentration in an aquatic organism to that in water, where exposure is from the combination of all possible routes, may be measured in either laboratory tests or using field monitoring data, and provides more information than BCF regarding accumulation of a substance by aquatic organisms.

BIOCONCENTRATION
Used to describe the concentration of a chemical in an organism derived from water uptake alone. The bioconcentration factor (BCF), the ratio of a chemical concentration in an aquatic organism to that in water, can only be measured in a laboratory experiment. This is the primary criterion used by regulators.

BIOMAGNIFICATION (BIODILUTION)
The relative increase (decrease) in concentration of a substance from one link in a food chain to one other (i.e. from one trophic level to the next.). The biomagnification factor (BMF), the ratio of a chemical concentration in an aquatic organism to that in its food or prey, may be measured in either laboratory tests or using field monitoring data. A BMF significantly greater than one (1.0) is indicative of biomagnification. A BMF significantly lower than one is indicative of biodilution. The BMF provides more information than BCF or BAF regarding accumulation of a substance by aquatic organisms.

BIOTA-SEDIMENT ACCUMULATION FACTOR (BSAF)
A point measure that is determined as the ratio of the lipid-normalized biota concentration to the organic carbon-normalized sediment concentration.

CES
CES - Silicones Europe, a sector group of the European Chemical Industry Council (Cefic)

cVMS
Cyclic volatile methylsiloxanes

DEMERSAL (ZONE)
The demersal zone is the part of the sea or ocean (or deep lake) comprising the water column that is near to (and is significantly affected by) the seabed and the benthos. The demersal zone is just above the benthic zone.

D4
Octamethylcyclotetrasiloxane

D5
Decamethylcyclopentasiloxane

ECHA	The European Chemicals Agency
FUGACITY (MODEL)	The fugacity model is a model in environmental chemistry that summarizes the processes controlling chemical behavior in environmental media by developing and applying of mathematical statements or "models" of chemical fate. Most chemicals have the potential to migrate from medium to medium. Multimedia fugacity models are utilized to study and predict the behavior of chemicals in different environmental compartments.
LTMP	Long Term Monitoring Program
NOEC	No Observed Effect Concentration
PBT	A compound that exceeds regulatory thresholds for all three factors of Persistence, Bioaccumulation and Toxicity. Regulatory thresholds for persistence, bioaccumulation and toxicity vary between regions of the world.
vPvB	A compound that exceeds regulatory thresholds for being both very persistent and very bioaccumulative. Toxicity is not considered in the designation of a vPvB compound.
PEC AND PNEC	A substance is judged environmentally compatible if the Predicted No Effect Concentration (PNEC) --that is, the concentration that causes no adverse effect to the Environment--is higher than the Predicted Environmental Concentration (PEC) --which is the concentration one expects to find in the environment.
PELAGIC (ZONE)	The pelagic zone is the part of the open sea or ocean that is not near the coast or sea floor.
POP	Persistent Organic Pollutant: a compound similar to PBT, but that is also transported to remote regions of the world *and* is detectable in surface waters or on land in those remote regions (i.e., it back deposits).
SEHSC	The Silicones Environmental, Health, and Safety Center, a sector group of the American Chemistry Council (ACC).
SIAJ	The Silicone Industry Association of Japan.
SILICONES	Silicones are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen.
TROPHIC MAGNIFICATION FACTOR (TMF) AND TROPHIC DILUTION FACTOR	The average relative increase (decrease) in concentration of a substance over an entire food chain. The trophic magnification factor (TMF) is calculated from concentrations of a chemical in multiple species in a food chain or food web in natural waters.
VMS	Volatile methylsiloxanes
WEIGHT OF EVIDENCE (WOE)	A method used to assess the strength (quality of the work) and relevance (to an assessment endpoint) of scientific data for the purposes of decision-making.
WWTP	Waste Water Treatment Plant

EXECUTIVE SUMMARY

Silicones are among the world's most important and adaptable raw materials, used in literally thousands of products and applications – from healthcare, aerospace and personal care, to electronics, transportation, construction and energy. Silicones are produced by reacting silicon—one of the earth's most common elements- with methyl chloride and further reaction with water which removes the chlorine atom. This reaction mainly produces linear and cyclic siloxanes characterised by a chain of alternating silicon and oxygen atoms. Siloxanes are then further reacted into longer chains to form silicone polymers.

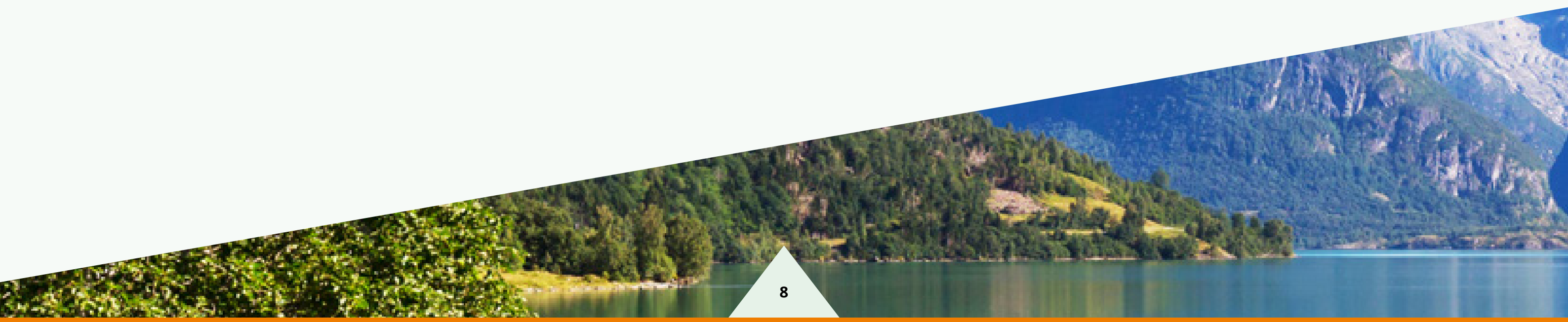
Their exceptional breadth of chemical and physical properties makes silicones important to achieving innovation in key sectors of the economy. Because they are flexible and resistant to moisture, chemicals, heat, cold and ultraviolet radiation, they also make products more stable, easier to use, more affordable and longer-lasting.

The common building blocks used to manufacture polymeric silicones are known as low molecular weight volatile methylsiloxanes (VMS), which have cyclic or linear oligomers. These oligomers share a common chemistry but each substance is different with regard to its specific properties and uses. The most common VMS in commercial use are the cyclic VMS compounds octamethylcyclotetrasiloxane (known as D4), decamethylcyclopentasiloxane (known as D5) and dodecamethylcyclohexasiloxane (known as D6). Common linear VMS compounds include hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and dodecamethylpentasiloxane (L5). The vast majority of VMS are used as building blocks to make silicone polymers; however, small quantities are used in 'direct uses', primarily in some cosmetic products.

VMS have come under scrutiny in the last few years for meeting strict bright line Persistence (P) and Bioaccumulation (B) criteria. Because of their widespread use, as part of the Silicones Industry's commitment to the safety of its products and its sound product stewardship practices, the industry has proactively conducted several VMS modelling and monitoring initiatives to enable active engagement in addressing concerns as they arise.

Models that can estimate a chemical's physicochemical properties and potential environmental fate and concentration are important tools for academics, industry, and regulators. The VMS materials have a unique combination of partition coefficients between air, octanol, and organic carbon, which differ significantly from the traditional organic chemicals (e.g. PCBs) that comprise many models' domain of applicability. Thus, the Silicones Industry has collaborated with modelling experts around the world to customize the input parameters of these models based on the properties of the chemical being modelled.

The Silicones Industry also has committed to several programs aimed at measuring concentrations of VMS around the world to customize and validate these models. These programs are focused on two environmental compartments; the atmosphere and aquatic environments. The volatile nature of VMS makes the atmosphere a relevant environmental compartment, while aquatic environments receive inputs of VMS materials from wastewater treatment plants (WWTPs). Data generated from these programs demonstrate



that concentrations of VMS do not pose a risk to the environment. These data can be used to determine whether any temporal and/or spatial trends in concentration of VMS are occurring in the environment. Additionally, data generated from these programs also demonstrate that concentrations of VMS do not pose a risk to the environment.

Although the use of silicone in general, including polymers and formulated silicone products, has grown in general[1], the Silicones Industry believes that concentrations of cyclic and linear siloxanes in the environment will decrease significantly in the future because the amounts in cosmetic products, which have wide dispersive uses with release to water, such as shampoos and conditioners, have been declining.

By monitoring releases and measured environmental concentrations whilst applying a probabilistic risk assessment approach that allows for inclusion of actual measured field data, the Silicone Industry has already demonstrated that the concentrations in the aquatic environment continue to be within safe limits. Based on multiple lines of evidence, which included persistence, bioaccumulation, toxicity, and long-range transport, a quantitative weight of evidence assessment concluded that D4, D5, and D6 should not be classified as P, B, or T, or as vP or vB, and that that there is no evidence that they are accumulating in remote regions.

Cyclic and linear VMS also will not deposit from the air to the earth's surface. Cyclic and linear VMS show significantly higher volatility due to an unusual combination of solubility and partitioning properties. They also are readily degraded in air. Model calculations and remote monitoring data from credible studies using appropriate quality controls support that back-deposition from the atmosphere to the earth's surface is negligible.

The Silicones Industry continues to work with scientists and regulators to demonstrate the safety of VMS materials so that the global society can continue to benefit from the multiple and unique attributes of silicones.

The Silicones Industry will continue to advocate for basing regulatory assessments on the best available science. With this approach, the industry believes that assessments of VMS materials will demonstrate both their safety and their positive impact on the global society.

Signatories

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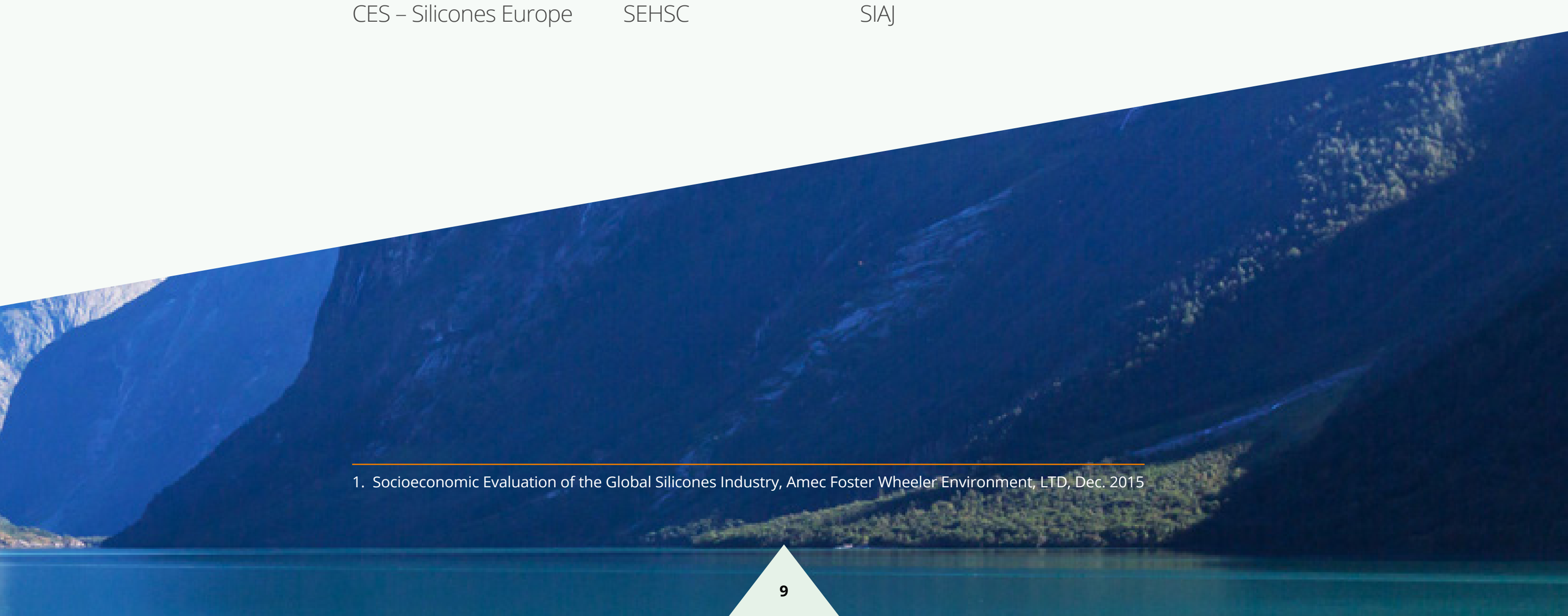


1. Socioeconomic Evaluation of the Global Silicones Industry, Amec Foster Wheeler Environment, LTD, Dec. 2015

WHY SILICONES MATTER

Silicones are high-performance polymers that can take a variety of physical forms – from solids to water-thin liquids, semi-viscous pastes and oils. They are used in nearly every industry and have revolutionized thousands of products in use today.

They are game changers for many critical applications in the fields of medicine, energy, transport, technology, and engineering.

Silicones are used in a wide range of health and medical applications. They serve as coatings for hypodermic needles, ensure high oxygen permeability in hydrogel contact lenses, and are used in tubing in a wide range of medical devices including insulin pumps. They are also particularly suitable in prosthetics devices due to their hypoallergenic properties and wide range of physical properties.

In aerospace and automotive applications, silicone products increase the efficiency and lifespan of vital components such as airbags, while in railway locomotives they provide tough, long-lasting motor insulation and lubricants for bearings.

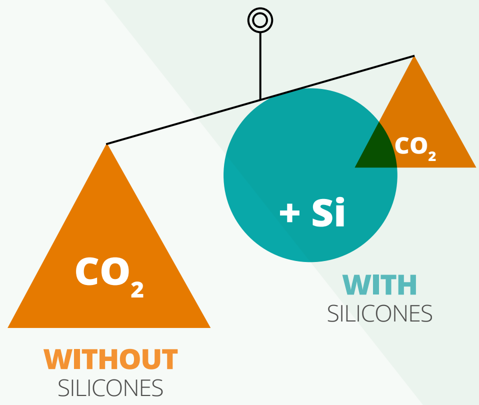
Silicones are used as sealants for windows, as caulking for bridges and bathroom tiles, and as coatings to protect facades and historical monuments.

In electronics, silicones are used as coolants in transformers, protective encapsulating material for semiconductors, and foam-control agents in the manufacture of many types of products.

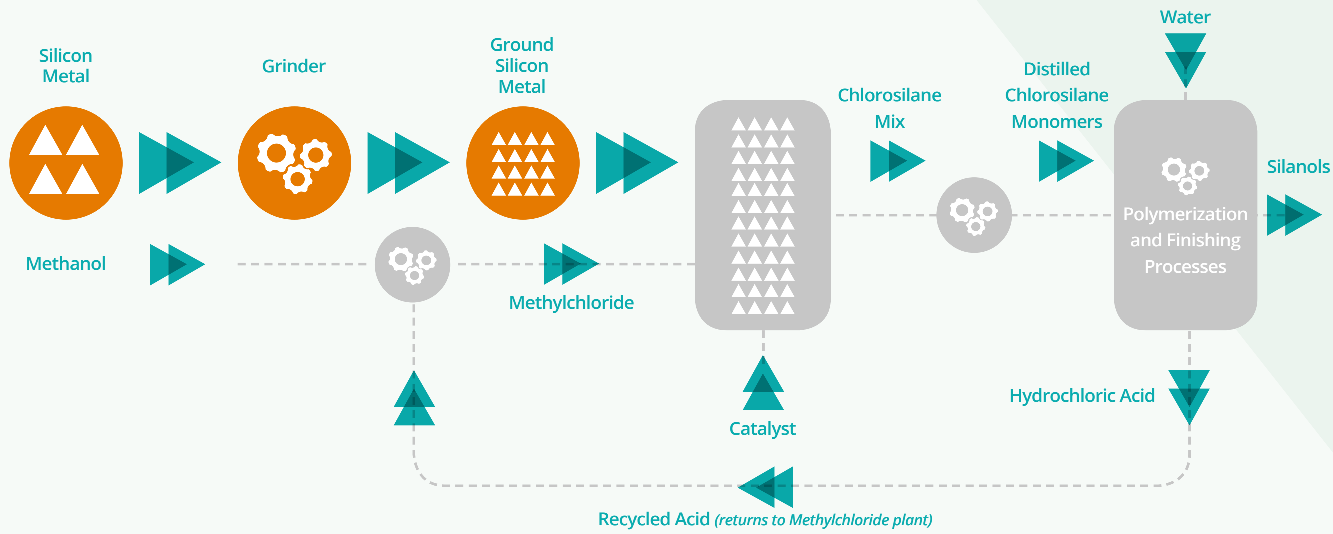
In our kitchens and throughout our homes, silicones are known for their versatility and convenience. Silicone kitchenware is durable, easy to clean, lightweight and stain-resistant. In the household, silicones are used as antifoams in detergents, which enable lower washing temperatures, thereby saving energy. Silicones spread easily and protect surfaces, making them an ideal component for polishes or cleaning agents for household surfaces.

Silicones also are used in products that produce renewable energy and in energy saving applications; everything from wind turbines, solar panels, LEDs and green tires rely on silicone technology.

Furthermore, the use of silicones, siloxanes and silanes generates energy savings and greenhouse-gas emission reductions that outweigh the impacts of production and end-of-life disposal by a factor of nine[2].



Silicones are produced by reacting silicon – one of the earth's most common elements – with methyl chloride and further reaction with water, which removes the chlorine atom. The chlorine atom is then recycled to make methyl chloride. This reaction is the first step in producing polymers resistant to both high and low temperatures.



Only a relatively small quantity of silicones, siloxanes or silanes can lead to a comparatively large increase in the efficiency of processes and the use of energy and materials. Examples include high-performance thermal insulation products, foam-control agents for washing, paint additives that increase the durability of vehicles and construction materials, and silanes used to reduce the rolling resistance of tires.

"Silicones help make things work better."

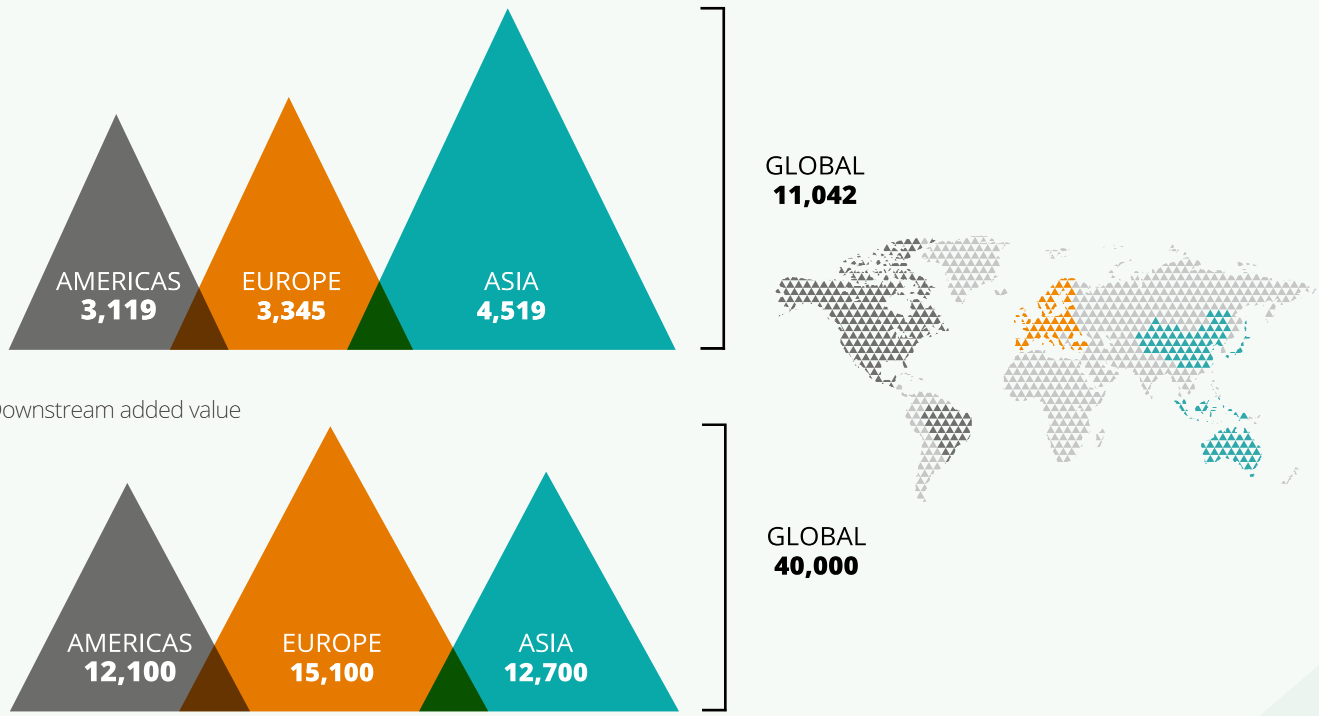
2. A study commissioned by the GSC from the sustainable development research firm Denkstatt in Austria, in association with Dekra, a German testing and certification company, assessed the greenhouse-gas emissions and emission-reduction effects linked to the manufacturing, use and waste management of silicon-chemistry products in Europe, North America and Japan. www.siliconescarbonbalance.eu

THE SILICONES INDUSTRY

In November 2014, the Global Silicones Council (GSC) commissioned Amec Foster Wheeler to carry out an independent socioeconomic evaluation of the contribution made by the silicones industry to the global economy. The study found that an estimated 2,122, 000 tons of formulated silicone products were sold worldwide to eight "key markets" and that these sales supported a further $39.9 billion of downstream added value globally. The study also revealed that silicone manufacturing alone directly employs just under 30,000 people across the globe and that up to 14 million employees may be involved in some form of economic activity that involves silicone products. The silicones supply chain in eight key markets is summarized in the chart below[3].

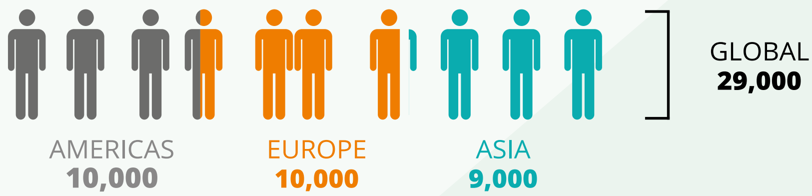
TURNOVER / REVENUE

Annual turnover of silicones by global regions ($ million, 2013)



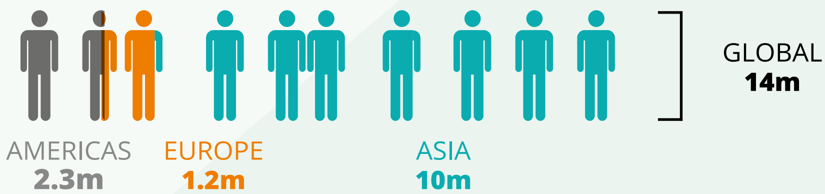
DIRECT EMPLOYMENT

Number of employees by region (2013)



EMPLOYMENT ALONG SILICONE SUPPLY CHAINS

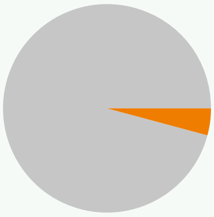
Number of employees by region (2013)



3. Socioeconomic Evaluation of the Global Silicones Industry, Amec Foster Wheeler Environment, LTD, Dec. 2015

GLOBAL INVESTMENT IN RESEARCH AND DEVELOPMENT (R&D)

Research and development expenditure related to silicones (2013)



THE SILICONE SUPPLY CHAIN — SALES TO KEY SECTORS

Downstream applications of silicones (tonnes and values, 2013)

	Transport	Construction materials	Electronics	Energy	Healthcare	Industrial processes	Personal care and consumer products	Special systems	**TOTAL**
TOTAL QUANTITY SOLD (000S OF TONNES)	118	548	61	42	28	746	357	222	**2,122**
TOTAL VALUE OF QUANTITY (€M)	1,204	2,176	1,006	280	379	2,867	1,900	1,440	**11,252**

The Global Silicones Council (GSC) (www.globalsilicones.org) is a not-for-profit, international organization representing companies that produce and sell silicone products around the world. The GSC brings together all the major global manufacturers via the three Regional Silicone Industry Associations in North America (Silicones Environmental, Health, and Safety Center – SEHSC), Europe (CES - Silicones Europe), and Japan (Silicones Industry Association of Japan – SIAJ), and encourages their cooperation and collaboration. These companies include Bluestar Silicones, Milliken, Evonik, Dow Corning, Momentive, Shin-Etsu Silicones, and Wacker.

Together they promote the safe use and stewardship of silicones and commission, co-ordinate and guide scientific research on questions of health, safety and the environment.

The Silicones Environmental, Health, and Safety Center (SEHSC) represents over 90 percent of silicone chemical manufacturing capacity in North America and is managed in the Chemical Products and Technology Division (CPTD) of the American Chemistry Council (sehsc.americanchemistry.com).

CES - Silicones Europe (www.silcones.eu) is a non-profit trade organization representing all major producers of silicones in Europe. CES is a sector group of the European Chemical Industry Council (Cefic).

The Silicone Industry Association of Japan (SIAJ) (www.siaj.jp/en) represents companies that produce and sell silicone products in Japan. SIAJ was founded in 1967 and consists of five companies today.

BRIEF OVERVIEW OF THE REGULATORY LANDSCAPE

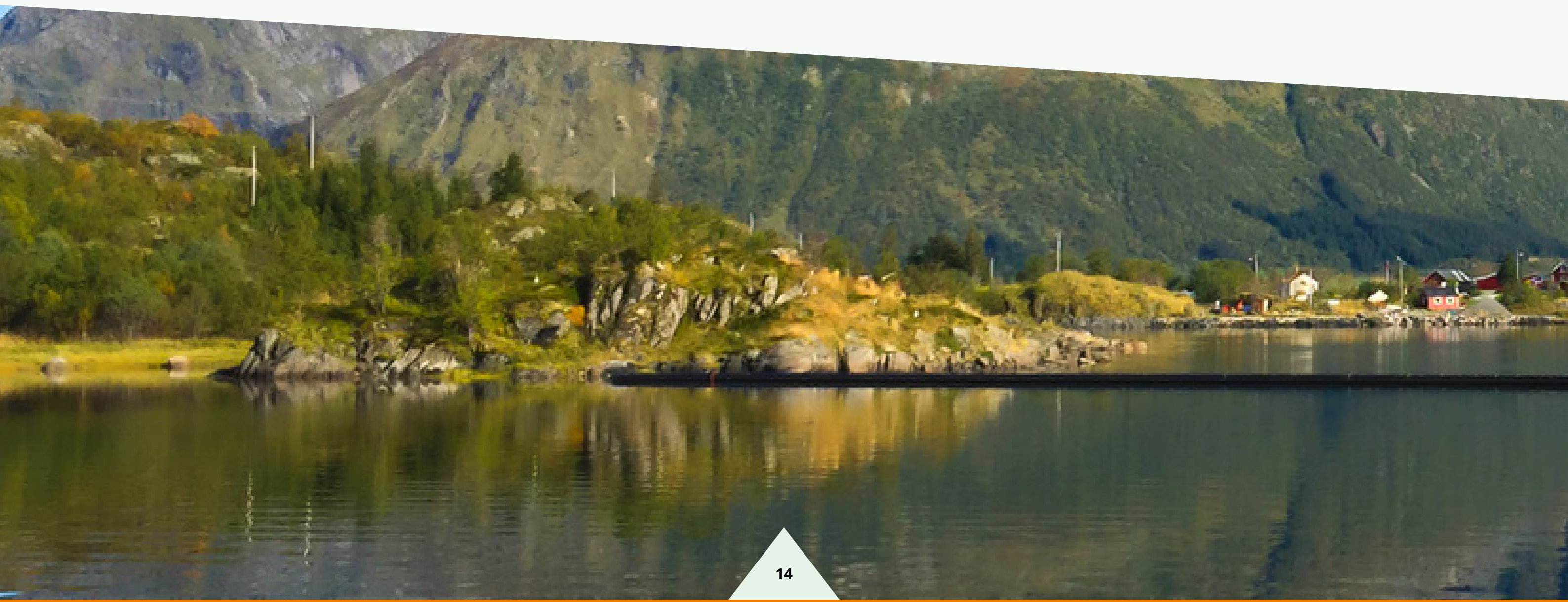
In Canada, an independent panel of scientists (known as a "Board of Review") reviewed all the data on D5 and concluded that "siloxane D5 does not pose a danger to the environment or its biological diversity", leading the Canadian Environment Minister to decide in 2012 that no action was needed to limit the use of the substance. In addition, Environment Canada, having reviewed the environmental data available for D4, has not imposed any product concentration restrictions on the use of D4 in any application but focused their Pollution Prevention Plan on D4 in industrial effluents[4]. The Government of Canada has also reviewed cyclic VMS D6 and the linear VMS compounds L2, L3, L4, and L5 and came to the same conclusions, that no action was needed to limit the use of these substances.

The United States Environmental Protection Agency (US EPA) released its intent to develop a chemical action plan ("CAP") for Siloxanes in March 2010. Six siloxanes deemed representative of the class were the subject of a 1996 Memorandum of Understanding (MOU) between the US EPA and Dow Corning Corporation. Dow Corning initiated a Product Stewardship Program under the MOU, from which a comprehensive human health of dataset was released in 2009. EPA indicated, "Following the theme of selecting chemicals for which chemical management actions have already been taken, these six "representative" siloxanes are likely to be singled out in the upcoming CAP for siloxanes." Subsequently, following submission of all Health and Environmental data on the six siloxanes to EPA and engagement with EPA health and environmental experts, EPA communicated it would be pursuing a CAP on D4 and D5 for an environmental assessment only. In a Federal Register Notice on May 24 2012, EPA considered both octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) for the collection of certain environmental monitoring data. In an April, 2014, FR Notice however, EPA withdrew the consideration of D5 in the official enforceable consent order and issued a testing consent order that incorporated an Enforceable Consent Agreement (ECA) with the members of the Silicone Industry of North America to collect certain environmental monitoring data on D4 only. The Silicones Industry members agreed to certain environmental testing that will be used by the EPA to characterize sources and pathways of release of D4 to the environment and resulting exposures of aquatic and sediment dwelling organisms, contributing to the Agency's efforts to understand potential environmental effects of D4. The environmental monitoring of D4 under the ECA was completed in 2017.

In Europe, a restriction prohibiting the use of D4 and D5 in wash-off cosmetic products was adopted in 2017 under the REACH legislative framework. This restriction was based on an Opinion from the European Chemicals Agency concluding that D4 meets the REACH criteria for Persistent, Bioaccumulative and Toxic (PBT) and very Persistent very Bioaccumulative (vPvB) substances and D5 meets the REACH Annex XIII criteria for a vPvB substance. Whilst this assessment is in sharp contrast with the conclusions reached in other jurisdictions and although the silicones industry does not believe that there is a need to restrict any uses of D4 and D5, the industry is committed to the successful implementation of this restriction. Other regulatory assessments of siloxanes are under way in Europe.

Other regions are also evaluating cVMS, and the silicones industry remains engaged with the authorities to address any questions and provide all of the robust data available on these substances.

4. www.cyclosiloxanes.org/D4_health_environment_properties



PRODUCT STEWARDSHIP – MODELLING INITIATIVES

Properties of VMS materials indicate that they may meet Persistent, Bioaccumulative or Toxic (PBT) and/or very Persistent and very Bioaccumulative (vPvB) criteria outlined in various regulatory frameworks. As a result, there has been an increased interest in the assessment of the VMS materials within these frameworks on a global scale. This prompted the Silicones Industry to voluntarily initiate modelling and monitoring projects and gather more data to better inform such assessments.

Models that can estimate a chemical's physico-chemical properties and potential environmental fate are important tools for academics, industry, and regulators. The VMS materials have a unique combination of partition coefficients between air, octanol, and organic carbon, which differ significantly from the traditional organic chemicals (e.g. PCBs) that comprise many models' domain of applicability. In an effort to make these models more useful in the evaluation of VMS materials, the silicone industry has supported research that has enabled significant strides to be made in the area of environmental modelling including siloxanes in their domain. These models have been further validated by comparison to actual field monitoring data. This progress provides value to the assessment of siloxanes, and increases the scientific and regulatory communities' understanding of complex chemistries.

UNIQUE CHEMISTRY OF SILOXANES

VMS are the base compounds for the silicone chemistry. Current standard tools to assess chemicals for regulatory review (e.g. environmental fate models and OECD guideline tests) were developed for organic substances that rely on a carbon (C-C) backbone. In contrast, VMS, as well as all silicones, rely on a silicon/oxygen (Si-O-Si) backbone that only uses organic chemistry as a reactant. The backbone of inorganic silicon and oxygen atoms combined with the organic functionality drives the unusual combination of physical/chemical properties that makes them distinctly different from carbon chemistry. This combination of fundamental intrinsic properties is not observed among carbon-based organic compounds, and is especially different from the traditional hydrophobic organic compounds.

Examples of such physical/chemical properties include:

- high hydrophobicity/lipophilicity
- low water solubility
- volatility (high vapor pressure relative to organic compounds of the same size and high air/water partitioning [Henry's Law Constant])
- large molecular size
- very low polarizability
- significant hydrogen bond acceptor character
- higher bond strength of Si-O bond compared to Si-C bond
- undergoes biotransformation in organisms (aquatic and terrestrial)

Consequently, siloxanes possess a different combination of solubility and partitioning properties that influence their distribution and fate in the environment compared to traditional hydrophobic organic compounds:

- High K_{AW} – will prefer air relative to water
- High K_{AW} and relatively low K_{OA} – will prefer air relative to lipid in organisms
- High K_{AW} and low K_{OC}/K_{AW} ratio – will prefer air relative to soil

The application of criteria developed around classic organic chemicals, such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) may not be appropriate for emerging chemistries, such as VMS. Given the importance of silicones for the day-to-day well-being of society, it is therefore crucial to assess the potential fate and effects of these materials correctly and with the highest confidence.

MODELS TO PREDICT ENVIRONMENTAL FATE

Use of fugacity-based modeling to estimate partitioning and distribution of a chemical in the environment was advocated as part of the High Production Volume (HPV) Challenge Program, and the Organization for Economic Cooperation and Development (OECD). In brief, the EQuilibrium Criterion (EQC) model is a fugacity-based mass balance of a defined chemical in a defined evaluative environment. The general aim is to provide a picture of the likely fate of the chemical in an evaluative environment or a "unit world" by applying a series of models with increasing data requirements and complexity. It is not intended to simulate fate and transport in a real environment, but it can be used to identify monitoring strategies and to suggest the key processes that must be addressed in subsequent real simulation models. It is most useful when applied to a new chemical or to a chemical of unusual properties for which there are few environmental monitoring data.

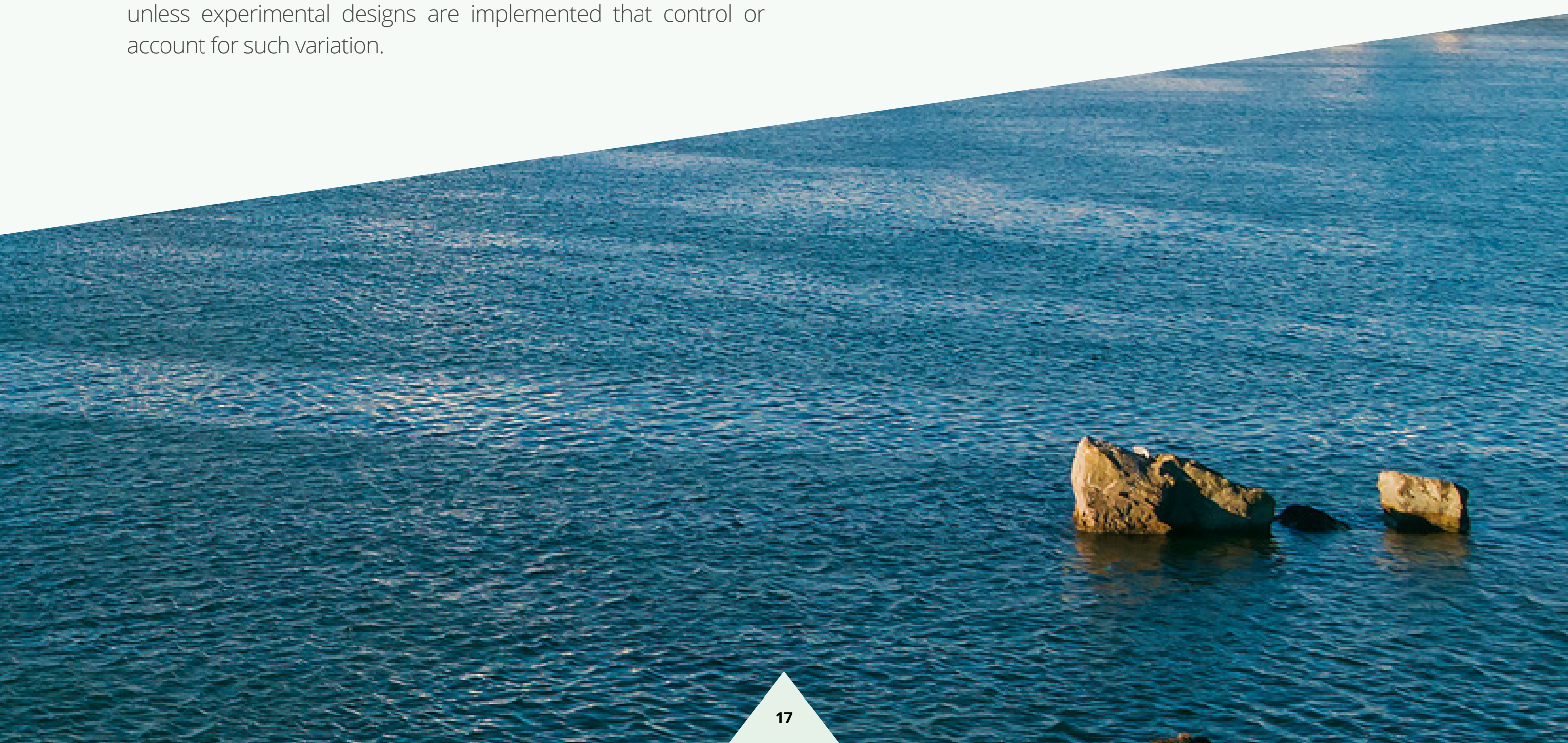
The original version of the EQC model was released in 1996. Based on scientific advancements and user feedback, the EQC model was subsequently updated to be more responsive to current regulatory needs and reflective of the state of the science. The new EQC model includes improved treatment of input partitioning and reactivity data, temperature dependence and provides a basis for facilitating sensitivity and uncertainty analysis (Hughes et al., 2012). D5 was considered a good example of a substance that requires evaluation using the updated EQC model because of its unusual combination of properties, namely a high vapor pressure and a low water solubility resulting in a very high K_{AW}, a large K_{OW} but only a moderately high K_{OC}, and a wide range of media-specific half lives. It is worth noting that the experimentally determined K_{OC} is three orders of magnitude lower than the K_{OW}. In the original EQC model, the K_{OC} is calculated from the K_{OW} using the Karickhoff approximation $K_{OC} = 0.41K_{OW}$, which results in greatly overestimated sorption coefficients for all solid media. It is also interesting that the reported K_{AW} of D5 is an order of magnitude higher than that, which would be calculated from the solubility and vapor pressure value reported from other sources. These differences could result in very different fate scenarios, thus highlighting the importance of being able to directly input known partition coefficients for substances that fall outside of the model's domain of applicability.

The Quantitative Water Air Sediment Interaction (QWASI) fugacity mass balance model has been widely used since 1983 for both scientific and regulatory purposes to estimate the concentrations of organic chemicals in water and sediment, given an assumed rate of chemical emissions, advective inflow in water or deposition from the atmosphere. It became apparent that an updated version was needed, especially to incorporate improved methods of obtaining input parameters such as partition coefficients. Accordingly, the model was revised and applied to two chemicals, D5 and PCB-180, in two lakes, Lake Pepin (MN, USA) and Lake Ontario (NY, USA and ON, CA), showing the model's capability of illustrating both the chemical-to-chemical differences and lake-to-lake differences (Mackay et al., 2014). The new QWASI water quality model can be of value for both evaluative and simulation purposes, thus providing a tool for obtaining an improved understanding of chemical mass balances in lakes, as a contribution to the assessment of fate and exposure, and as a step towards the assessment of risk.

MODELS TO PREDICT BIOACCUMULATION POTENTIAL

Several metrics for assessment of chemical bioaccumulation in aquatic organisms and food webs can be considered, including the octanol-water partition coefficient (K_{OW}), bioconcentration factor (BCF), bioaccumulation factor (BAF), biomagnification factor (BMF), and trophic magnification factor (TMF). The BCF is often preferred over K_{OW} (considered a surrogate for lipid-water partitioning in aquatic biota) because the BCF is predictive of biomagnification for hydrophobic chemicals that undergo little to no metabolism. However, the BCF is determined under laboratory conditions that are often not realistic for poorly soluble, volatile chemicals. In addition, the BCF does not include dietary exposures and hence excludes the potential for biomagnification via the diet. In the environment, the diet is often the dominant exposure pathway for very hydrophobic chemicals and the need to consider bioaccumulation metrics that include dietary exposures is generally well recognized. Field-derived BMFs and TMFs are environmentally relevant because they include all routes of chemical exposure and ecosystem processes. It is notable that TMF and BMF, which were proposed as the most relevant metrics for the identification and categorization of bioaccumulative chemicals, are explicitly included in weight-of-evidence assessments of bioaccumulation under REACH. Similarly, it has been proposed that the greatest weight-of-evidence ought to be given to high quality field studies when assessing the potential for bioaccumulation and biomagnification (Bridges and Solomon, 2016). However, interpretation of field data is susceptible to systematic bias because of uncertainty due to spatial heterogeneity and temporal variability in environmental concentrations, uncertainty in trophic interactions, species migrations and organism home range, limited statistical power, and other ecosystem-specific factors such as sediment-water disequilibrium conditions. In some cases, the between-study and within-study variability in exposure conditions is so great that the field data may be questionable and its usefulness severely limited unless experimental designs are implemented that control or account for such variation.

The Silicones Industry has recognized these challenges during the course of conducting field studies to assess the trophic transfer of the cyclic VMS materials in aquatic ecosystems. In an effort to advance the field of bioaccumulation assessment, a collaborative study was initiated with Drs. Don Mackay, Frank Gobas, and Jon Arnot, recognized experts in the field of bioaccumulation science. As a result of this work, two recent publications have been published in the peer-reviewed literature (Kim, et al., 2016; Mackay, et al., 2016) illustrating advancements in understanding factors that influence a chemicals ability to biomagnify in the aquatic environment.



PRODUCT STEWARDSHIP – MONITORING INITIATIVES

The Silicones Industry has committed to several product stewardship initiatives to better understand the presence and behavior of cyclic and linear siloxanes, the chemical building blocks used in many silicones, in the environment. This research focuses on two environmental compartments; the atmosphere and aquatic environment. The volatile nature of VMS makes the atmosphere a relevant environmental compartment, while aquatic environments may receive inputs of VMS materials from WWTPs, which process influent from residential and industrial sources. Sponsored research programs include:

Presence and Behavior of VMS in Air

- Presence of VMS in air
- Estimates of degradation half-lives
- Assessment of the potential for long-range transport

Long-Term Monitoring of VMS Concentrations in Aquatic Environments

- Lake Ontario, Canada & United States
- Lake Pepin, Minnesota, United States
- Oslofjord, Norway
- Tokyo Bay, Japan

Monitoring of VMS Concentrations in Waste Water Treatment Plants

- Support of JRC WWTP study
- D4 Enforceable Consent Agreement in the United States
- Monitoring influent to WWTPs in Europe

PRESENCE AND BEHAVIOR OF VMS IN AIR

PRESENCE OF VMS IN AIR

VMS tends to be distributed mainly to air (> 95%). In air, it is well established that VMS readily degrades by interaction with OH radicals. VMS are mainly released from urban centers where the OH radical concentrations are much higher than the global average OH radical concentration used to estimate their current half-lives. As a consequence, only a small fraction of VMS may reach the remote parts of the atmosphere. For example, the measured VMS concentrations in the Arctic air are hundreds of times lower than those in the source region (Yucuis et al., 2013; Krogseth et al., 2013).

Very recent work using actual monitoring data demonstrates that the real life degradation of VMS in air may be much faster than what is currently estimated (Xu and Warner et al., 2017 submitted publication) and involve other mechanisms beyond OH radical degradation. This work suggests a calculated real-life half-life closer to 2 days. Discussions with experts from Norway, Stockholm University and Canada at the 2016 SETAC conference provided support for this hypothesis and an ongoing collaboration with these experts is underway to further explore this hypothesis.

Very little airborne VMS will deposit from air to surface compartments in the environment due to their unique combination of partition coefficients (high K_{AW} and relatively low K_{OA}, or High K_{AW} and low K_{OC}/K_{AW} ratio), and thus airborne VMS in the remote part of the atmosphere will result in little exposure to surface media.

The conclusion that VMS will not deposit to the terrestrial environment of remote regions, regardless of their half-lives in the atmosphere, is further supported by multimedia modeling assessments (Xu and Wania, 2013), using the OECD overall persistence and long range transport screening tool (Wegmann et al., 2009) and the GloboPOP model (Wania, 2006).

POTENTIAL FOR LONG-RANGE TRANSPORT

Until now the half-life of VMS has been modeled using a model that relies on only one known degradation mechanism (indirect photolytic degradation), which led to the following estimates for Long-Range Atmospheric Transport/Deposition Potential.

Compound	τ_A (Day)	P_{OV} (Day)	mCTD (km)	TE (%)	$eACP_{10}$ (%)
D4	10.6	15.3	5260	0.016	5.4E-6
PCB 28	10.3	540	4930	2.1	0.2
HCB	396	12080	153000	1100	2.7

τ_A = Half-lives in air (OH radical mechanism only)
P_{OV} = Overall persistence
mCTD = Model-estimated characteristic travel distance
TE = Transfer Efficiency
$eACP_{10}$ = Absolute Arctic contamination Potential after 10 years' constant release

It needs to be noted that the accuracy of the estimated CTD (Characteristic Travel Distance) values is dependent on the accuracy of τ_{AIR} of all combined degradation mechanisms:

- CTD (km) ≈ 497 τ_{AIR} (day)
- Half-life of D4 in air (τ_{AIR}) used in modeling is not accurate
- Reaction with OH• is the only mechanism considered
- Multiple sets of rate constants (1-2.2x10^{-12} cm^3/molec-s)*
- Multiple values of average [OH] conc (5x10^5 (EU)- 7.5x10^5 molec/cm^3 (Global)

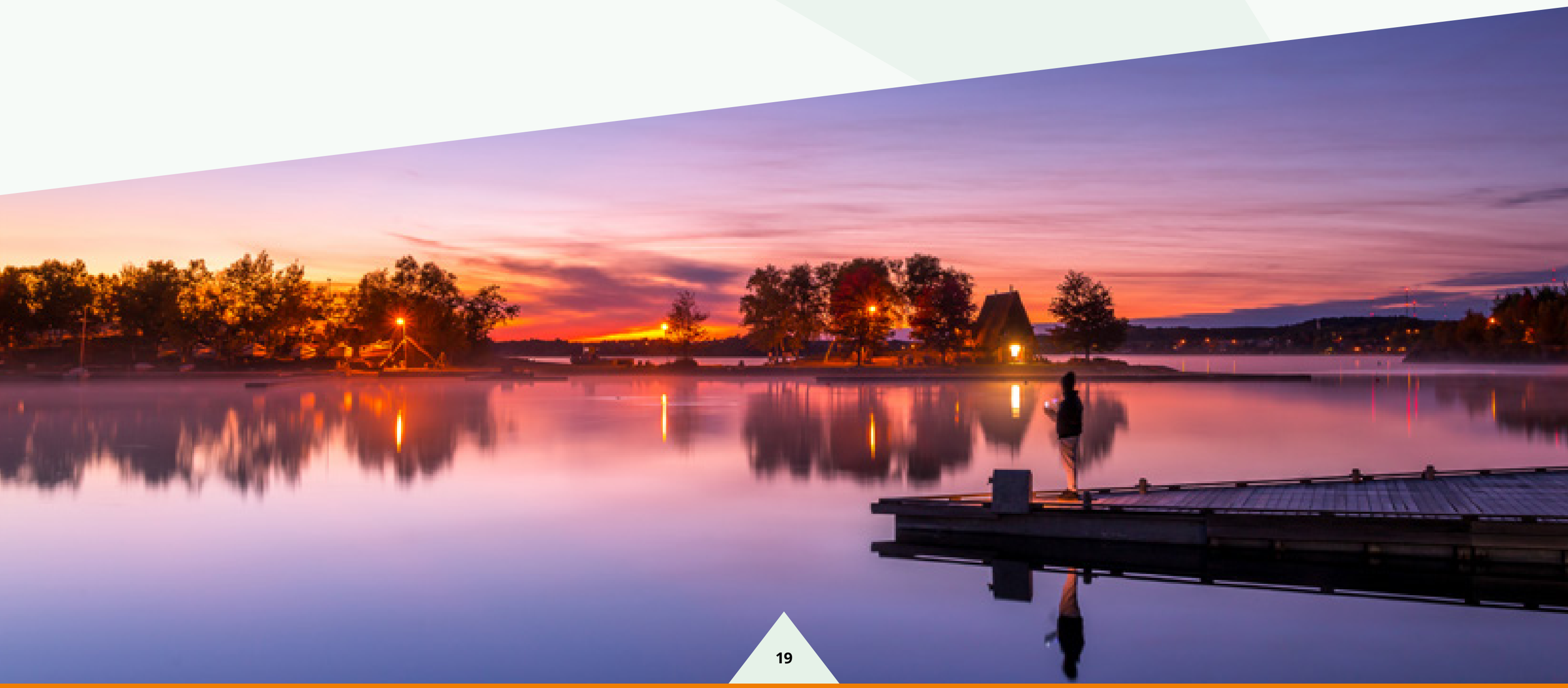
Available air monitoring data suggest a very different picture:

Data Sources: Published reports. Air Sampling Locations: All N-Hemisphere; Source regions (black) in NA and Europe; European rural (orange) and Arctic (green) locations. Sampled Times: 2004, 2005, 2009-2015

Log concentrations of cVMS decreased linearly as the sample latitude increased from the source region (around 40 °N) to the remote locations at high latitude. The decrease was much steeper than what may be predicted using the known cVMS half-lives based on either the global or the European hydroxyl radical concentrations.

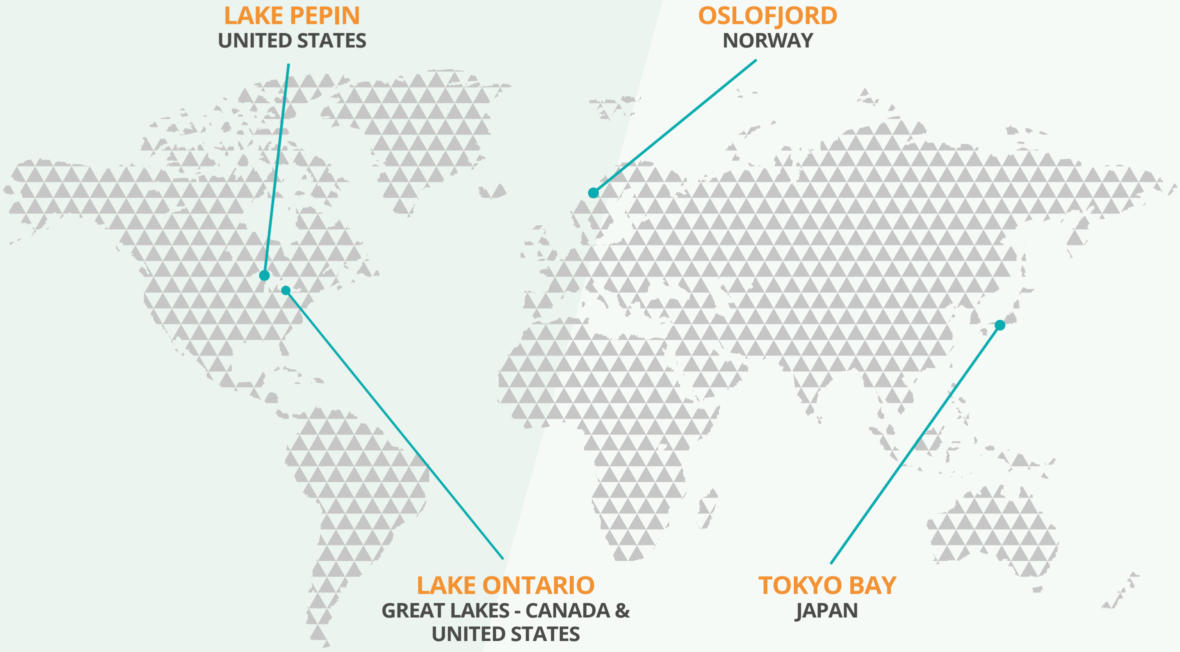
cVMS concentrations were highly correlated with each other from the same samples; the none-unit slopes suggest the removal rates of D5 > D4 > D6.

In contrast to the modeled air half-life of >10d (10.6 days for D4) it is now thought that the air half-life in the real environment is significantly smaller (2.2 days for D4, 2.0 days for D5 and 3.1 days for D6) based on the spatial patterns of concentrations and concentration ratios. Currently GSC is seeking to conduct more studies in collaboration with regulators and academia to substantiate and validate these findings.



OVERVIEW OF LONG TERM MONITORING OF VMS IN AQUATIC ENVIRONMENTS

The Silicones Industry is conducting a long-term monitoring program for VMS at four locations around the world in order to provide a representative picture of their presence and behavior in the aquatic environment. These locations are representative of a wide range of aquatic environments, including both freshwater and marine ecosystems and spanning subtropical to cool temperate climates. All study areas are located near highly populated areas, thereby experiencing significant anthropogenic impacts.



The sites selected for inclusion in the LTMP are:

1. Lake Ontario, Great Lakes, Canada & United States
2. Lake Pepin, Minnesota, United States
3. Oslofjord, Norway
4. Tokyo Bay, Japan

The primary objective of this monitoring program is to determine if concentrations of cyclic VMS materials in surface sediments and aquatic biota are stable or changing over the five-year duration of the project. Specifically, the program has identified a target of being able to detect a +/-6% change in concentrations of cyclic VMS. In addition to understanding the temporal trends in environmental concentrations of the cyclic VMS (D4, D5, D6), each site has conducted a survey of the linear VMS as well (L3, L4, and L5).

Collection of surface sediment and aquatic biota was initiated in 2011 and has occurred on an annual basis through 2016. Biota species collected from each site were representative of a range of trophic levels and feeding guilds, and included invertebrate and fish species, with the exception of in Tokyo Bay where only fish were collected.

Concentrations of the cyclic VMS compounds were found to be greatest in aquatic environments adjacent to areas with the highest population density. Of the four study areas included in the monitoring program, samples from Tokyo Bay, which is surrounded by a population of approximately 36 million people, had the greatest concentrations of cyclic VMS. With increased distance from point sources, concentrations of the cyclic VMS were found to decrease. Following analysis of the cyclic VMS data for temporal trends, the Silicones Industry may decide to extend the program for additional years, on a site-by-site basis.

Results of the survey of linear VMS in surface sediments and aquatic biota showed that concentrations were at or below method detection limits (MDLs).

EVALUATION OF EMISSIONS FROM WASTEWATER TREATMENT PLANTS

The use patterns of VMS make WWTPs a conduit of their release to aquatic environments. As such, the Silicones Industry has initiatives that investigate the levels of VMS materials in media from WWTPs and the aquatic environments receiving direct WWTP effluent.

SUPPORT FOR THE JRC WWTPS STUDY

At the outset of the initiatives in 2010, the Silicones Industry provided support for a major European project, coordinated by the European Commission's Joint Research Centre (JRC) in Ispra, Italy[5].

Effluents from 90 European wastewater treatment plants (WWTPs) were collected and analyzed for levels of 168 organic chemicals and 20 inorganic trace elements.

The analyses were complemented by applying effect-based monitoring approaches aimed at estrogenicity and dioxin-like toxicity analyzed by in vitro reporter gene bioassays.

The analytical work was performed in six European expert laboratories:

- The Institute of Environment and Sustainability of the European Commission's Joint Research Centre (JRC) in Ispra, Italy
- IWW Water Centre, Mühlheim a.d. Ruhr, Germany
- Federal Environmental Agency (Umweltbundesamt; UBA), Vienna, Austria
- RECETOX, Masaryk University, Brno, Czech Republic
- VITO, Mol, Belgium
- UMEA University, Umea, Sweden

Although the Silicones Industry was not directly involved in this project, it contributed €15,000 towards the costs through cooperation with the UBA in Austria.

Importantly, this study found no evidence of D4 and D5 with the exception of one local wastewater treatment in Belgium, which was at the analytical detection limit.

D4 ENFORCEABLE CONSENT AGREEMENT – WWTP IN UNITED STATES

To provide the U.S. Environmental Protection Agency (EPA) with environmental monitoring data on the siloxane D4, members of the Silicones Environmental, Health, and Safety Center (SEHSC) have conducted an environmental monitoring program, designed in partnership with the EPA, to assess levels of D4 in the aquatic environment. This monitoring evaluated D4 concentrations near municipal WWTPs as well as several locations corresponding to D4 manufacturing, processing and formulating facilities owned or operated by GSC members, for a total of 14 sites.

The data generated in the program will facilitate EPA's environmental risk assessment for D4, using actual environmental concentrations, rather than predicting concentrations using computer models. Concentrations of D4 were determined in WWTP influent, effluent, and bio-solids, as well as in surface water, sediment, benthic invertebrate, and fish collected from within the mixing zone of the receiving waters.

Sample collection for this program occurred throughout 2016. Final results are anticipated to be reported to EPA by September 2017.

MONITORING INFLUENT OF WWTP IN EUROPE

In recent years, there has been an increase in the regulatory scrutiny of siloxane materials in Europe. One specific area of interest has been the release of D4 and D5 to aquatic environments via WWTPs. As a result, a Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) restriction of D4 and D5 has been adopted, limiting their concentration in wash-off personal care products to less than 0.1% by weight. To gain a more comprehensive understanding of this type of release and the impact of the restriction, the Silicones Industry has initiated a monitoring program. The objective of this program is to determine the loading of D4 and D5 in wastewater from residential sources and monitor for temporal trends. Sampling for this program is scheduled to begin in late 2017 and is slated to continue for several years.

REFINEMENT OF CHEMICAL ASSESSMENT PRACTICES

An example of how models and data generated by the Silicones Industry were used can be seen in the Canadian assessments of the VMS materials. In Canada, the cyclic and linear VMS were screened under the Canadian Environmental Protection Act (CEPA) to determine whether these substances present a risk to the environment or human health. Screening assessments of cyclic and linear VMS determined that D6, L2, L3, L4, and L5 were not entering the environment in quantities or concentrations that had the potential to cause ecological harm. Similar screening assessments of D4 and D5 determined these materials were entering the environment in quantities or concentrations that had the potential to cause ecological harm.

Following the screening assessment of D4, the Government of Canada developed measures to control the potential risks posed by D4, including industrial Pollution Prevention Plans with respect to D4 in industrial effluents; reassessment of D4 contained in pesticides, as part of the Pest Management Regulatory Agency's formulant reassessment program; and ongoing monitoring of D4 in the environment. However, no product or product concentration restrictions on the use of D4 in any application have been imposed.

The Environment Canada screening assessment of D5 was challenged and a scientific Board of Review was convened, as per section 333(1) of CEPA, to review all available data on D5. The Board conducted an extensive review of the available data and interviewed experts in the fields of bioaccumulation, environmental fate, and ecotoxicology. Following this review, the Board concluded in late October 2011, "Siloxane D5 does not pose a danger to the environment or its biological diversity." Furthermore, the Board added that, "based on the information presented, siloxane D5 will not pose a danger to the environment or its biological diversity in the future". In February 2012, the Canadian Environment Minister removed D5 from a proposed list of toxic substances under CEPA.

That a more thorough review of the physicochemical properties, detailed modelling estimates, measured environmental concentrations, and subsequent risk assessment of D5 resulted in a reversal of the screening assessment findings - which were based only on generic criteria - highlights the importance of incorporating all available data.

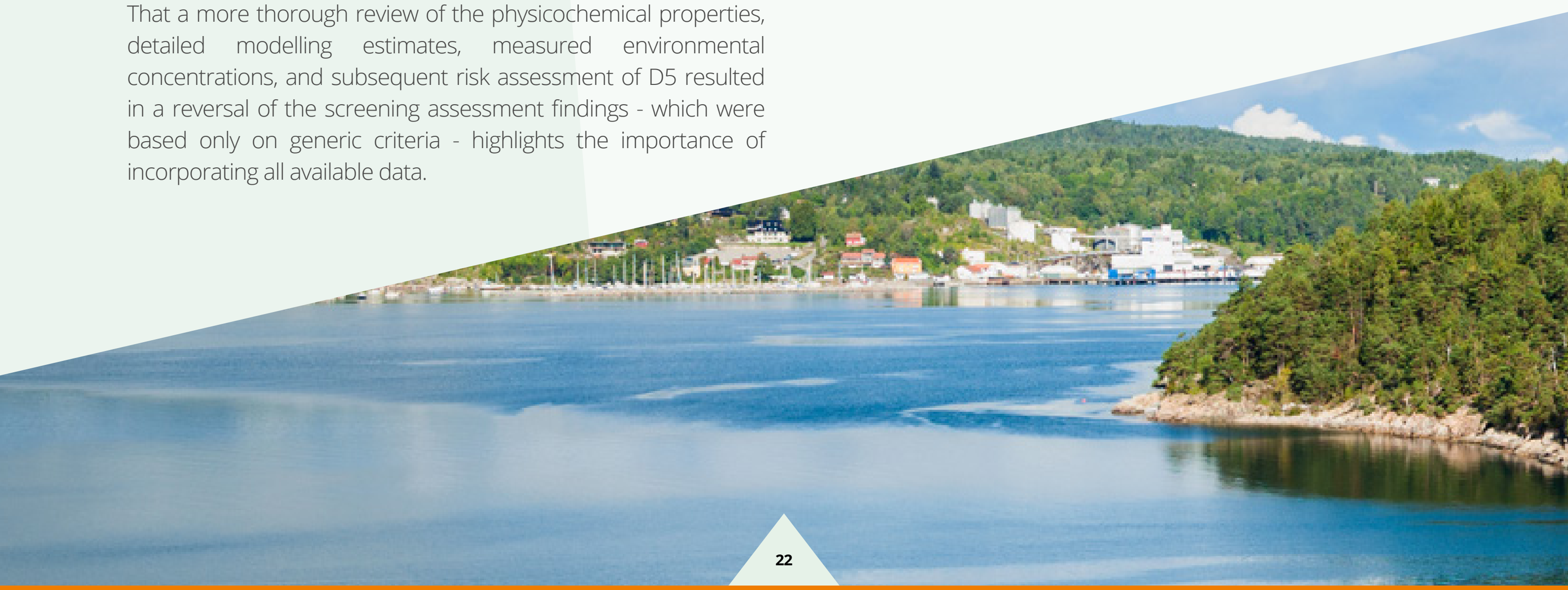
As discussed in previous sections, the Silicones Industry has been engaged in the improvement of available models to estimate environmental fate and bioaccumulation potential, as well as generating data detailing the concentration of siloxanes around the world. Furthermore, the industry also has initiatives on how to advance risk assessment practices and review all available information using a quantitative weight of evidence approach.

SILICONES INDUSTRY SUPPORT OF PROBABILISTIC RISK ASSESSMENTS

The simplest risk assessment method compares a measure of exposure with a threshold level for detrimental effects. Since conservative assumptions apply to both the exposure and toxicity endpoints, the method is inherently protective in nature, but not predictive as to the level of potential risk.

The term "risk" implies an element of likelihood or probability, which cannot be calculated from the comparison of point estimates. Higher tiered methods utilize more probabilistic approaches, in which one can calculate the probability of an exposure concentration exceeding some probability of effect or non-effect. Probabilistic risk assessment (PRA) methods allow the risk assessor to examine stochastic properties of both exposure and toxicity. The PRA method is still protective in nature, as the risk assessor can determine the level of risk that is acceptable.

A PRA assessing the aquatic risk of D4 has been conducted (Fairbrother and Woodburn, 2016). In this assessment, the 95th percentile D4 water concentration was 0.1 µg/L, or 2 times lower than either the of ecotoxicology trigger values and greater than 40 times lower than measured LC10 values. The lack of overlap between measured environmental concentrations of D4 in the water column and the toxicity threshold values for the aquatic species indicates a lack of risk in aquatic systems.



SILICONES INDUSTRY SUPPORT OF QUANTITATIVE WEIGHT OF EVIDENCE IN CHEMICAL ASSESSMENTS

Multiple lines of evidence are relevant to characterizing the safety profile of a chemical. These may include data of a chemical's physicochemical properties, toxicity, environmental fate, and bioaccumulation potential. Having more data will lend greater certainty to the assessment of a chemical, but it can also make the interpretation of the comprehensive dataset complex. One method of doing this is through a qualitative weight of evidence approach, but this approach introduces more uncertainty and complexity by trying to compare dissimilar lines of evidence. To overcome these limitations, the assessment can be conducted using a quantitative framework that allows for the interpretation and integration of varied lines of evidence into the assessment.

The use of a quantitative weight of evidence (QWoE) approach allows for a transparent and consistent manner of reviewing all available data. Within the QWoE framework, all available studies are included. Studies receive scores based on quality and relevance of observations. Results of higher quality studies receive a higher score relative to those from studies of lesser quality, and more relevant observations receive a higher score relative to those of lesser relevance. This method of including and scoring all studies reduces potential selection bias that could be introduced by the assessors.

One area where QWoE assessments can be very valuable is in the assessment of a chemical's properties relative to criteria for classification as PBT or as a persistent organic pollutant (POP). These assessments require information pertaining to a chemical's potential for persistence (P), bioaccumulation (B), toxicity (T), and long-range transport (LRT). When assessing the volume and breadth of information that needs to be considered as part of the assessment for classifying a chemical as PBT or a POP, having a structured and transparent method such as QWoE is very beneficial, lending clarity and credibility to the ultimate decision.

Recently, a QWoE assessment was conducted for the environmental fate and toxicity of D4, D5, and D6 (Bridges and Solomon, 2016). This assessment focused on the environment and whether these chemicals possess physical, chemical, and biological properties that would result in their classification as POPs and/or demonstrate the potential for LRT under the criteria of the Stockholm Convention or as PBT and/or vPvB under REACH. Based on multiple lines of evidence, which included persistence, bioaccumulation, toxicity, and long-range transport, the assessment concluded that D4, D5, and D6 should not be classified as P, B, or T, or as vP or vB, and that that there is no evidence that they are accumulating in remote regions. Additionally, the authors state that D4, D5, and D6 have physical, chemical, and biological properties that are dissimilar to those of legacy POPs, and that the traditional criteria used to classify these materials are not suitable for cVMS.

CONCLUSIONS

Silicones are among the world's most important and adaptable raw materials, used in literally thousands of different products and applications. Their remarkable breadth of chemical and physical properties makes silicones essential to innovation and function in diverse critical economic sectors. In addition, the use of silicones, siloxanes, and silanes generates energy savings, reduces greenhouse gas emissions, and reduces waste by protecting buildings and infrastructure and extending the lifespan of many valuable products.

VMS materials have a unique combination of partition coefficients between air, octanol, and organic carbon, which differ significantly from traditional organic chemicals (e.g. PCBs) that comprise many models' domain of applicability.

To expand the usability of important environmental fate modelling tools, the Silicones Industry collaborated with modelling experts. These efforts have increased the level of customization of the input parameters in available models, allowing them to be more specific to the chemical of interest. Models that have been updated include the Equilibrium Criterion Model (EQC), the Quantitative Water Air Sediment Interaction Model (QWASI), and the AQUAWEB model.

The Silicones Industry has committed to several voluntary monitoring product stewardship initiatives to better understand the presence and behavior of VMS in the environment. This research has focused on two environmental compartments, the atmosphere and aquatic environments.

A long-term monitoring program of VMS is being conducted at four highly populated locations around the world. The data from this program is being used to understand temporal trends in concentrations of cyclic VMS. In addition, concentrations of linear VMS were determined to be at or below method detection limits at these locations.

The Silicones Industry has engaged with the relevant regulatory agencies during the planning and execution of programs monitoring VMS in the wastewater stream in both the United States and Europe. Data generated from the program in the United States will be used to inform a risk assessment of D4. The program in Europe has the objective of monitoring temporal trends in the mass loading of D4 and D5 in WWTP influent and how that relates to their restricted use in wash-off PCPs.

Based on multiple lines of evidence, which included persistence, bioaccumulation, toxicity, and long-range transport, a quantitative weight of evidence assessment concluded that D4, D5, and D6 should not be classified as P, B, or T, or as vP or vB, and that that there is no evidence that they are accumulating in remote regions. Other assessments have reached similar conclusions for the linear VMS.

The Silicones Industry will continue to advocate for basing regulatory assessments on the best available science. With this approach, the industry believes that assessments of VMS materials will demonstrate both their safety and their positive impact on the global society.

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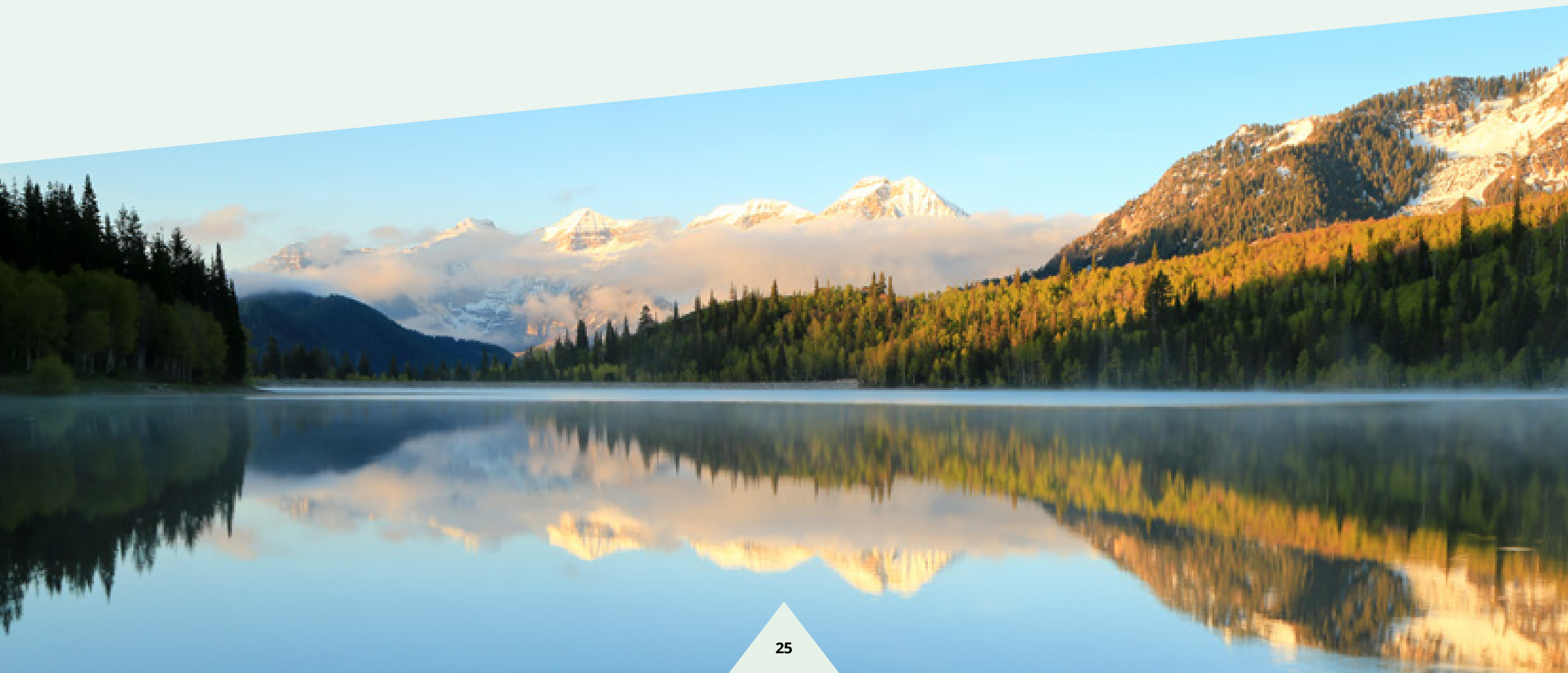

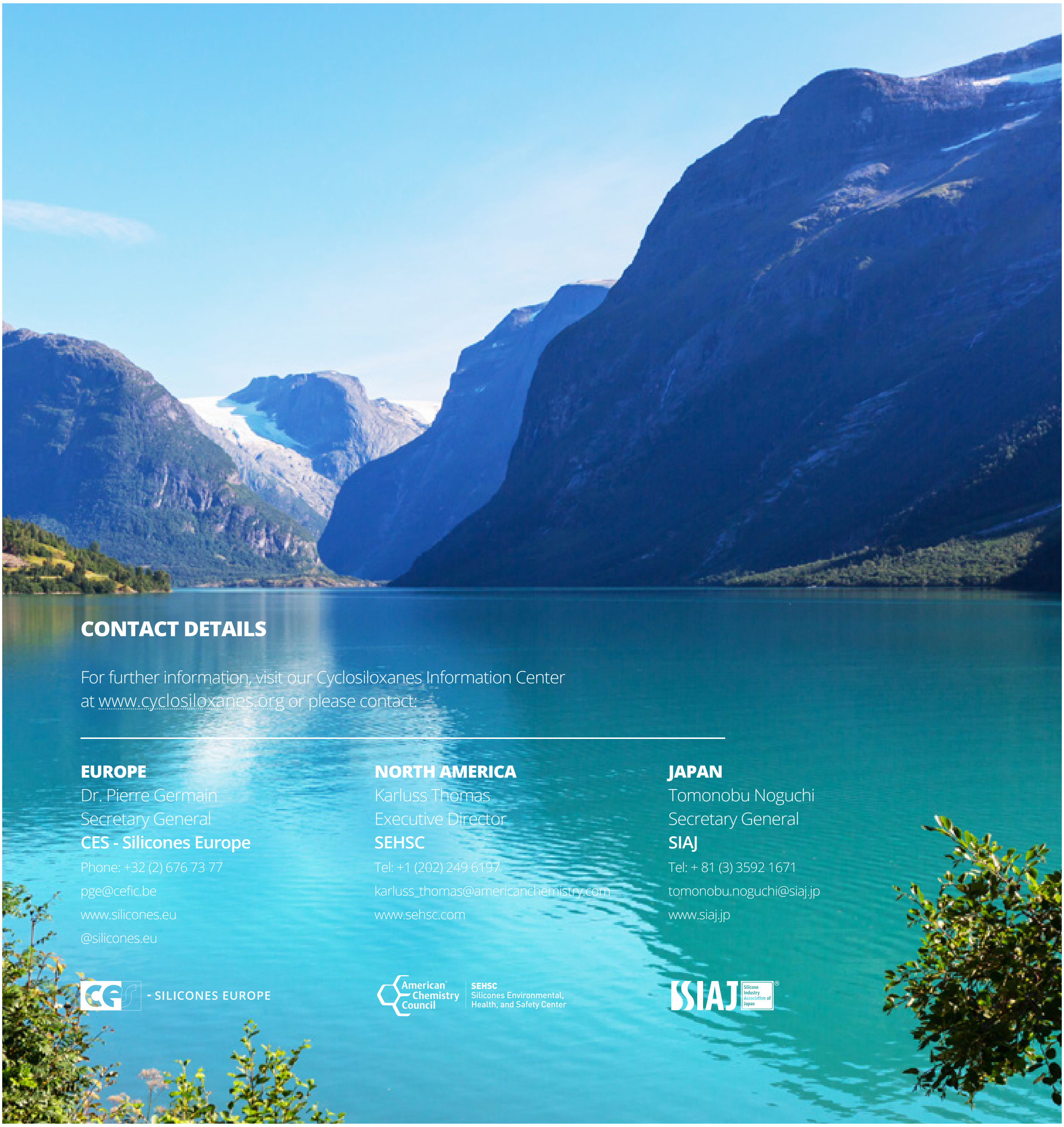

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