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UNIVERSITÄT LÜNEBURG

# Struktur-Abbaubarkeits-Beziehungen von siliziumorganischen Substanzen

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WINNERS…
ARE NOT
THOSE WHO
NEVER FAIL

BUT…
THOSE WHO
NEVER QUIT.

– Banksy –

# Zusammenfassung

Siliziumorganische Substanzen sind aus dem Alltag kaum wegzudenken. Sie kommen in vielfältiger Form vor und finden durch ihre Stabilität in vielen Produkten des Haushalts und der Industrie Anwendung. Da sie zum Beispiel auch in Körperpflegeprodukten und Pflanzenschutzmitteln angewendet werden, ist eine Freisetzung in die Umwelt unvermeidbar. Siliziumorganische Substanzen konnten bereits in allen Umweltkompartimenten (Luft, Wasser, Boden) analytisch nachgewiesen werden. Welche Risiken von dieser Stoffgruppe ausgehen, ist noch nicht abschließend geklärt, dennoch gibt es Hinweise auf negative Auswirkungen auf Mensch und Umwelt. Deshalb sollten Strukturen in siliziumorganischen Substanzen untersucht werden, die einen Abbau in der Umwelt begünstigen, um die Akkumulation dieser Stoffe in der Umwelt zu verringern.

Dafür wurden diverse biotische und abiotische Abbautests mit unterschiedlichen siliziumorganischen Substanzen durchgeführt. Der Fokus der vorliegenden Arbeit lag vor allem in der biologischen Abbaubarkeit der Substanzen. Es wurden die *Organisation for Economic Co-operation and Development* (OECD)-konformen Tests *Closed-Bottle*-Test (CBT, OECD 301D) und Manometrischer Respirationstest (MRT, OECD 301F) durchgeführt. Die Hydrolysierbarkeit wurde mithilfe des Hydrolysetests OECD 111 bei unterschiedlichen pH-Werten untersucht. Bei bestimmten Substanzgruppen ohne biologischen Abbau wurde das Verhalten der Substanzen bei Bestrahlung mit verschiedenen Bestrahlungsquellen untersucht. Die Analyse der Primärelimination der siliziumorganischen Substanzen erfolgte je nach Substanzeigenschaften mithilfe der Hochleistungsflüssigkeitschromatografie gekoppelt mit einem Spektrometer mit ultraviolettem und sichtbarem Licht (HPLC-UV/Vis) oder der Gaschromatografie gekoppelt mit einem Massenspektrometer (GC-MS). Die Transformationsprodukte wurden hingegen mithilfe der Flüssigkeitschromatografie gekoppelt mit einem Mehrfach-Massenspektrometer (LC-$MS^n$) analysiert. Für eine umfassende Bewertung des biologischen Abbaus von siliziumorganischen Substanzen wurden ein Vergleich mit analogen Kohlenstoffverbindungen und eine Aufstockung mit Daten aus der Datenbank der Europäischen Chemikalien Agentur (ECHA) durchgeführt. Die Gruppierung der Substanzen nach ihren Strukturmerkmalen wurde hinzugezogen, um Rückschlüsse auf die Abbaubarkeit zu ziehen.

Eine besser biologisch abbaubare Grundstruktur brachte für die Benzenderivate keine Verbesserung der biologischen Abbaubarkeit. Dennoch hatte die Einführung von +M-Gruppen am Aromaten einen positiven Einfluss auf die Geschwindigkeit und den Grad des photolytischen Abbaus. Die Bestrahlungsquelle hatte ebenfalls einen deutlichen Einfluss auf die Eliminierungsrate während des Photolyseexperiments. Mit einer Veränderung der Wellenlängen in den kurzwelligen Bereich und der daraus resultierenden energiereicheren Strahlung konnten die Substanzen schneller und teilweise vollständig primär eliminiert werden. Bei allen Abbaupfaden hatte die Hydrolyse eine entscheidende Rolle und wurde als einer der Hauptabbauprozesse charakterisiert. Bei einer Verbindung wurde im

Nachgang an die biotischen und abiotischen Abbautests eine ausführliche Aufklärung der elf gebildeten Transformationsprodukte vorgenommen.

Um den Einfluss von Silizium in organischen Substanzen auf die biologische Abbaubarkeit zu untersuchen, wurde der direkte Vergleich von siliziumorganischen Substanzen und deren Kohlenstoffanaloga im CBT durchgeführt. Dabei hat sich gezeigt, dass drei von fünf Kohlenstoffverbindungen und keine siliziumorganische Verbindung als leicht biologisch abbaubar eingestuft werden konnten. In allen bis auf einen Fall konnten für die Kohlenstoffverbindungen höhere Abbauraten im CBT beobachtet werden. Die Hydrolyse wurde als erforderlicher Schritt vor dem biologischen Abbau von siliziumorganischen Substanzen identifiziert. Das siliziumfreie Produkt der Hydrolyse bestimmte den Grad des biologischen Abbaus. Die gute biologische Abbaubarkeit der einen siliziumorganischen Verbindung resultierte aus der leicht hydrolysierbaren Silizium-Stickstoff-Bindung und der leichten biologischen Abbaubarkeit des siliziumfreien Hydrolyseproduktes. Die siliziumhaltigen Reaktionsprodukte der Hydrolyse waren nicht biologisch abbaubar.

Bioabbaudaten aus eigenen Experimenten, aus vorhergehenden in der Arbeitsgruppe durchgeführten analogen Arbeiten und aus der ECHA-Datenbank wurden zusammengetragen, um einen Datensatz zu generieren. Die 182 Substanzen des Datensatzes wurden hinsichtlich ihrer Struktur gruppiert, um allgemeine Erkenntnisse für die biologische Abbaubarkeit von siliziumorganischen Verbindungen abzuleiten. Es gab Gruppen mit Substanzen, die überhaupt nicht biologisch abbaubar waren (z. B. zyklische, lineare und verzweigte Siloxane). Gruppen, die Substanzen mit Ethern, Estern, Oximen, Aminen und Amiden enthielten, waren hydrolyseanfällig, sodass auch leicht biologisch abbaubare Zwischenprodukte gebildet werden konnten. Die siliziumfreien Hydrolyseprodukte waren meist biologisch abbaubar, während die siliziumhaltigen Hydrolyseprodukte persistent waren.

Allgemein hat sich gezeigt, dass Modifikationen am Molekül einen positiven Einfluss auf die Abbaubarkeit haben können. Beispielsweise können Heteroatome eine Veränderung der Polarität bzw. der Elektronendichte hervorrufen, was die Photolyse- und Hydrolysefähigkeit und folglich auch den Bioabbau zum Positiven verändern kann. Das Einführen solcher Heteroatome oder funktioneller Gruppen in Polysiloxanketten kann demnach ein vielversprechender Ansatz für leichter abbaubare siliziumorganische Verbindungen sein. Nicht abbaubare Stoffe sollten vermieden werden, wenn sie nach ihrer Verwendung in die Umwelt gelangen.

Diese Erkenntnisse tragen unter anderem zur Spurenstoffstrategie des Bundes, zum *European Green Deal* und zu den *Sustainable Development Goals* bei. Ziel dieser Ansätze ist die Verringerung der Schadstoffemissionen, um uns Menschen auch zukünftig Zugang zu sauberem Wasser und einer lebenswerten Erde zu gewährleisten.

# Abstract

Organosilicon substances are an indispensable part of everyday life. They occur in a variety of forms and are used in many household and industrial products due to their stability. Since they are also used, for example, in personal care products and pesticides, their release into the environment is unavoidable. Organosilicon substances have already been analytically detected in all environmental compartments (air, water, soil). The risks posed by this group of substances have not yet been conclusively clarified, but there are indications of negative effects on human health and the environment. Therefore, structures in organosilicon substances that support degradation in the environment should be investigated in order to reduce the accumulation of these substances in the environment.

For this purpose, various biotic and abiotic degradation tests were carried out with different organosilicon substances. The focus of the present work was mainly on the biodegradability of the substances. The Organization for Economic Co-operation and Development (OECD)-compliant closed bottle test (CBT, OECD 301D) and manometric respirometry test (MRT, OECD 301F) were performed. The ability to hydrolyse was investigated using the hydrolysis test OECD 111 at different pH values. For certain groups of substances without biodegradation, the behaviour of the substances was studied upon irradiation with different irradiation sources. The analysis of the primary elimination of the organosilicon substances was carried out using high performance liquid chromatography coupled to a spectrometer using ultraviolet and visible light (HPLC-UV/Vis) or gas chromatography coupled to a mass spectrometer (GC-MS), depending on the substance properties. The transformation products, on the other hand, were analysed using liquid chromatography coupled with a multiple mass spectrometer ($LC\text{-}MS^n$). For a comprehensive assessment of the biodegradation of organosilicon substances, a comparison with analogous carbon compounds and a supplementation with data from the European Chemicals Agency (ECHA) database were performed. Grouping of substances according to their structural features was added to draw conclusions on degradability.

A more biodegradable basic structure did not improve biodegradability for the benzene derivatives. Nevertheless, the introduction of +M groups on the aromatic ring had a positive effect on the rate and degree of photolytic degradation. The irradiation source also had a significant effect on the elimination rate during the photolysis experiment. With a change in wavelengths to the shorter wavelength range and the resulting higher energy radiation, the substances were eliminated faster and in some cases completely primary eliminated. In all degradation pathways, hydrolysis had a decisive role and was characterized as one of the main degradation processes. For one compound, a detailed elucidation of the eleven formed transformation products was performed following the biotic and abiotic degradation tests.

In order to investigate the influence of silicon in organic substances on biodegradability, the direct comparison of organosilicon substances and their carbon analogues was carried out in the CBT. This showed that three out of five carbon compounds and no organosilicon compound could be classified as readily biodegradable. In all but one case, higher degradation rates were observed for the carbon

compounds in CBT. Hydrolysis was identified as a mandatory step prior to biodegradation of organosilicon compounds. The silicon-free product of hydrolysis determined the rate of biodegradation. The good biodegradability of one organosilicon compound resulted from the easily hydrolysable silicon-nitrogen bond and the ready biodegradability of the silicon-free hydrolysis product. The silicon-containing reaction products of the hydrolysis were not biodegradable.

Biodegradation data from own experiments, from previous analogous work carried out in the working group, and from the ECHA database were assembled to generate a data set. The 182 substances in the data set were grouped according to their structure in order to derive general findings for the biodegradability of organosilicon compounds. There were groups with substances that were not biodegradable at all (e.g. cyclic, linear and branched siloxanes). Groups containing substances with ethers, esters, oximes, amines and amides were susceptible to hydrolysis, so that readily biodegradable intermediates could also be formed. The silicon-free hydrolysis products were mostly biodegradable, whereas the silicon-containing hydrolysis products were persistent.

In general, it has been shown that modifications to the molecule can have a positive influence on degradability. For example, heteroatoms can cause a change in polarity or electron density, which can positively change the photolysis and hydrolysis ability and consequently also the biodegradation. The introduction of such heteroatoms or functional groups into polysiloxane chains can thus be a promising approach for more readily degradable organosilicon compounds. Non-degradable substances should be avoided if they are released into the environment after use.

These findings contribute, among other things, to the federal government's trace substance strategy, the European Green Deal and the Sustainable Development Goals. The aim of these approaches is to reduce pollutant emissions in order to ensure that people will have access to clean water and a liveable earth in the future.

# Inhaltsverzeichnis

# Abbildungsverzeichnis



# Tabellenverzeichnis

# Abkürzungsverzeichnis

| | |
|---|---|
| CBT | *Closed-Bottle*-Test (OECD 301D) |
| $D_4$ | Octamethylcyclotetrasiloxane |
| $D_5$ | Decamethylcyclopentasiloxane |
| $D_6$ | Dodecamethylcyclohexasiloxane |
| DMSO | Dimethylsulfoxid |
| ECHA | Europäische Chemikalien Agentur |
| GC | Gaschromatografie |
| HPLC | Hochleistungsflüssigkeitschromatografie |
| $L_2$ | Hexamethyldisiloxan |
| $L_3$ | Octamethyltrisiloxan |
| $L_4$ | Decamethyltetrasiloxan |
| $L_5$ | Dodecamethylpentasiloxan |
| LC | Flüssigkeitschromatografie |
| MRT | Manometrischer Respirationstest (OECD 301F) |
| MS | Massenspektrometrie/Massenspektrometer |
| $MS^n$ | Mehrfach-Massenspektrometer mit *n*, der Anzahl der Fragmentierungsschritte |
| OECD | *Organisation for Economic Co-operation and Development* |
| PDMS | Polydimethylsiloxane |
| TOC | *total organic carbon* |
| UV/Vis | Spektroskopie mit ultraviolettem und sichtbarem Licht |

# 1 Einleitung

## 1.1 Struktur und Verwendung siliziumorganischer Substanzen

Silikone sind gekennzeichnet durch Ketten aus alternierenden Silizium- und Sauerstoffatomen, mit an Silizium gebundenen organischen Seitenketten. Ursprünglich stammt der Name davon Silizium-Analoge von Ketonen zu beschreiben, wobei jedoch keine Silizium-Sauerstoff-Doppelbindungen existieren. Sie liegen in Form von längeren Ketten oder Ringen vor. Zu den Silikonen gehören unter anderem Polydimethylsiloxane (PDMS), Polyethermethylsiloxane, flüchtige Methylsiloxane und andere Siloxane mit Silizium-Sauerstoff-Grundgerüsten (Rücker und Kümmerer, 2015). Kleinere Moleküle mit alternierenden Silizium- und Sauerstoffatomen werden als Siloxane bezeichnet. Weitere organische Verbindungen ohne die Silizium-Sauerstoff-Ketten werden im Folgenden als siliziumorganische Verbindungen bezeichnet, welche durch Silizium-Kohlenstoff-Bindungen charakterisiert sind. Die Silizium-Kohlenstoff-Bindungen werden synthetisch hergestellt und kommen nicht in der Natur vor (Hirner et al., 2003). Die Verbindungen wurden so konzipiert, dass sie in den Produkten und während der Anwendung sehr stabil sind. Sie werden durch ihre vielfältigen Einsatzmöglichkeiten z. B. in Tensiden, Entschäumern, Klebstoffen, Schmiermitteln, Beschichtungen, Kosmetik, im Baugewerbe, in der Landwirtschaft und für medizinische Materialien in hohen Mengen produziert (Andriot et al., 2007, Knoche, 1994, O'Lenick und O'Lenick, 2014). Im Jahr 2019 wurden weltweit 2,4 Mio t Silikone produziert (imarc, 2020).

## 1.2 Siliziumorganische Substanzen in der Umwelt und damit verbundene Risiken

Zum Vorkommen von Silikonen in der Umwelt gibt es umfassende Studien. Die zyklischen Methylsiloxane Octamethylcyclotetrasiloxane ($D_4$), Decamethylcyclopentasiloxane ($D_5$) und Dodecamethylcyclohexasiloxane ($D_6$) wurden bereits in diversen Umweltkompartimenten detektiert. $D_4$ konnte beispielsweise in Konzentrationen um 80 ng $L^{-1}$ im Meerwasser in der Antarktis gemessen werden (Desideri et al., 1991). Sparham et al. (2008) konnten $D_5$ in britischen Flüssen und van Egmond et al. (2013) konnten $D_5$ und $D_6$ jeweils in Kläranlagenzu- und -abläufen nachweisen. Die linearen Siloxane Hexamethyldisiloxan ($L_2$), Octamethyltrisiloxan, ($L_3$), Decamethyltetrasiloxan ($L_4$) und Dodecamethylpentasiloxan ($L_5$) wurden in spanischen Flüssen (Companioni-Damas et al., 2012), in Kläranlagenzu- und -abläufen in nordischen Ländern (z. B. Norwegen, Kaj et al., 2005), in Klärschlamm in China (Liu et al., 2014) und in Deponiesickerwasser in Deutschland detektiert (Grümping et al., 1998, Grümping et al., 1999).

Durch bestimmte Anwendungen, vor allem im Kosmetikbereich und der Landwirtschaft, gelangen die Silikone ins Abwasser bzw. in die Umwelt. In der Kläranlage werden Silikone nur unzureichend abgebaut oder sie adsorbieren am Klärschlamm (Graiver et al., 2003, Rücker und Kümmerer, 2015).

PDMS verteilt sich im Wesentlichen auf der Biomasse und wird nur in geringer Konzentration in Oberflächengewässern detektiert (Watts et al., 1995). Wenn der Klärschlamm zur Erzeugung von Biogas verwendet wird, gelangen die Silikone auch ins Biogas, wo diese nachgewiesen werden konnten (Grümping et al., 1998). Neben den bereits beschriebenen Kompartimenten kommen Siloxane auch in der Luft, dem Boden, Staub und in Lebensmitteln vor (Rücker und Kümmerer, 2015).

Siliziumorganische Substanzen müssen für die Gefährdungsbeurteilung näher beleuchtet werden, da sie ubiquitär vorkommen. Bisher sind die Gesundheitsrisiken nicht abschließend geklärt. Es gibt jedoch Hinweise auf ein mögliches Gefahrenpotenzial, weswegen die zyklischen Siloxane $D_4$, $D_5$ und $D_6$ von der ECHA als besonders besorgniserregende Substanzen eingestuft und für den Einsatz in Kosmetikprodukten stark limitiert wurden (ECHA, 2019). Die Diskussion, diese Substanzen auf die Zulassungsliste zu setzen, dauert weiter an (ECHA, 2021). Eine Verwendung dieser Stoffe wäre dann ausschließlich mit einer Genehmigung möglich.

Anhand des *ex vivo* Hautmodells konnte eine Diffusion von $D_4$, $D_5$ und $D_6$ in tiefer liegende Hautschichten wie der Epidermis und Dermis nachgewiesen werden (Krenczkowska et al., 2020). $D_6$ hatte eine besonders hohe Affinität zur Hornschicht (*Stratum corneum*), was auf die hohe Lipophilie zurückzuführen ist. $D_4$ diffundierte am leichtesten durch die verschiedenen Hautschichten, während die Diffusion von $D_5$ schwieriger und die von $D_6$ stark limitiert war. Daher gehen von $D_4$ und $D_5$ größere Risiken aus als von $D_6$, da sie durch dieses Verhalten das Blut- und Lymphsystem erreichen können (Krenczkowska et al., 2020). Eine Bioakkumulation in der Dermis und somit auch eine spätere unkontrollierte Freisetzung in den Blutkreislauf können potenzielle Folgen sein. Kala et al. (1997) konnten mithilfe der Entwicklung einer analytischen Methode zur Bestimmung von Siloxangehalten in Geweben nachweisen, dass diese Stoffe das Potential zur Bioakkumulation besitzen. Obwohl Silikonimplantate bei sachgemäßer Verwendung als sicher gelten (U.S. Food and Drug Administration, 2011), beschreiben viele Frauen Krankheitssymptome, die erst nach dem Implantieren auftraten und nach der Entfernung der Implantate wieder verschwanden (Magnusson et al., 2019). Zudem wurde bereits berichtet, dass $D_4$ toxische Effekte auf verschiedene biologische Prozesse in Ratten haben können. Dazu gehören eine beeinträchtigte Fruchtbarkeit (Meeks et al., 2007), Leberschäden (McKim et al., 2001) und die Affinität von $D_4$ zu einem Östrogenrezeptor (Quinn et al., 2007). Ebenso konnten die Leber (McKim, JR et al., 1999) und die Lunge (Burns-Naas et al., 1998) von Ratten als Zielorgane für $D_5$ identifiziert werden, wo Entzündungsreaktionen beobachtet werden konnten.

## 1.3 Abbau von siliziumorganischen Substanzen und mögliche Transformationsprodukte

Silikone und weitere siliziumorganische Verbindungen weisen aufgrund ihrer stabilen Silizium-Kohlenstoff-Bindung eine hohe Persistenz in der Umwelt auf. Um die in Kapitel 1.2 erwähnten Risiken einzudämmen, gibt es verschiedene Strategien zur Verminderung der Umweltkonzentration. Eine

weitverbreitete Strategie Schadstoffe in der Umwelt zu reduzieren, zielt zusätzlich zur Behandlung in der Kläranlage darauf ab, den Kläranlagenablauf in einer vierten Reinigungsstufe nachzubehandeln, um die Konzentration der noch enthaltenen Schadstoffe zu verringern. Dafür werden beispielsweise Aktivkohlefilter eingesetzt. Die Adsorption an Aktivkohle wurde bisher nur für die Entfernung von Siloxanen (z. B. $D_4$) aus Biogas untersucht (Dewil et al., 2006, Schweigkofler, Niessner, 2001, Yu et al., 2013). Inwiefern eine Übertragung der Ergebnisse auf die Entfernung von Siloxanen aus dem Abwasser möglich ist, müsste noch untersucht werden. Neben Aktivkohlefiltern gibt es die erweiterte Oxidation, bei der durch den Einsatz von z. B. Fentons Reagenz ($H_2O_2$/Fe (II) (Pfister et al., 1997)), Ozon, UV-Strahlung und/oder Ultraschall (Mahamuni und Adewuyi, 2010) hochreaktive Hydroxylradikale entstehen, die die Schadstoffe oxidieren und deren Eliminierung verursachen (von Sonntag, 2008). Diese resultieren oft in einer unvollständigen Mineralisierung, was sich z. B. an der Bildung von Transformationsprodukten zeigt (Alfiya et al., 2017, Herrmann et al., 2016). Das Gefahrenpotenzial der Transformationsprodukte kann sowohl kleiner als auch größer als das der Ausgangssubstanzen sein und kann in Transformationsproduktmischungen sehr schlecht abgeschätzt werden. Außerdem entstehen hohe Kosten durch den Einsatz großer Mengen von Chemikalien und Energie (Mahamuni und Adewuyi, 2010).

Da die Nachbehandlung des Abwassers viele Nachteile mit sich bringt, ist eine Schadstoffreduktion durch ein gezieltes Design von Substanzen der bessere Ansatz. Das 10. Prinzip der Grünen Chemie „Design für den Abbau“ adressiert einen solchen Lösungsansatz (Anastas und Warner, 2000). Um Substanzen zu entwickeln, die nach ihrer Anwendung leicht in der Umwelt abgebaut werden, müssen die beteiligten Abbauprozesse verstanden werden, welche stark von den chemischen Strukturen der Substanzen abhängig sind. Ein vollständiger Abbau, auch Mineralisierung genannt, ist erst erfolgt, wenn nur Grundbausteine wie Wasser, Kohlenstoffdioxid, Siliziumdioxid und Mineralsalze übrig bleiben.

Daten über den biotischen oder abiotischen Abbau von siliziumorganischen Verbindungen in der Umwelt sind sehr begrenzt. Meist werden nur Siloxane und deren Hydrolyse betrachtet. Michel et al. (2014) haben gezeigt, dass Silwet L-77, ein kommerzielles Polyethermethylsiloxan, bei pH 9 schneller hydrolysiert als bei pH 7. Sie fanden heraus, dass Silwet L-77 unter Umweltbedingungen eine Halbwertszeit von mehreren Wochen hat (12 °C, pH 7). Die Hydrolyse von PDMS-Flüssigkeiten wurde unter extremen chemischen Bedingungen beobachtet (pH 2–4 und 9–12). Bei pH 6 war die Hydrolysegeschwindigkeit von PDMS jedoch sehr langsam (Ducom et al., 2013). Daher scheint die Hydrolyse von PDMS säure- bzw. basekatalysiert zu sein (Issa und Luyt, 2019). Dieses Wissen und das von Rücker und Kümmerer (2013) könnte dazu genutzt werden Substanzen zu entwickeln, bei denen die Hydrolysegeschwindigkeit durch gezielte Modifikationen so beeinflusst wird, dass die Substanzen erst in der Kläranlage oder bei Erreichen der Umwelt zerfallen.

Xu (1999) zeigte in seiner Studie, dass einige flüchtige zyklische Methylsiloxane einschließlich $D_4$, $D_5$ und $D_6$ vollständig durch Verflüchtigung, biologischen Abbau und mehrstufige Hydrolyse im Boden abgebaut wurden. Zum Beispiel wurde $D_4$ direkt über eine Ringöffnung zum Tetramerdiol

($HO–[SiMe_2O]_4–H$) hydrolysiert. Dieses Produkt hydrolysierte zu kleineren Diolen und schließlich zu Dimethylsilandiol ($SiMe_2(OH)_2$, Xu, 1999). Der biologische Abbau wurde in dieser Studie jedoch nicht hinreichend definiert bzw. beschrieben. Xu et al. (2013) schlussfolgerten aus ihrer Studie über die Abbaubarkeit von flüchtigen zyklischen Methylsiloxanen, dass die biokatalysierte Hydrolyse neben der Verflüchtigung und Adsorption der Hauptabbauweg von $D_4$ und $D_5$ war. Sie berichteten auch, dass die Hydrolysegeschwindigkeit mit zunehmender Kettenlänge abnahm, was hauptsächlich auf eine sterische Hinderung zurückzuführen ist. Weitere Gründe wurden nicht diskutiert.

Meistens sind Silikone in der Kläranlage nicht biologisch abbaubar oder sie adsorbieren am Klärschlamm (Graiver et al., 2003). Da sie eine sehr stabile Silizium-Kohlenstoff-Bindung haben, gibt es die Vorstellung, dass es keine Mikroorganismen in der Umwelt gibt, die diese Bindung spalten können (Hirner et al., 2003). Bletsou et al. (2013) analysierten Siloxane in Kläranlagenabläufen. Sie nahmen an, dass die hohen detektierten Konzentrationen verschiedener linearer Oligosiloxane (z. B. Dodecamethylpentasiloxan ($L_5$), Tetradecamethylhexasiloxan ($L_6$) und Hexadecamethylheptasiloxan ($L_7$)) oder auch zyklischer Siloxane zu den Bioabbauprodukten von PDMS gehören. Diese Schlussfolgerung war jedoch weder durch biologische Abbaubarkeitstests nachgewiesen noch durch die gezeigten Ergebnisse dargestellt worden. Weitere Studien verwendeten die Mikroorganismen *Pseudomonas aeruginosa S240* (Li et al., 2014) und *Methylibium sp.* (Boada et al., 2020) in Biotropffiltern, um flüchtige Methylsiloxane (z. B. $D_4$ und $D_5$) aus Biogas zu entfernen. Siloxane im Biogas verringern die energetische Ausbeute des Biogases, da durch die Verbrennung $SiO_2$-Ablagerungen entstehen. Diese führen zum Abrieb an Motorenteilen und zur Hemmung der notwendigen Wärmeleitung (Boada et al., 2020, Li et al., 2014). Auch wenn die Verwendung dieser Spezies zur Entfernung von Siloxanen vielversprechend scheint, werden solche spezifischen Organismen in der Umwelt meist durch schneller wachsende Mikroorganismen verdrängt (Rücker und Kümmerer, 2015), was den Einsatz dieser Mikroorganismen zur Reinigung von Abwässern begrenzt.

Die photochemische Spaltung von Silizium-Kohlenstoff-Bindungen wurde z. B. anhand von Benzyltrimethylsilan und substituierten Benzyltrimethylsilanen untersucht. Mithilfe von UV-Licht mit einer Wellenlänge von 254 nm konnte eine $Si–C_{Benzyl}$-Bindungsspaltung hervorgerufen werden (Kira et al., 1985). Drake et al. (1998) sind zu dem Schluss gekommen, dass die durch UV-Licht verursachte Oxidation von Polysiloxanen mit zunehmender Energie des UV-Lichts, also mit kürzeren Wellenlängen, zunimmt (123 und 147 nm (Skurat, Dorofeev, 1994), 147 nm (Vasilets et al., 1994), 193 und 248 nm (Joubert et al., 1991), 313 nm (Imakoma et al., 1994) und <300 nm (Israëli et al., 1992)). Da die Strahlung der Sonne mit diesen Wellenlängen durch die Ozonschicht absorbiert wird, kommen solche energiereichen Strahlungen nicht natürlich in der Umwelt vor (Heister, 1998). Ein direkter photolytischer Abbau von siliziumorganischen Substanzen in der Umwelt ist daher nicht zu erwarten.

# 2 Ziele und Aufbau der Arbeit

## 2.1 Zielstellung

Siliziumorganische Substanzen kommen ubiquitär vor, da es kaum einen Anwendungsbereich gibt, in dem sie nicht vertreten sind und weil sie schlecht in der Umwelt abgebaut werden. Obwohl siliziumorganische Substanzen so weit verbreitet sind, gibt es keine Studien, die sich systematisch mit der Abbaubarkeit bzw. mit der Verbesserung der Abbaubarkeit in der Umwelt befasst haben.

Ziel dieser Arbeit war es daher unterschiedliche Modifikationen an siliziumorganischen Substanzen auf deren Beitrag zur Abbaubarkeit zu untersuchen und abbaubarkeitsfördernde Strukturen zu identifizieren. Die Identifizierung von Sollbruchstellen und Strukturmerkmalen, die einen Abbau begünstigen, sind der Schlüssel zu besser abbaubaren Silikonen. Die Auswahl der Substanzen sollte deshalb eine Vielfalt an Strukturen beinhalten (z. B. Ester-, Ether-, Amino- und Benzenderivate, siehe Kapitel 3.1), um Angriffspunkte für verschiedene Abbauprozesse zu bieten. Als mögliche Abbaupfade wurden sowohl biotische (CBT und MRT) als auch abiotische Prozesse (Hydrolyse und Photolyse) untersucht. Damit sollte ein umfassender Einblick in die Prozesse gewonnen werden, die auch in der Umwelt stattfinden können. Die energiereichere Strahlung (Hg-Lampe) kommt zwar nicht in der Umwelt vor, simuliert aber die vierte Reinigungsstufe mittels UV-Licht. Für weitere Erkenntnisse über den Abbau von organischen Substanzen wurden zusätzlich zu den siliziumorganischen Substanzen auch deren Kohlenstoffanaloga analysiert. Im Fokus dieser Teilarbeit stand der direkte Vergleich der biologischen Abbaubarkeit der Analoga und welche Prozesse maßgeblich beteiligt sind. Neben den eigenen experimentellen Untersuchungen wurde erstmals für die Substanzgruppe der siliziumorganischen Substanzen eine umfängliche Recherche, Zusammentragung und Auswertung von Bioabbaudaten aus der ECHA-Datenbank vorgenommen, mit deren Hilfe eine größere Substanzvielfalt und eine umfangreichere Datenlage erreicht wurden.

Im Rahmen dieser Arbeit wurden aufgrund der vorhandenen Datenlage (Kapitel 1.3) und umfassender Überlegungen die folgenden Hypothesen aufgestellt und untersucht:

- Amino- und Methoxygruppen am aromatischen Ring verbessern die biologische und photolytische Abbaubarkeit von aromatischen siliziumorganischen Substanzen.
- Kohlenstoffverbindungen sind besser biologisch abbaubar als ihre siliziumanalogen Substanzen.
- Es gibt funktionelle Gruppen (z. B. Ester), die die biologische Abbaubarkeit von siliziumorganischen Verbindungen begünstigen.

## 2.2 Aufbau

Die praktischen Arbeiten wurden von Mai 2016 bis Februar 2020 an der Leuphana Universität Lüneburg am Institut für Nachhaltige Chemie und Umweltchemie in der Arbeitsgruppe von Prof. Dr. Kümmerer durchgeführt. Die dabei entstandenen Ergebnisse und Erkenntnisse wurden in drei Publikationen in internationalen Fachzeitschriften mit Peer-Review-Verfahren veröffentlicht, welche im Folgenden dargestellt und zusammengefasst diskutiert werden (Kapitel 5).

**Publikation 1**

Grabitz, E.; Olsson, O.; Amsel, A.-K.; Rummel, B.; Mitzel, N.; Kümmerer, K. (2020).
Abiotic and biotic degradation of five aromatic organosilicon compounds in aqueous media – Structure degradability relationships.
*Journal of Hazardous Materials*, 392, 122429,
DOI: 10.1016/j.jhazmat.2020.122429

**Publikation 2**

Grabitz, E.; Reich, M.; Olsson, O.; Kümmerer, K. (2020).
Using structure biodegradability relationships for environmentally benign design of organosilicons – An experimental comparison of organosilicons and their carbon analogues.
*Sustainable Chemistry and Pharmacy*, 18, 100331,
DOI: 10.1016/j.scp.2020.100331

**Publikation 3**

Grabitz, E.; Olsson, O.; Kümmerer, K. (2021).
Towards the design of organosilicon compounds for environmental degradation by using structure biodegradability relationships.
*Chemosphere*, 279, 130442
DOI: 10.1016/j.chemosphere.2021.130442

# 3 Methoden

Im Fokus der Arbeit stand die biologische Abbaubarkeit der siliziumorganischen Substanzen in der Kläranlage und der aquatischen Umwelt, da diese angestrebt werden sollte. In Deutschland ist für diese Art des biologischen Abbaus keine weitere Behandlung als die in der Kläranlage erforderlich. Allerdings werden weltweit nur 20 % der Abwässer behandelt (UNESCO World Water Assessment Programme, 2017). Daher sollte die biologische Abbaubarkeit auch bei geringen Bakterienmengen gewährleistet sein. Aus diesem Grund wurden die biologischen Abbautests CBT und MRT gewählt (Kapitel 3.2.1), in denen nur geringe Mengen unspezialisierter Mikroorganismen als Inokulum verwendet werden. Zudem sind diese Tests OECD-konform und gewährleisten somit eine gute Vergleichbarkeit von Ergebnissen.

Da die Hydrolyse der Substanzen im wässrigen Medium ebenfalls eine tragende Rolle spielen kann, wurden auch hierzu Tests bei unterschiedlichen pH-Werten durchgeführt (Kapitel 3.2.2).

Für manche Substanzen, für die keine biologische Abbaubarkeit gemessen werden konnte (hier Benzenderivate), wurden verschiedene Photolysetests mit unterschiedlichen Strahlungsquellen (Xe- und Hg-Lampe) und Lösungsmitteln durchgeführt (Kapitel 3.2.3).

Zudem wurden verfügbare Bioabbaudaten siliziumorganischer Substanzen aus der ECHA-Datenbank extrahiert und für die Erstellung eines Datensatzes genutzt (siehe Kapitel 3.4).

Eine Übersicht, welche Substanzen und welche Experimente in welchen Publikationen zu finden sind, ist in Tabelle 1 dargestellt.

**Tabelle 1:** Übersicht über die Substanzen und die durchgeführten Abbautests mit Kennzeichnung der Publikation, in der die Ergebnisse veröffentlicht wurden. * auch weitere OECD-Tests, die den biologischen Abbau bestimmen.

| **Substanzen** | **Bioabbau** | | **Hydrolyse** | **Photolyse** | | **Publikation** |
|---|---|---|---|---|---|---|
| | **CBT** | **MRT** | | **Xe-Lampe** | **Hg-Lampe** | |
| Benzen-derivate | X | X | X | X | X | 1 |
| Silizium- und Kohlen-stoffanaloga | X | | | | | 2 |
| 50 weitere silizium-organische Substanzen | X | X | | | | 3 |
| Substanzen aus der ECHA-Datenbank | | X* | | | | 3 |

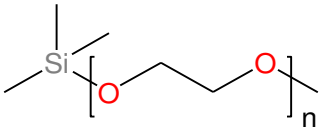
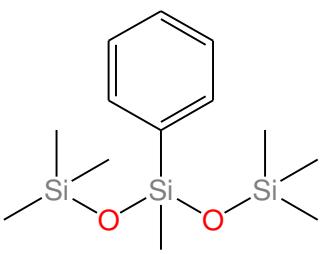
## 3.1 Auswahl der Substanzen

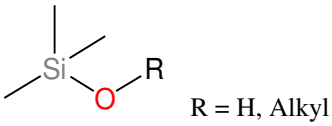
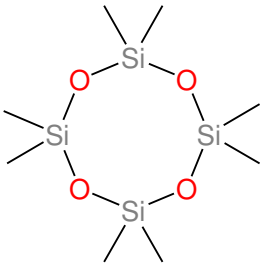
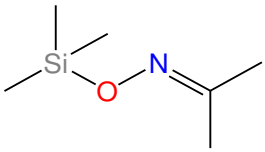
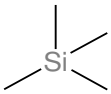
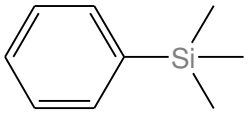
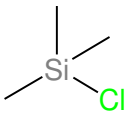
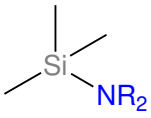
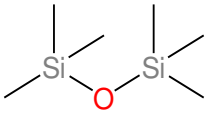
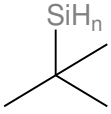
Für die vorliegende Arbeit wurde eine Vielzahl von Substanzen untersucht (Strukturformeln im Anhang). Ausschlaggebend für die Auswahl der Substanzen waren die kommerzielle Verfügbarkeit, die Synthetisierbarkeit (durch Projektpartner) und die Vielfalt an funktionellen Gruppen (Tabelle 2). Es wurden funktionelle Gruppen ausgewählt, von denen eine gute biologische Abbaubarkeit (z. B. primäre Alkohole und Carbonsäuren (Boethling et al., 2007)), eine gute Hydrolysierbarkeit (z. B. Ester (Boethling et al., 2007)) und eine gute photolytische Abbaubarkeit (z. B. +M-substituierte Benzenderivate (Hallas, 1979)) erwartet wurde.

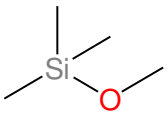
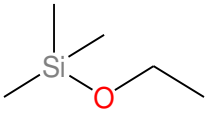
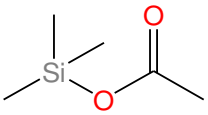
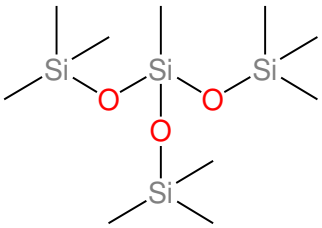
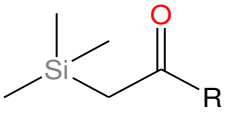
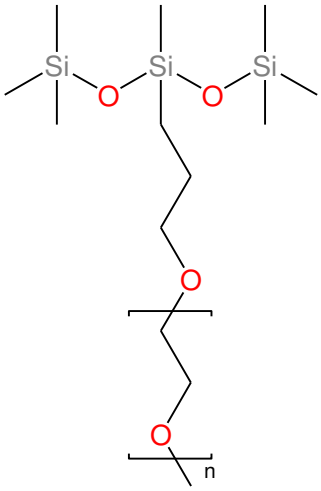
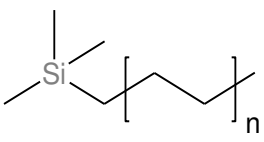
In Publikation 1 wurden 5 Benzenderivate mit einer Di-/Trimethylsilylgruppe und einer Methoxy- bzw. *N*,*N*-Dimethylaminogruppe in *para*- bzw. *ortho*-Position untersucht (*o*-MeOPhSiMe$_3$, *p*-MeOPhSiMe$_3$, (*p*-MeOPh)$_2$SiMe$_2$, *o*-Me$_2$NPhSiMe$_3$, *p*-Me$_2$NPhSiMe$_3$). Für Publikation 2 wurde neben 5 weiteren siliziumorganischen Substanzen (MeCONHSiMe$_3$, Me$_2$Si(OEt)$_2$, PrSi(OMe)$_3$, PhSi(OMe)$_2$Me und PhSi(OMe)$_3$) ein Vergleich der biologischen Abbaubarkeit mit 5 kohlenstoffanalogen Substanzen vorgenommen. In Publikation 3 wurden zusätzlich zu den eigenen experimentellen Daten (weitere 50 Substanzen) verfügbare Bioabbaudaten siliziumorganischer Substanzen aus der ECHA-Datenbank (siehe Kapitel 3.4) hinzugezogen und ausgewertet. Durch die Aufnahme von Daten aus der ECHA-Datenbank wurden auch kommerziell eingesetzte Siloxane und andere siliziumorganische Substanzen untersucht und bewertet (z. B. D$_4$, D$_5$ und D$_6$), von denen eine schlechtere biologische Abbaubarkeit erwartet wurde.

Insgesamt wurden valide Abbaudaten für 60 siliziumorganische Substanzen generiert und durch Bioabbaudaten von weiteren 122 Substanzen aus der ECHA-Datenbank ergänzt.

**Tabelle 2:** Überblick über die funktionellen Gruppen aller 182 Substanzen mit Gruppennummer, Gruppenname, einer Beispielstruktur und der Anzahl der Substanzen pro Gruppe (Publikation 3, * korrigierte Fassung).

| Gruppe | Name | Beispielstruktur | Anzahl |
|---|---|---|---|
| **1** | Oligoether |  | 3 |
| **2** | Aromatische Trisiloxane |  | 9 |

| | | | |
|---|---|---|---|
| **3** | O–$SiC_3$ |   R = H, Alkyl | 4 |
| **4** | Zyklische Siloxane |   | 5 |
| **5** | Oxime |   | 4 |
| **6** | Organosilane (Si–$C_4$) |   | 7 |
| **7** | Aromatische Organosilane |   | 13 |
| **8** | Chloride |   | 8 |
| **9** | Amine, Amide (Si–N) |   | 11 |
| **10** | Lineare Siloxane |   | 14 |
| **11** | Silane (Si–H) |   n = 3 | 1* |

| | | | |
|---|---|---|---|
| **12** | Methoxysiloxane |  | 40 |
| **13** | Ethoxysiloxane |  | 31* |
| **14** | Siloxanester |  | 10 |
| **15** | Verzweigte Siloxanes |  | 6 |
| **16** | Ketone, Carbonsäuren und (Thio)Ester |  R = Me, OH, OR', SR'' | 8 |
| **17** | Polyethertrisiloxane |  | 3 |
| **18** | Lineare Alkylkette |  | 5 |

## 3.2 Abbaubarkeitsstudien

### 3.2.1 Biologische Abbaubarkeit

Die biologische Abbaubarkeit der ausgewählten Substanzen wurde mithilfe des *Closed-Bottle*-Tests (CBT, OECD 301D) und des Manometrischen Respirationstests (MRT, OECD 301F) bestimmt. Beide Tests wurden OECD-konform über 28 Tage durchgeführt (OECD, 1992a). Der Abbau wurde über den Verbrauch an Sauerstoff durch die Mikroorganismen mittels verschiedener Messmethoden untersucht. Für den CBT wurde ein optischer Sauerstoffsensor verwendet. Im Test wurde eine geringe Menge an Bakterien aus Kläranlagenablauf (AGL Lüneburg) und Mineralstoffen, die die Bakterien für Ihren Stoffwechsel benötigen, eingesetzt. Für den MRT wurde ein drucksensitives Respirometer (OxiTop ®) verwendet, um die Sauerstoffzehrung zu ermitteln. Die Bakteriendichte im MRT ist etwa 1.600-fach höher als im CBT, wodurch auch die Diversität an Mikroorganismen erhöht wird. Zu Beginn und am Ende des Tests wurden Proben für eine spätere Analytik genommen.

Trotz der stark unterschiedlichen Bakteriendichte gelten Substanzen in beiden Tests als „leicht biologisch abbaubar“, wenn innerhalb von 28 Tagen ein Abbau von mindestens 60 % des theoretischen Sauerstoffbedarfs innerhalb eines 10-Tage-Fensters ermittelt wurde. Weitere Validitätskriterien sind: die Unterschiede der Duplikate am Ende des Tests dürfen nicht größer als 20 % sein, der Sauerstoffverbrauch der Blindkontrolle sollte 1,5 mg $L^{-1}$ nicht überschreiten, die Abbaurate der Toxizitätskontrolle muss am Tag 14 höher als 25 % sein, die Sauerstoffkonzentration in den Flaschen mit Testsubstanz muss am Ende des Tests höher als 0,5 mg $L^{-1}$ sein und die Abbaurate der Positivkontrolle muss am Tag 14 mindestens 60 % betragen.

In der Praxis kommen neben der korrekten Durchführung der Tests unter Berücksichtigung der Validitätskriterien noch weitere Herausforderungen hinzu. Viele der siliziumorganischen Substanzen haben mit einem Log P weit über 3 eine sehr schlechte Wasserlöslichkeit. Um dennoch Tests im wässrigen Medium durchführen zu können, wurden Lösungsvermittler verwendet. Für die biologischen Abbautests wurde Dimethylsulfoxid (DMSO) gewählt, da DMSO im Vergleich zur eingesetzten Menge (1 % v/v) nur einen sehr geringen Sauerstoffverbrauch verursacht hat. Ein weiteres Problem stellte die Flüchtigkeit einiger weniger Substanzen dar. Auch in diesem Fall konnte das Problem durch Lösungsvermittler eingedämmt werden. Weitere Angaben sind den Publikationen 1, 2 und 3 zu entnehmen.

### 3.2.2 Hydrolytische Abbaubarkeit

Die hydrolytische Abbaubarkeit von den 5 siliziumorganischen Benzenderivaten (*o*-$MeOPhSiMe_3$, *p*-$MeOPhSiMe_3$, (*p*-$MeOPh)_2SiMe_2$, *o*-$Me_2NPhSiMe_3$, *p*-$Me_2NPhSiMe_3$) wurde bei verschiedenen pH-Werten und Puffersystemen untersucht (OECD 111, Publikation 1). Dazu wurden die Substanzen unter kontrollierten Bedingungen bei 25 °C im Dunkeln im wässrigen Medium hydrolysiert und in

regelmäßigen Abständen beprobt (OECD, 2004). Diese Proben wurden dann mithilfe der HPLC-UV/Vis (Primärelimination) und der LC-$MS^n$ (Transformationsprodukte) analysiert. Detaillierte Angaben sind in Publikation 1 zu finden.

### 3.2.3 Photolytische Abbaubarkeit

Der Test, mit dem Sonnenlicht simuliert werden sollte, wurde unter Verwendung einer Xe-Lampe mit einem optischen Filter (300–800 nm) durchgeführt. Die Versuche an den 5 siliziumorganischen Benzenderivaten wurden im wässrigen Medium unter Zuhilfenahme verschiedener Lösungsvermittler (Isopropanol und Acetonitril) und in reinem Acetonitril durchgeführt. Die Lösungsvermittler wurden zum einen dafür verwendet die schlecht in Wasser löslichen siliziumorganischen Substanzen in Lösung zu bringen und zum anderen, um als Radikalfänger zu agieren (Faraggi et al., 1984, Newton und Milligan, 2006). Der Versuch in 100 % Acetonitril sollte zudem den Einfluss des Wassers während der Bestrahlung ausschließen, sodass die direkte Photolyse betrachtet werden konnte. Um den Verlauf der 480-minütigen Bestrahlung zu dokumentieren, wurden alle 120 min Proben genommen und unmittelbar mit der HPLC-UV/Vis analysiert (Kapitel 3.3.1).

In einem weiteren Versuch wurden die gleichen 5 siliziumorganischen Benzenderivate mit einer Mitteldruck Quecksilberlampe (Hg-Lampe, 200–400 nm) bestrahlt, um die Desinfektion mit UV-Licht nach der Kläranlage zu simulieren. Dem wässrigen Medium wurde hierfür Acetonitril als Lösungsvermittler und Radikalfänger zugesetzt. Aufgrund der energiereichen Strahlung und der Vermutung, dass ein Abbau mit der Hg-Lampe schneller ablaufen würde als bei der Bestrahlung mit der Xe-Lampe, wurden die Proben engmaschiger nach 0, 2, 4, 8, 16, 32, 64, 128 und 256 min genommen und direkt mittels HPLC-UV/Vis analysiert (Kapitel 3.3.1).

Parallel zu beiden Bestrahlungsversuchen wurden Dunkelproben (Blindwert) unter denselben Bedingungen betrachtet. Diese dienten dem direkten Vergleich und sollten Rückschlüsse auf den Effekt der Bestrahlung liefern. Alle Proben von *p*-$Me_2NPhSiMe_3$ aus diesen Versuchen wurden ebenfalls für die Analyse der Transformationsprodukte verwendet. Weitere Details können Publikation 1 entnommen werden.

## 3.3 Analyse der siliziumorganischen Substanzen

Die Analyse der siliziumorganischen Substanzen gestaltete sich oft schwierig, da sie entweder schlecht detektierbar (z. B. keine Absorption > 200 nm, schlecht oder nicht ionisierbar) oder schlecht aus dem wässrigen Medium extrahierbar (oftmals zu polar) waren. Es wurde zwischen Substanzen, die UV/Vis-aktiv und GC-MS-gängig waren, unterschieden. Zusätzlich wurde die Primärelimination der Muttersubstanzen (Kapitel 3.3.1) anders ermittelt als die Bestimmung der Transformationsprodukte (Kapitel 3.3.2).

### 3.3.1 Analyse der Primärelimination

Das „Verschwinden“ der Muttersubstanz wird als Primärelimination bezeichnet. Dabei können Prozesse wie Sorption, Verflüchtigung, Hydrolyse, biologischer und photolytischer Abbau eine Rolle spielen. Eine Bildung von Transformationsprodukten kann bei der Hydrolyse und dem Abbau nicht ausgeschlossen werden. Im Gegensatz zur Bestimmung des biologischen Abbaus wird bei der Bestimmung der Primärelimination nur ein erster Teilschritt betrachtet. Besser wäre es an dieser Stelle die Mineralisierung anhand des gesamten organischen Kohlenstoffgehalts (*total organic carbon*, TOC) zu bestimmen. Da aufgrund der schlechten Löslichkeit der Substanzen mit kohlenstoffhaltigen Lösungsvermittlern gearbeitet werden musste, ist der Kohlenstoffgehalt der Lösung sehr hoch (ca. 10.000 mg $L^{-1}$), sodass das Signal der Testsubstanzen (ca. 5–10 mg $L^{-1}$) im Rauschen untergehen würde.

Der Nachweis der Primärelimination kann je nach Eigenschaften der Substanzen auf unterschiedliche Weise erfolgen. Für die siliziumorganischen Benzenderivate (Publikation 1) konnte die Analyse mithilfe der HPLC-UV/Vis durchgeführt werden. Dazu wurde ein substanzgruppenspezifisches Eluentenprofil entwickelt, um die Muttersubstanzen von den gebildeten Transformationsprodukten zu trennen. Anschließend wurden die Substanzen im UV/Vis-Detektor mit spezifischen Wellenlängen (227 nm (*o*-$MeOPhSiMe_3$), 228 nm (*p*-$MeOPhSiMe_3$), 236 nm ((*p*-$MeOPh)_2SiMe_2$), 256 nm (*o*-$Me_2NPhSiMe_3$) und 264 nm (*p*-$Me_2NPhSiMe_3$)) angeregt und deren Absorptionsspektren detektiert. Weitere Details zum Eluentenprofil sind Publikation 1 zu entnehmen.

Die Substanzen aus Publikation 2 wurden mithilfe von GC-MS analysiert. Dazu wurde zunächst ein geeignetes Temperaturprofil entwickelt, um die Substanzen aufzutrennen und anhand ihrer Retentionszeiten näher zu charakterisieren. Die im Anschluss generierten Massenspektren konnten mithilfe einer Software eigenen Spektrenbibliothek eindeutig den Substanzen zugeordnet werden. Eine der Substanzen ($PhC(OMe)_2Me$) war nicht in der Spektrenbibliothek enthalten und wurde deshalb mithilfe einer Fragmentierungsmodellierungssoftware (http://cfmid.wishartlab.com/predict) berechnet und mit dem gemessenen Spektrum verglichen.

Für die GC-Analyse der Substanzen in wässrigen Proben musste zunächst das Lösungsmittel substituiert werden, da Wasser ein ungeeignetes Lösungsmittel für die GC-Messung ist. Ein Lösungsmittel mit geringem Siedepunkt, welches im Injektor schnell verdampft und somit bei kurzer Retentionszeit im Chromatogramm erscheint, wird bevorzugt, da die Analyten auf diese Weise nicht vom Lösungsmittelsignal überlagert werden. Gängige Lösungsmittel für die GC-Analytik sind z. B. *n*-Hexan und Cyclohexan. Es wurden zwei unterschiedliche Extraktionen durchgeführt. Die flüssig-flüssig-Extraktion wurde mit einem Gemisch aus Chloroform und Methanol (2:1 v/v) durchgeführt. Dazu wurden 2 mL des Extraktionsmittels mit 1 mL wässriger Probe gemischt. Nach der Phasentrennung wurden 1,2 mL der Chloroformphase in ein Zentrifugenglas überführt und unter einem sanften Stickstoffstrom bis zur Trockne eingedampft. Die Festphasenextraktion wurde mit HR-X-Kartuschen

(6 mL/200 mg, Macherey Nagel, Düren, Deutschland) durchgeführt. Die Konditionierung der Kartuschen wurde mit 10 mL Methanol und 10 mL Wasser durchgeführt. Danach wurde 1 mL der wässrigen Probe in die Kartuschen gesaugt. Die Kartuschen wurden für 20 min unter Vakuum getrocknet. Der Analyt wurde mit 5 mL Chloroform/Methanol (1:1) eluiert und unter leichtem Stickstoffstrom zur Trockne reduziert. Der Rückstand wurde bei beiden Extraktionsarten mit 100 µL *n*-Hexan aufgenommen und mittels GC-MS analysiert. Weitere Details können Publikation 2 entnommen werden.

### 3.3.2 Analyse der Transformationsprodukte

Die Transformationsprodukte eines der siliziumorganischen Benzenderivate (*p*-$Me_2NPhSiMe_3$) wurden mittels LC-$MS^n$ untersucht, um die Strukturen der Transformationsprodukte näher zu charakterisieren. Proben aus den Hydrolyse- und Photolyseversuchen sowie dem Bioabbau wurden mithilfe der entwickelten HPLC-Methode getrennt und mittels $MS^n$ analysiert. Genauere Informationen zu den Einstellungen am Gerät können Publikation 1 entnommen werden. Rückschlüsse auf die Konzentration der entstandenen Transformationsprodukte konnten nur relativ im Verhältnis zur Konzentration der Muttersubstanz gezogen werden, da keine Standards der jeweiligen Transformationsprodukte vorlagen. Ebenso konnte vermutlich keine allumfassende Analyse der Transformationsprodukte mit dieser Methode durchgeführt werden, da die Ionisationseigenschaften der Transformationsprodukte stark variieren können und somit die Detektion als limitierender Faktor zu betrachten ist.

## 3.4 Datenerhebung und Bewertung von Abbaudaten aus der ECHA-Datenbank

Die ECHA-Datenbank ist eine frei zugängliche Datenbank, in der Informationen zu physikalisch-chemischen Eigenschaften (z. B. Schmelz- und Siedepunkt, Dichte und Dampfdruck), zur Ökotoxizität (z. B. Toxizität für Fische, Algen und Cyanobakterien) und zum biologischen Abbau von in der Europäischen Union registrierten Stoffen hinterlegt sind. Aus dieser Datenbank konnten Bioabbaudaten sämtlicher registrierter siliziumorganischer Substanzen inklusive der Testart, -dauer, -parameter und Verlässlichkeit entnommen werden. Diese Daten wurden zusammen mit den eigens experimentell ermittelten Bioabbaudaten in einen Datensatz bestehend aus den Daten von 182 Substanzen (Anhang) zusammengetragen, der hinsichtlich Struktur-Abbaubarkeits-Beziehungen ausgewertet wurde. Dazu wurden die Substanzen zunächst gruppiert und anschließend die Bioabbaudaten im Detail betrachtet. So konnten Substanzgruppen und Strukturmerkmale identifiziert werden, die einen biologischen Abbau begünstigen oder hemmen (Publikation 3).

# 4 Ergebnisse und Diskussion

In den folgenden Abschnitten werden die Ergebnisse der drei Publikationen vorgestellt und diskutiert.

## 4.1 Abbaubarkeit der Benzenderivate und gebildete Transformationsprodukte

Die detaillierten Ergebnisse zur Abbaubarkeit der Benzenderivate sind in Publikation 1 veröffentlicht. Eine Zusammenfassung der Ergebnisse aus den verschiedenen Abbautests ist in Tabelle 3 dargestellt. Die fünf Substanzen zeigten einen biologischen Abbau von −10–8 %. Bis auf Substanz (*p*-MeOPh)$_2$SiMe$_2$ hatten alle Substanzen eine Halbwertszeit von maximal einem Tag während der Hydrolyse. Die Hydrolyse von Substanz (*p*-MeOPh)$_2$SiMe$_2$ war deutlich langsamer als die der anderen Substanzen und stark pH abhängig. Die Photolyse mit der Xe-Lampe resultierte in Abbauraten von 13–100 % und die Photolyse mit der Hg-Lampe verursachte Abbauraten von 92–100 %. Bei beiden Bestrahlungsexperimenten hatte *p*-Me$_2$NPhSiMe$_3$ die höchste und (*p*-MeOPh)$_2$SiMe$_2$ die geringste Photolyserate.

Aus den Ergebnissen lässt sich ableiten, dass die Benzenderivate weder im CBT noch im MRT biologisch abbaubar waren. Somit konnte die Annahme, dass die Verwendung einer biologisch abbaubaren Grundstruktur (hier Anisol) in einer verbesserten biologischen Abbaubarkeit der siliziumorganischen Verbindung resultiert, nicht bestätigt werden. Die schlechte Abbaubarkeit kann demnach auf die Trimethylsilylgruppe der Verbindung zurückgeführt werden, da dies der einzige Unterschied zum leicht biologisch abbaubaren Anisol ist (ECHA, 2020a). Ebenso haben die zwei Methylgruppen an der Aminogruppe einen negativen Einfluss auf die biologische Abbaubarkeit (Kuhn und Suflita, 1989). Die Verwendung leicht biologisch abbaubarer Grundstrukturen hat für diese Substanzklasse mit den hier angewendeten Methoden nicht die gewünschten Effekte gebracht und keine leicht abbaubaren siliziumorganischen Substanzen generiert.

Alle fünf getesteten Substanzen zeigten eine Anfälligkeit gegenüber Hydrolyse bei den vorherrschenden Bedingungen. Die beiden Methoxy-substituierten Benzenderivate zeigten eine schnelle pH unabhängige Hydrolyse innerhalb von 4 Tagen. Die beiden *N*,*N*-Dimethylamino-substituierten Verbindungen hydrolysierten ebenfalls schnell (4–7 Tage), jedoch hydrolysierte die *para*-substituierte Substanz bei pH 4 deutlich schneller als bei pH 7 und 9. Das zweifach *para*-Methoxybenzen-substituierte Derivat war gegenüber der Hydrolyse am stabilsten, zeigte von allen fünf Verbindungen allerdings die stärkste pH-Abhängigkeit. Diese Stabilität im wässrigen Medium könnte auf eine sterische Abschirmung der hydrolysierbaren Bindungen durch die aromatischen Ringe zustande kommen (Bruice et al., 2011, Xu et al., 2013). Wenn eine pH-Abhängigkeit der Hydrolyse bei den Substanzen vorlag, hydrolysierten sie bei niedrigen pH-Werten schneller als bei hohen. Man spricht in diesem Fall von einer säurekatalysierten Hydrolyse. In der wasserfreien Umgebung waren die Substanzen über den getesteten Zeitraum stabil.

Demnach ist die Primärelimination eindeutig auf eine Reaktion mit Wasser zurückzuführen. Dieses Wissen kann für das gezielte Design von Substanzen verwendet werden. Solche Substanzen könnten beispielsweise unter neutralen/basischen oder wasserfreien Bedingungen ihre Funktion während der Anwendung erfüllen und danach mittels saurer Hydrolyse eliminiert werden. Wenn zusätzlich funktionelle Gruppen als Schutzgruppen eingesetzt werden, um die Hydrolysegeschwindigkeit zu steuern (Gitto und Wooley, 1995), unterstützt das die These der „gerichteten Hydrolyse“ (Rücker und Kümmerer, 2013). Das bedeutet, dass die Moleküle so konzipiert sind, dass sie sich in einer bestimmten Zeit bzw. unter bestimmten Bedingungen abbauen und sich nicht in der Umwelt anreichern.

Die unterschiedlichen Lösungsvermittler hatten während der Bestrahlung mit der Xe-Lampe keinen merklichen Einfluss auf die Geschwindigkeit der Eliminierung. Eine wasserfreie Umgebung hingegen stellte den rein photolytisch abgebauten Anteil dar, der zum Teil stark von den Ergebnissen im wässrigen Medium abwich. Die Bestrahlung in der wasserfreien Umgebung (dargestellt in Publikation 1) brachte zum Vorschein, dass lediglich die *para*-substituierte Aminoverbindung mithilfe der Xe-Lampe primär eliminiert wurde. Die Überlappung von Emissionsspektrum der Lampe und Absorptionsspektrum der Substanz war hier am größten. Daraus ist abzuleiten, dass die Einführung von +M-Gruppen einen positiven Effekt auf die photolytische Abbaubarkeit bei Verwendung der Xe-Lampe hat und in der wasserfreien Umgebung auf direkte Photolyse zurückzuführen ist.

Die fünf getesteten Substanzen sind innerhalb der 256 min zu mindestens 92 % mithilfe der Hg-Lampe primär eliminiert worden. Trotz ähnlich hoher Eliminierungsraten nach den 256 min konnten unterschiedliche Geschwindigkeitskonstanten *k* ermittelt werden. Aus den Geschwindigkeitskonstanten lässt sich ableiten, dass die *para*-substituierte Aminoverbindung (*p*-$Me_2NPhSiMe_3$, $k = 0{,}158\ min^{-1}$) am schnellsten und das zweifach *para*-Methoxy-Benzen-substituierte Derivat ((*p*-$MeOPh)_2SiMe_2$, $k = 0{,}024\ min^{-1}$) am langsamsten eliminiert wurde. Das einfach *para*-Methoxy-Benzen-substituierte Derivat (*p*-$MeOPhSiMe_3$) wurde schneller als das zweifach substituierte Derivat eliminiert ($k = 0{,}089\ min^{-1}$), aber langsamer als die *para*-substituierte Aminoverbindung. Diese Erkenntnisse stehen im Einklang mit der Vermutung, dass eine größere Überlappung des Absorptionsspektrums der Substanzen mit dem Emissionsspektrum der Lampe eine höhere photolyseinduzierte Eliminierung hervorruft.

Im Photolyseversuch mit der Hg-Lampe wurden jeweils die *para*-substituierten im Vergleich zu den *ortho*-substituierten Verbindungen schneller primär eliminiert. Mit der Xe-Lampe konnte dieser Effekt nicht beobachtet werden. Gegenüber des Bestrahlungsexperiments mit der Xe-Lampe wurden die Substanzen mit der Hg-Lampe deutlich schneller eliminiert. Das ist zum einen auf die unterschiedlich emittierten Wellenlängen der Lampen und zum anderen auch auf die Intensität der Strahlung zurückzuführen.

Die eventuell auftretende Abnahme der Kohlenstoffkonzentration der Muttersubstanzen und gegebenenfalls gebildeter Transformationsprodukte konnte aufgrund der Verwendung der organischen

Lösungsvermittler nicht bestimmt werden. Die Konzentration der Lösungsvermittler hätte die vergleichsweise geringe Konzentration der getesteten Substanzen überlagert. Um dennoch weitere Informationen gewinnen zu können, wurden im nächsten Schritt die Transformationsprodukte der *para*-substituierten Aminoverbindung bestimmt.

**Tabelle 3:** Zusammenfassung der generierten Ergebnisse aus den biotischen und abiotischen Abbauversuchen. CBT und MRT wurden über einen Zeitraum von 28 Tagen durchgeführt (n = 2, * n = 4). Die Hydrolyseexperimente (n = 2) wurden bei verschiedenen pH-Werten durchgeführt bis die Substanzkonzentration unterhalb von 10 % lag oder 28 Tage erreicht waren. In der Tabelle sind die Halbwertszeiten ($t_{1/2}$) dargestellt. Die Photolyseversuche (n = 3) mit der Xe-Lampe dauerten 480 min und die mit der Hg-Lampe 256 min. Die prozentuale primäre Eliminierung (Elim.) bei der Photolyse ist inklusive der auftretenden Hydrolyse dargestellt.

| | **Bioabbau** | | **Hydrolyse** | | **Photolyse** | |
|---|---|---|---|---|---|---|
| | CBT | MRT | | | Xe-Lampe | Hg-Lampe |
| **Substanz** | Abbau in % | Abbau in % | $t_{1/2}$ in d | | Elim. in % | Elim. in % |
| *o*-MeOPhSiMe$_3$ | −2 | −10 | pH 4, 7, 9 | 0,5 | 96±2 | 99±2 |
| *p*-MeOPhSiMe$_3$ | 3±2* | −7 | pH 4, 7, 9 | 0,7 | 88±4 | 99±2 |
| (*p*-MeOPh)$_2$SiMe$_2$ | 0±2* | 8 | pH 4 | 7,5 | 13±3 | 92±3 |
| | | | pH 7 | 58,7 | | |
| | | | pH 9 | 169,1 | | |
| *o*-Me$_2$NPhSiMe$_3$ | −2 | −3 | pH 4 | 0,7 | 84±3 | 100±7 |
| | | | pH 7, 9 | 1,0 | | |
| *p*-Me$_2$NPhSiMe$_3$ | 6±8* | −4 | pH 4 | 0,3 | 100±0 | 100±1 |
| | | | pH 7, 9 | 1,0 | | |

Von der *para*-substituierte Aminoverbindung *p*-Me$_2$NPhSiMe$_3$ wurden elf Transformationsprodukte mittels $MS^n$ detektiert und näher charakterisiert. Außerdem wurden das Auftreten und die Konzentration der Transformationsprodukte in den unterschiedlichen biotischen und abiotischen Tests untersucht. Einige Transformationsprodukte enthielten weiterhin Silizium, was anhand des Isotopenmusters im Massenspektrum eindeutig zugeordnet werden konnte. Die Massen des Molpeaks, des Molpeaks plus eins und des Molpeaks plus zwei stehen im Verhältnis 100 : 5,1 : 3,3 (Gross, 2019). Wenn kein Silizium mehr enthalten war, ist es wahrscheinlich, dass die Trimethylsilylgruppe abgespalten wurde.

Die Hydroxylierung ist eine der häufigsten Transformationen im wässrigen Medium (Mahmoud et al., 2013). Die resultierenden Produkte sind polarer als die Muttersubstanz und haben daher bei den verwendeten Trennsäulen (Umkehrphase) kürzere Retentionszeiten als die Muttersubstanz. Während der Bestrahlung im wasserfreien Medium traten diese Transformationsprodukte nicht auf, sodass darauf geschlossen werden kann, dass diese Transformationsprodukte durch indirekte Photolyse, also durch die

Reaktion mit durch Strahlung generierte Hydroxylradikale, entstanden sind. Die Anzahl der gebildeten Transformationsprodukte war unabhängig von der Bestrahlungsquelle. Lediglich die Konzentration und die Bildungs- und Eliminierungsrate wurden dadurch beeinflusst. Am Ende der Bestrahlung mit der Hg-Lampe waren alle zuvor detektierten Transformationsprodukte eliminiert worden. Eine Aussage zu zuvor nicht detektierten Transformationsprodukten kann leider nicht getroffen werden. Auch hier wäre ein Nachweis der Mineralisierung bzw. eine Messung der Kohlenstoffkonzentration sinnvoll gewesen, was aber aufgrund der Verwendung des organischen Lösungsvermittlers zu keinem eindeutigen Ergebnis geführt hätte.

## 4.2 Vergleich von Silizium- und Kohlenstoffanaloga

Keine der Siliziumverbindungen war im CBT leicht biologisch abbaubar. Drei von fünf Kohlenstoffverbindungen waren leicht biologisch abbaubar, was bedeutet, dass deren Abbau größer als 60 % war. Eine Kohlenstoffverbindung ($MeCONHCMe_3$) zeigte gar keinen Abbau. Die anderen Substanzen waren mindestens zu 20 % abbaubar. Der Vergleich der analogen Paare zeigte, dass eine siliziumhaltige Substanz ($MeCONHSiMe_3$) besser abbaubar war als die Kohlenstoffverbindung, eine zeigte annähernd das gleiche Abbauverhalten wie die Kohlenstoffverbindung ($Me_2Si(OEt)_2$ und $Me_2C(OEt)_2$) und drei siliziumhaltige Substanzen ($PrSi(OMe)_3$, $PhSi(OMe)_2Me$ und $PhSi(OMe)_3$) waren deutlich schlechter biologisch abbaubar als ihre analogen Kohlenstoffverbindungen. Besonderes Strukturmerkmal der besser abbaubaren Siliziumverbindung ist eine Silizium-Stickstoff-Bindung, welche leicht durch Hydrolyse gespalten werden kann (Rücker und Kümmerer, 2013). Daher wird angenommen, dass diese Bindung zunächst hydrolysierte und anschließend das siliziumfreie Hydrolyseprodukt Acetamid biologisch abgebaut wurde. Der per Sauerstoffmessung festgestellte Abbau der Muttersubstanz wäre demnach nur durch den Abbau der leicht abbaubaren Verbindung Acetamid erreicht worden. Das zweite gebildete Hydrolyseprodukt Trimethylsilanol war nicht biologisch abbaubar (ECHA, 2020b). Eine solche Silizium-Stickstoff-Bindung könnte als Sollbruchstelle in größere siliziumorganische Polymere eingebaut werden, um eine Spaltung im wässrigen Medium zu provozieren. Daher sollten auf diese Weise modifizierte Verbindungen in einer wasserfreien Umgebung Anwendung finden. Erst nach der Anwendung und mit Erreichen der aquatischen Umwelt würde ein Zerfall der Verbindung beginnen.

Die drei leicht abbaubaren Kohlenstoffverbindungen hydrolysierten im ersten Schritt. Im zweiten Schritt wurden alle entstandenen Hydrolyseprodukte biologisch abgebaut. Es handelte sich bei den Hydrolyseprodukten um Methanol, Butansäure, Acetophenon und Benzoesäure, welche für ihre leichte biologische Abbaubarkeit bekannt sind (Ahmad et al., 1979, Cordes und Bull, 1974, Wagner, 1976). Die analogen Siliziumverbindungen waren schlechter abbaubar, weil immer ein nicht biologisch abbaubares Silanol gebildet wurde. Die gebildeten Silanole sind allerdings fähig zu größeren Oligomeren zu kondensieren (Issa und Luyt, 2019), welche eine schlechtere Löslichkeit und demnach eine noch schlechtere Bioverfügbarkeit aufweisen.

Die Ergebnisse aus dem Bioabbautest wurden anschließend noch durch Analysen der Bioabbauproben zu Beginn und am Ende des Tests ergänzt. Die Extraktion und Analytik der Substanzen aus dem wässrigen Medium war eine große Herausforderung. Extrahierbar mit flüssig-flüssig-Extraktion waren die Substanzen $MeCONHCMe_3$, $PrSi(OMe)_3$, $PhC(OMe)_2Me$ und $PhC(OMe)_3$. Einige Substanzen waren zu polar, um sie aus der Wasserphase mit organischen, mit Wasser nicht mischbaren Lösungsmitteln zu extrahieren. Mittels Festphasenextraktion konnten auch nicht alle Substanzen extrahiert werden (nur $PhSi(OMe)_2Me$ und $PhSi(OMe)_3$). Die Substanzen $MeCONHSiMe_3$, $Me_2Si(OEt)_2$, $Me_2C(OEt)_2$ und $PrC(OMe)_3$ konnten weder mit flüssig-flüssig-Extraktion noch mit Festphasenextraktion extrahiert werden. Ursache für die schlechte Extrahierbarkeit könnte die Polarität der Substanzen sein, durch die entweder zu wenige oder zu starke Wechselwirkungen mit dem Säulenmaterial der festen Phase vorlagen. Bei zu wenigen Wechselwirkungen adsorbiert der Analyt nicht an der festen Phase, sondern läuft mit dem Lösungsmittel direkt durch die Kartusche. Bei zu starken Wechselwirkungen mit dem Säulenmaterial bleibt der Analyt auch nach der Elution auf dem Säulenmaterial. In beiden Fällen kann keine Analyse der Substanz erfolgen.

Durch die Analyse konnte bestätigt werden, dass die nicht abbaubare Kohlenstoffverbindung ($MeCONHCMe_3$) vor und nach dem Bioabbau in nahezu gleichen Konzentrationen vorgelegen hat und sich demnach im Verlauf der 28 Tage nicht verändert hat. Zwei der drei leicht abbaubaren Kohlenstoffverbindungen ($PhC(OMe)_2Me$ und $PhC(OMe)_3$) konnten in Proben von Tag 0, aber nicht in Proben von Tag 28 nachgewiesen werden. Dadurch wurde bestätigt, dass die Substanzen im Verlauf der Zeit vollständig eliminiert wurden. Da keinerlei Transformationsprodukte nachgewiesen wurden und der biologische Abbau bei über 85 % lag, ist bei diesen Verbindungen von einer vollständigen Mineralisierung auszugehen.

## 4.3 Auswertung des erstellten Datensatzes

Für die Erstellung des Datensatzes wurden sämtliche Bioabbaudaten von siliziumorganischen Verbindungen aus der ECHA-Datenbank extrahiert und mit experimentellen Daten dieser Arbeit und früher in der Arbeitsgruppe durchgeführten Tests aus dem Labor ergänzt. Die Bioabbaudaten wurden durch folgende Tests generiert: OECD 301A (11 Substanzen), OECD 301B (36 Substanzen), OECD 301C (21 Substanzen), OECD 301D (63 Substanzen), OECD 301F (63 Substanzen) (OECD, 1992a), OECD 306 (OECD, 1992b, 2 Substanzen), OECD 310 (OECD, 2014, 14 Substanzen), OECD 302C (OECD, 2009, 1 Substanz) und einen Bioabbautest beschrieben durch Bourquin (Bourquin, 1975, 1 Substanz). Von den insgesamt 254 Messwerten (für 182 Substanzen) lagen 154 Werte unterhalb von 30 %, 70 Werte zwischen 30 und 60 % und nur 30 Werte oberhalb von 60 % (Abbildung 1). Ausgehend von den Bioabbauwerten und den Kriterien für leichte biologische Abbaubarkeit konnten nur 12 Substanzen als leicht biologisch abbaubar klassifiziert werden. Bei den übrigen Substanzen (Abbau ≥ 60 %) wurde das Validitätskriterium des 10-Tage-Fensters nicht erfüllt, der Bioabbau wurde über den gelösten Kohlenstoff bestimmt (Schwellenwert von ≥70 %) oder es wurde ein Test durchgeführt, der keine Aussagekraft über die leichte biologische Abbaubarkeit hat (z. B. OECD 306 marine Abbaubarkeit). Die Substanzen, zu denen die 70 Abbauwerte zwischen 30 und 60 % gehören, sind laut OECD-Kriterien nicht leicht biologisch abbaubar, können aber als moderat biologisch abbaubar bezeichnet werden. Diese Klassifizierung ist nicht OECD-konform, kann aber aus Erfahrungswerten abgeleitet werden. Substanzen, deren Abbauwerte unterhalb von 30 % liegen, werden als nicht leicht biologisch abbaubar bezeichnet.

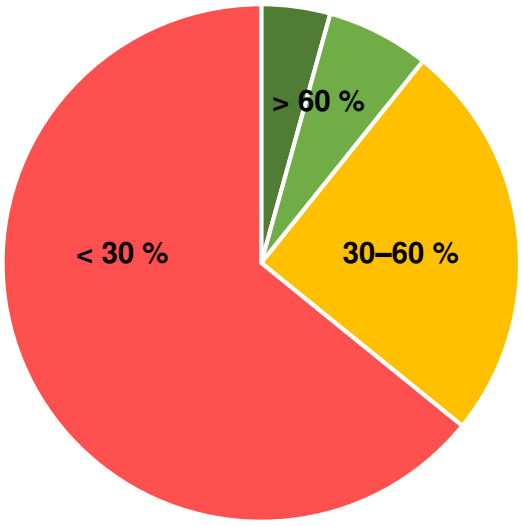



**Abbildung 1:** Anteile der biologischen Abbauwerte der siliziumorganischen Substanzen. Werte unter 30 % sind rot dargestellt, zwischen 30 und 60 % gelb und über 60 % grün. Der Anteil der leicht biologisch abbaubaren Substanzen ist dunkelgrün dargestellt.

Für die Identifizierung von Strukturmerkmalen, die einen Abbau begünstigen, wurden die 182 Substanzen in 18 Gruppen eingeteilt (Tabelle 2). Einteilungskriterien wurden anhand der funktionellen Gruppen festgelegt. Gruppe 1 enthält Oligoether, Gruppe 2 aromatische Trisiloxane mit Substituenten in *para*-Position, Gruppe 3 Verbindungen mit $O–SiC_3$, die zu keiner anderen Gruppe passen, Gruppe 4 zyklische Siloxane, Gruppe 5 Oxime, Gruppe 6 Organosilane, Gruppe 7 aromatische Organosilane, Gruppe 8 Organosilane mit mindestens einer Si–Cl-Bindung, Gruppe 9 Amine und Amide, Gruppe 10 lineare Siloxane, Gruppe 11 Silane, Gruppe 12 Methoxysiloxane, Gruppe 13 Ethoxysiloxane, Gruppe 14 Siloxanester, Gruppe 15 verzweigte Siloxane, Gruppe 16 Organosilane mit Keto-, Carbonsäure- und Esterfunktionen in der Kohlenstoffkette, Gruppe 17 Polyethertrisiloxane und Gruppe 18 Organosilane mit linearen Kohlenstoffketten. Von den 18 Gruppen enthalten nur 5 Gruppen leicht biologisch abbaubare Substanzen (Gruppen 1, 9, 12, 13 und 14). In diesen Gruppen sind aber auch nicht biologisch abbaubare Substanzen enthalten (außer in Gruppe 1). Die gute bis sehr gute biologische Abbaubarkeit ist meist auf die Hydrolyse der Muttersubstanz und die anschließende Mineralisierung der siliziumfreien Hydrolyseprodukte wie lineare Alkohole, Carbonsäuren, Ketone, Aldehyde und Amide zurückzuführen (Boethling et al., 2007, ECHA, 2020a). Substanzen der Gruppen 1, 9, 12, 13, 14, 16 und 17 reagieren mit Wasser zu solchen Hydrolyseprodukten und diversen Silanolen. Verzweigte Kohlenwasserstoffverbindungen sind schlechter abbaubar als lineare Verbindungen mit gleicher Kohlenstoffanzahl (Boethling et al., 2007). Zudem gibt es auch Gruppen, die fast ausschließlich nicht abbaubare Substanzen beinhalten (Gruppen 2, 3, 4, 6, 7, 8, 10 und 15). Bei diesen Substanzen ist entweder die Hydrolyse eingeschränkt oder es entstehen nicht biologisch abbaubare Hydrolyseprodukte. Eine leichte biologische Abbaubarkeit konnte nur dann beobachtet werden, wenn neben dem Siliziumanteil auch größere kohlenstoffbasierte Anteile im Molekül vorhanden sind, die von Mikroorganismen verstoffwechselt werden können. Die weiteren Gruppen (5, 11 und 18) zeigten eine wenig bis moderate biologische Abbaubarkeit abhängig vom Kohlenstoffanteil der Verbindungen.

# 5 Allgemeine Diskussion

Im Folgenden werden die Ergebnisse der Prüfung der drei Hypothesen aus Kapitel 2.1 dargestellt. Des Weiteren werden Gemeinsamkeiten und Unterschiede der drei Publikationen aufgezeigt. Neben diesem Vergleich werden neue Erkenntnisse dieser Arbeit verdeutlicht und Empfehlungen für verschiedene Anwendungsbereiche gegeben.

## 5.1 Prüfung der Hypothesen

Die erste Hypothese, dass Amino- und Methoxygruppen am aromatischen Ring die biologische und photolytische Abbaubarkeit von aromatischen siliziumorganischen Substanzen verbessern können, konnte zum Teil bestätigt werden. Auch wenn die biologische Abbaubarkeit nicht verbessert werden konnte, war der Unterschied zwischen den unterschiedlich substituierten Verbindungen in den Bestrahlungsversuchen eindeutig. Die Einführung einer Aminogruppe in *para*-Position hatte aufgrund des bathochromen Effekts (Pohorecki et al., 2010) einen positiven Einfluss auf die photolytische Eliminierung bei beiden Strahlungsquellen. Die Bestrahlung in der wasserfreien Umgebung zeigte, dass lediglich die *para*-substituierte Aminoverbindung mithilfe der Xe-Lampe primär eliminiert wurde. Die Überlappung von Emissionsspektrum der Lampe und Absorptionsspektrum der Substanz war hier am größten.

Die zweite Hypothese, dass Kohlenstoffsubstanzen besser biologisch abbaubar sind als ihre siliziumanalogen Substanzen, konnte nur teilweise bestätigt werden. Die Verbindung mit der Silizium-Stickstoff-Bindung war gegenüber ihrem Kohlenstoffanalogon besser abbaubar, weil eine schnelle Hydrolyse in zum Teil biologisch abbaubare Substanzen stattgefunden hat. Die analoge Kohlenstoffverbindung war gegenüber Wasser und Mikroorganismen sehr stabil, da die *tert*-Butylgruppe eine Reaktion verhindert. Die anderen Kohlenstoffverbindungen waren gleich gut oder besser biologisch abbaubar als ihre Siliziumanaloga. Nach der vorangegangenen Hydrolyse wurden bei den Kohlenstoffverbindungen nur Hydrolyseprodukte gebildet, die anschließend durch die Mikroorganismen leicht biologisch abbaubar waren.

Die dritte Hypothese, dass es funktionelle Gruppen gibt, die die biologische Abbaubarkeit von siliziumorganischen Verbindungen begünstigen, konnte bestätigt werden. Methoxy-, Ethoxy-, Acetoxy-, Amino- und Amidgruppen üben einen positiven Einfluss auf die Abbaubarkeit aus, da diese leicht hydrolysierbare Bindungen enthalten, was in diesen Fällen in leicht biologisch abbaubaren Hydrolyseprodukten resultierte. Genauso wie es begünstigende Gruppen gibt, konnten Strukturmerkmale identifiziert werden, die einen biologischen Abbau einschränken oder sogar verhindern. Hierzu zählen vor allem die klassische Siloxanstruktur (linear, zyklisch und verzweigt) und Organosilane mit vier Kohlenstoffatomen am Siliziumatom.

## 5.2 Vergleich der Publikationen

Allen drei Publikationen ist gemein, dass sie den Bioabbau von siliziumorganischen Substanzen beschreiben. Die Ergebnisse aus den ersten beiden Publikationen sind in die dritte Publikation eingeflossen. Die Bestimmung der biologischen Abbaubarkeit wurde vor allem mittels CBT durchgeführt und teilweise durch Ergebnisse aus dem MRT ergänzt. Obwohl im MRT eine ca. 1.600-fach höhere Bakteriendichte vorlag, unterschieden sich die Abbauwerte meist nur unwesentlich (5–25 %). Dadurch wird gezeigt, dass durch die Erhöhung der Bakteriendichte und -diversität nur ein bestimmter maximaler Bioabbau erreicht werden kann, der durch die Struktur des Moleküls vorgegeben ist. Es blieben immer Substanzen mit Silizium-Kohlenstoff-Bindungen übrig (z. B. Silanole oder aromatische Organosilane), da die hierfür benötigten Mikroorganismen im Lüneburger Kläranlagenablauf nicht ausreichend vorhanden sind. Die, die solche Bindungen spalten könnten, würden von anderen schneller wachsenden Mikroorganismen verdrängt werden.

Bei den gut abbaubaren Strukturen hat sich gezeigt, dass oftmals eine Hydrolyse als obligatorischer Schritt vorangegangen sein muss, damit die Mikroorganismen einen Angriffspunkt haben. Bei Substanzen, wo die Hydrolyse eingeschränkt stattgefunden hat, z. B. wenn die hydrolyseanfälligen Bindungen durch voluminöse Gruppen abgeschirmt wurden, konnte auch kein Bioabbau in den 28 Tagen Testzeitraum beobachtet werden. Dieses Wissen unterstützt die Idee der gerichteten Hydrolyse. Dabei können leicht hydrolysierbare Bindungen mit Schutzgruppen kombiniert werden, die die Hydrolyse entweder über die Zeit oder über z. B. den pH-Wert steuerbar machen (Rücker und Kümmerer, 2013). Wenn die Anwendung der Substanz mit einer säurestabilen Schutzgruppe (z. B. Fluorenylmethoxycarbonyl-Gruppe (Fmoc)) unter sauren Bedingungen stattfindet, kann diese Schutzgruppe nach dem Eintrag ins Abwasser in der Kläranlagen unter basischen Bedingungen gespalten werden (Schönherr, 2009).

Die schlechte Wasserlöslichkeit der siliziumorganischen Verbindungen brachte viele Herausforderungen mit sich. Durch den Einsatz geeigneter Lösungsvermittler – DMSO im Bioabbau und Acetonitril im Photoabbau – konnten zwar die verschieden Tests zur Bestimmung der Eliminierung und Abbaubarkeit durchgeführt werden, aber die Überprüfung der Ergebnisse wurde dadurch eingeschränkt. Beispielsweise konnte keine Bestimmung der Mineralisierung über den Kohlenstoffgehalt in den Proben erfolgen, da die organischen Lösungsvermittler die Ergebnisse verfälscht hätten.

Unterschiede in den Publikationen ergeben sich vor allem durch die angewendeten Methoden und die daraus resultierenden Ergebnisse. In Publikation 1 wurden zusätzlich zum Bioabbau die Hydrolyse und Photolyse der Benzenderivate untersucht und potentielle Transformationsprodukte identifiziert. Hier zeigte sich, dass, wenn eine pH-Abhängigkeit vorlag, die Hydrolyse säurekatalysiert stattgefunden hat. Die Photolyserate der Benzenderivate konnte durch eine Aminogruppe in *para*-Position positiv beeinflusst werden. Die zweifach substituierte Benzenverbindung zeigte die größte Photostabilität, da

zwei konjugierte Systeme (Benzenringe) statt einem vorlagen, welche Strahlung absorbieren können. In Publikation 2 wurde zusätzlich zur biologischen Abbaubarkeit der siliziumorganischen Substanzen die Abbaubarkeit der analogen Kohlenstoffverbindungen untersucht und mittels Analysen überprüft. Bei diesen Versuchen zeigte sich, dass die Silizium-Stickstoff-Bindung besonders hydrolyselabil ist. Die analoge Kohlenstoffverbindung war hingegen gar nicht biologisch abbaubar, was auf die Abschirmung und Polarität der Bindung zwischen Kohlenstoff und Stickstoff zurückzuführen ist. Besondere Herausforderung bei den in Publikation 2 untersuchten Substanzen war die schlechte Extrahierbarkeit aus dem wässrigen Medium für die Analyse mittel GC-MS.

In Publikation 3 wurden in Ergänzung zu den Bioabbauergebnissen aus eigenen Versuchen experimentelle Daten aus der ECHA-Datenbank hinzugezogen. Durch diese Vorgehensweise konnte die Datengrundlage für die Auswertung der Struktur-Eigenschafts-Beziehungen erheblich verbessert werden (etwa Faktor 3). So konnten nicht nur siliziumorganische Substanzen, die eigens für Forschungszwecke synthetisiert worden waren, untersucht werden, sondern auch im großen Maßstab kommerziell verwendete Substanzen. Die klassischen Siloxane wie $D_4$, $D_5$, $D_6$ und $L_2$ waren nicht biologisch abbaubar, wohingegen Verbindungen mit Ether-, Ester- und Aminogruppen besser biologisch abbaubar waren. Dadurch konnte gezeigt werden, dass die Einführung von Heteroatomen in siliziumorganische Substanzen einen positiven Einfluss auf die biologische Abbaubarkeit dieser haben kann, was meist auf eine Veränderung der Polarität der Bindung zurückzuführen ist.

## 5.3 Ergebnisse der Arbeit im wissenschaftlichen Kontext

Die Datenlage zur biologischen Abbaubarkeit von siliziumorganischen Substanzen ist wie bereits in Kapitel 1.3 dargestellt sehr begrenzt und oftmals nicht ausreichend beschrieben bzw. definiert. Beispielsweise schrieb Xu, (1999), dass die zyklischen Siloxane $D_4$, $D_5$ und $D_6$ vollständig durch Verflüchtigung, biologischen Abbau und mehrstufige Hydrolyse im Boden abgebaut wurden. Die These von Xu, dass ein Teil der Substanzen durch Mikroorganismen abgebaut wurden, wird durch die vorliegenden Ergebnisse der zyklischen Siloxane aus dem Bioabbau widerlegt. Die siliziumorganischen Substanzen der Gruppe 4, zu denen auch $D_4$, $D_5$ und $D_6$ gehören, waren nicht biologisch abbaubar. Allerdings hat Xu den biologischen Abbau nicht weiter erläutert. Der festgestellte Abbau von Xu ist wahrscheinlich eher als eine Art Eliminierung zu verstehen, die nur durch Verflüchtigung und mehrstufige Hydrolyse stattgefunden hat (Xu, 1999). Das bestätigen auch die Ergebnisse von Xu et al. (2013), die die biokatalysierte Hydrolyse neben Verflüchtigung und Adsorption als Hauptabbauwege von $D_4$ und $D_5$ beschreiben.

Allgemein ist die Abbaubarkeitsstudie der vorliegenden Arbeit zum biologischen Abbau für die Substanzklasse der siliziumorganischen Substanzen neu. Die bekannten Regeln zur biologischen Abbaubarkeit organischer Substanzen sind zum Teil aber auch auf siliziumorganische Substanzen anwendbar. Boethling et al. (2007) haben dieses Wissen über das Design von organischen Molekülen zur biologischen Abbaubarkeit in ihrer Publikation zusammengefasst. Sie beschreiben, dass funktionelle

Gruppen, die für enzymatische Hydrolyse anfällig sind, wie Ester, Amide, Hydroxyl-, Aldehyd- und Carbonsäuregruppen, wahrscheinlich auch Ketone, lineare Alkylketten ab vier Kohlenstoffatomen und Phenylringe die aerobe biologische Abbaubarkeit verbessern. Diese Erkenntnisse stehen im Einklang mit den vorliegenden Ergebnissen aus dieser Arbeit. Widersprüchlich zu den vorliegenden Ergebnissen ist die Aussage von Boethling et al., dass Ether (außer Ethoxylate) keinen positiven Einfluss auf die biologische Abbaubarkeit haben. Es muss jedoch beachtet werden, dass ihre Zusammenfassung auf Kohlenstoffverbindungen beruht. Von daher kann diese Aussage nicht eindeutig auf siliziumorganische Verbindungen übertragen werden. Dadurch dass ein Siliziumatom (Atomvolumen 12,1 $cm^3\ mol^{-1}$) mehr als doppelt so groß ist wie ein Kohlenstoffatom (Atomvolumen 5,3 $cm^3\ mol^{-1}$) ergeben sich andere Polaritäten (Hoppe, 2020) und somit andere Bindungseigenschaften. In der vorliegenden Arbeit waren Substanzen mit Strukturmerkmalen wie –Si–OR (mit R = Me oder Et) moderat biologisch abbaubar, was auf den biologischen Abbau von Methanol bzw. Ethanol nach vorangegangener Hydrolyse zurückzuführen ist. Die Ethoxylate der vorliegenden Arbeit (Gruppe 1) waren wie von Boethling et al. (2007) beschrieben sehr gut biologisch abbaubar. Sie betonen aber auch, dass es einige Ausnahmen bezüglich der biologischen Abbaubarkeit gibt, die im Einzelfall zu betrachten sind (Boethling et al., 2007).

Ebenso wie die systematische Betrachtung der biologischen Abbaubarkeit wurde erstmalig die ECHA-Datenbank als Datengrundlage für siliziumorganische Substanzen angewendet. Da diese Datenbank kostenlos verfügbar ist und durch Aktualisierungen in der REACH-Verordnung (EG Nr. 1907/2006) auch regelmäßig aktualisiert wird, eignet sie sich besonders gut als Quelle für Informationen. Nichts desto trotz gibt es Limitierungen. Sie enthält z. B. nur registrierungspflichtige Stoffe des europäischen Wirtschaftsraums, die ein Produktionsvolumen von 1 $t\ a^{-1}$ pro Hersteller bzw. Importeur überschreiten.

Die Hydrolyse hat einen großen Einfluss auf die Abbaubarkeit von siliziumorganischen Verbindungen und ist oftmals als obligatorischer Schritt vor dem biologischen Abbau nötig. Doch auch wenn kein biologischer Abbau stattfand, hydrolysierten einige der Verbindungen. Für die eigens für Forschungszwecke synthetisierten Benzenderivate wurde erstmalig das Hydrolyseverhalten bei verschiedenen pH-Werten untersucht. Wenn bei den Verbindungen eine pH-Abhängigkeit der Hydrolyse vorlag, war diese unter sauren Bedingungen schneller als bei neutralen oder basischen Bedingungen. Ein ähnliches Verhalten beobachteten Ducom et al., (2013) bei PDMS-Flüssigkeiten. Sie konnten ebenfalls bei niedrigen pH-Werten eine Hydrolyse der Verbindung beobachten. Im Gegensatz zu den Ergebnissen der vorliegenden Arbeit trat bei ihnen aber auch unter basischen Bedingungen eine Hydrolyse auf. Das zeigt, dass ebenso wie der biologische Abbau die Hydrolyse stark von der Struktur des Moleküls abhängt.

Die Photolyse von siliziumorganischen Substanzen und Siloxanen wurde bisher vor allem bei niedrigen Wellenlängen zwischen 123 und 313 nm beobachtet (123 und 147 nm (Skurat, Dorofeev, 1994), 147 nm (Vasilets et al., 1994), 193 und 248 nm (Joubert et al., 1991), 313 nm (Imakoma et al., 1994) und <300 nm (Israëli et al., 1992)). Diese Ergebnisse stützen die Beobachtungen der vorliegenden Arbeit,

dass siliziumorganische Substanzen durch Strahlung eliminiert werden können. Die Wellenlänge und auch die Struktur der Verbindungen haben einen großen Einfluss auf das Photolyseverhalten der Substanzen. Wie auch Drake et al. (1998) bereits feststellten, nahm die durch Strahlung verursachte Oxidation von siliziumorganischen Substanzen mit kürzeren Wellenlängen zu. In der vorliegenden Arbeit hat sich das durch die Verwendung der Xe- und Hg-Lampe gezeigt. Die Photolyseexperimente mit der Hg-Lampe hatte eine viel schnellere Eliminierung zur Folge als die Bestrahlung mit der Xe-Lampe (vergleichbar mit dem Sonnenspektrum). Allerdings hat sich gezeigt, dass sich durch die Einführung von +M-Substituenten am aromatischen Ring die Photolyseeigenschaften verbessern lassen und eine Eliminierung auch unter Bedingungen wie in Oberflächengewässern durch Sonneneinstrahlung auftreten kann. Somit konnte bewiesen werden, dass die Einführung von +M-Substituenten auch bei siliziumorganischen Substanzen eine Verbesserung der Eliminierung durch Photolyse hervorruft.

## 5.4 Empfehlungen für verschiedene Anwendungsbereiche

Aus den Erkenntnissen und Methoden der drei Publikationen lassen sich einige Schritte und Empfehlungen ableiten. Es könnten weitere aromatische siliziumorganische Verbindungen mit unterschiedlichen Substituenten auf ihre Photolyseeigenschaften getestet werden. In Publikation 3 wurden Substanzen im Bioabbau untersucht, die auch für einen Photolyseversuch geeignet wären (z. B. Substanzen aus Gruppe 2 und 7). Zudem könnte die Kinetik der Hydrolyse weiterer Substanzen näher untersucht werden. Grundlegende Voraussetzung für diese Untersuchungen ist eine verlässliche Analysemethode, um den Verlauf der Reaktion zu dokumentieren. Ebenso könnten die Transformationsprodukte der Substanzen aus Publikation 2 und 3 näher untersucht werden, um die Vermutungen, die bisher durch bestehende Literatur belegt wurden, analytisch zu bestätigen. Die Herausforderung die Mineralisierung zu bestimmen, könnte durch eine Verringerung der Stoffkonzentration in den Proben angegangen werden. Die Konzentration sollte so gering sein, dass die Wasserlöslichkeit gegeben ist, sie sollte aber hoch genug sein, um sie mittels TOC-Analyser zu messen.

Das generierte Wissen kann ebenfalls genutzt werden, um für verschiedene Anwendungsbereiche geeignete Substanzen zu entwickeln. Für eine Anwendung von Substanzen, die erhöhter Strahlung ausgesetzt sind und in dieser Umgebung stabil sein sollen, eignen sich Substanzen, die mehrere aromatische Ringe tragen (wie Substanz (*p*-MeOPh)$_2$SiMe$_2$). Wenn eine Substanz leicht durch Strahlung eliminiert werden soll, sollte diese +M-Substituenten am aromatischen Ring tragen und möglichst im Bereich oberhalb von 250 nm absorbieren (z. B. *p*-Me$_2$NPhSiMe$_3$). Für die untersuchte Substanz hatte das aber keine Verbesserung der biologischen Abbaubarkeit zur Folge. Allerdings schien die Aminogruppe am aromatischen Ring die Hydrolyse im sauren Milieu positiv zu beeinflussen. Somit kann daraus geschlussfolgert werden, dass die Aminogruppe bei dieser Substanz eine Verbesserung der abiotischen Eliminierung (Hydrolyse und Photolyse) bewirkt hat.

Substanzen, die in der aquatischen Umgebung möglichst stabil sein sollen, könnten mithilfe von *tert*-Butylgruppen oder pH abhängigen Schutzgruppen modifiziert werden, um hydrolyseanfällige

Bindungen vor der Reaktion mit Wasser abzuschirmen. Hydrolyselabile Substanzen wiederum benötigen keine dieser Gruppen für die Abschirmung, da sie direkt bei Kontakt mit Wasser zerfallen sollen. Eine Anwendung ist daher nur in einer wasserfreien Umgebung möglich. Solche Substanzen enthalten beispielsweise Silizium-Stickstoff- oder Silizium-Sauerstoff-Bindungen (Ester oder Ether), welche schnell hydrolysieren und oftmals leicht biologisch abbaubare organische Substanzen zur Folge haben. Neben den leicht biologisch abbaubaren Substanzen entstanden aber auch immer siliziumhaltige Substanzen, die nicht biologisch abbaubar waren.

In einer Umgebung mit degradierenden Mikroorganismen sind klassische Siloxane besonders stabil wie zum Beispiel die Substanzen der Gruppen 2, 4, 10 und 15. Siliziumorganische Substanzen mit Hydroxylgruppen oder linearen Alkylketten sind hingegen gut biologisch abbaubar und das auch ohne vorangegangene Hydrolyse (z. B. Gruppe 18).

Mit den hier beschriebenen Modifikationen könnten Polysiloxane ausgestattet werden, um je nach Anwendungsbereich Sollbruchstellen zu generieren. Diverse Stickstoffverbindungen sind besonders vielversprechend, da sie Angriffspunkte für verschiedene Abbaumechanismen (z. B. Hydrolyse, Photolyse und biologischen Abbau) bieten.

Von dem hier generierten Wissen profitieren vor allem Entwicklungsabteilungen in der Silikonindustrie, da sie die Erkenntnisse nutzen können, um besser abbaubare Substanzen zu designen. Auch wenn durch die vorliegende Arbeit ein guter Ansatzpunkt geschaffen wurde, ist noch viel Forschung und Entwicklung nötig, um dem Ziel abbaubarer Siliziumverbindungen ein Stück näher zu kommen. Zudem ist diese Arbeit ein gutes Argument gegen den Einsatz von klassischen Siloxanen (z. B. $D_4$, $D_5$, $L_2$ und PDMS), wenn ihre Verwendung vorsieht, dass sie während ihres Lebenszyklus die aquatische Umwelt erreichen.

Diese Arbeit bietet zudem wissenschaftlich bestätigte Aussagen, die als Grundlage für regulatorische Maßnahmen gelten können. Die ECHA hat bereits durch die Beschränkung von $D_4$, $D_5$, und $D_6$ in Kosmetikartikeln einen entscheidenden Schritt getätigt (ECHA, 2019) und verfolgt diese Strategie weiter, indem sie diese drei Stoffe auf die Zulassungsliste setzen möchte (ECHA, 2021). Die Spurenstoffstrategie des Bundes (Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit, 2016) sieht verschiedene Maßnahmen zur Reduktion von Schadstoffen vor. Mit den Erkenntnissen aus dieser Arbeit werden Maßnahmen an der Quelle adressiert. Durch das gezielte Design von siliziumorganischen Substanzen können weniger bedenkliche Ersatzstoffe gefunden werden, die in Waschmitteln, Kosmetika, Haushalts- und Industriechemikalien und Pflanzenschutzmitteln zum Einsatz kommen könnten. Im *European Green Deal* (Europäische Kommission, 2020) bzw. im *Zero Pollution Action Plan* heißt es, dass Investitions- und Innovationskapazitäten für die Produktion und Verwendung von Chemikalien, die durch ihr Design und während ihres gesamten Lebenszyklus sicher und nachhaltig sind, gefördert werden sollen. Dadurch können der Menschheit sauberes Wasser ermöglicht und die besonders schädliche Verschmutzung durch Mikroplastik und Arzneimittel verringert werden. In der

vorliegenden Arbeit konnten Erkenntnisse zur verbesserten biologischen Abbaubarkeit siliziumorganischer Substanzen gewonnen werden, die das Ziel verfolgen sichere und nachhaltige Stoffe zu entwickeln. Die meisten getesteten siliziumorganischen Substanzen sind nicht leicht biologisch abbaubar, aber mit gezielten Modifikationen kann der leicht biologisch abbaubare Anteil an Substanzen erhöht werden. Zudem können aus dem generierten Wissen Design-Regeln für weitere Spurenstoffe abgeleitet werden, um diese besser biologisch abbaubar zu gestalten.

# 6 Schlussfolgerungen und Ausblick

Die Datenlage zur Abbaubarkeit von siliziumorganischen Substanzen ist sehr überschaubar, wenn man bedenkt wie vielfältig und heterogen diese Substanzklasse ist. Die vorliegende Arbeit bietet daher einen ersten Ansatz diese Datenlücke systematisch zu schließen und mit den gewonnenen Erkenntnissen besser abbaubare Substanzen zu entwickeln. Mit den in der Arbeit angewendeten Methoden konnten Ergebnisse generiert werden, die einen entscheidenden Beitrag zu *Benign by Design*, der Spurenstoffstrategie des Bundes, zum *European Green Deal* sowie nachhaltiger Chemie im Allgemeinen leisten. Zudem werden 3 der 17 *Sustainable Development Goals* adressiert (6 sauberes Wasser, 14 Leben unter Wasser, 15 Leben an Land (United Nations, 2015)).

Die siliziumorganischen Substanzen waren meist nur zu einem bestimmten Anteil biologisch abbaubar, wenn funktionelle Gruppen wie Ether, Ester, Oxime, Amine und Amide enthalten waren. Diese Gruppen hydrolysierten schnell, sodass leicht biologisch abbaubare siliziumfreie Zwischenprodukte gebildet werden konnten. Die siliziumhaltigen Hydrolyseprodukte waren hingegen persistent. Wenn eine mögliche verbesserte biologische Abbaubarkeit der siliziumorganischen Substanzen nur durch eine Veränderung der Hydrolyseeigenschaften erreicht werden kann, sind Substanzen mit einer Anwendung in einer wasserfreien Umgebung für diese Modifikation geeignet. Eine solche Substanz würde erst nach dem Eintrag in die aquatische Umwelt zerfallen. Geeignete Hydrolyseprodukte wären leicht biologisch abbaubare Substanzen wie lineare Carbonsäuren oder Amine und *ortho*-Kieselsäure. Da die Hydrolyse in den meisten untersuchten Fällen als Voraussetzung für den biologischen Abbau galt, könnte über eine gesteuerte Hydrolyse nachgedacht werden.

Neben der Hydrolyse und dem biologischen Abbau konnten die getesteten Substanzen auch durch energiereiche Strahlung eliminiert werden. Je kurzwelliger die Strahlung war, desto schneller wurden die Substanzen eliminiert. Eine aromatische Substanz mit einer +M-Gruppe in *para*-Stellung konnte auch durch sichtbares Licht eliminiert werden. Durch die hochauflösende Massenspektroskopie konnten gebildete Transformationsprodukte der untersuchten Prozesse näher charakterisiert werden.

Trotz allem werden mehr verlässliche Daten benötigt, besonders bei Substanzen, die einen vielversprechenden Abbau zeigen könnten. Über mehr standardisierte Tests könnte eine bessere Vergleichbarkeit erzielt werden, wobei durch die REACH-Verordnung (EG Nr. 1907/2006) schon sehr viele OECD-konforme Tests verwendet werden. Dennoch wäre es ratsam sich wegen der Vergleichbarkeit und der geringen Bakteriendichte auf zwei Tests zu beschränken wie z. B. den CBT und MRT. Ein Trend in diese Richtung ist bereits erkennbar. Des Weiteren sollte die ECHA-Datenbank auch für andere Substanzklassen als Quelle für Daten (z. B. physikalisch-chemische Eigenschaften, Umweltverhalten und Ökotoxizität) genutzt werden, da sie leicht zugänglich ist und eine Vielzahl von Substanzen des europäischen Markts oberhalb einer Tonne Produktionsvolumen pro Jahr enthält.

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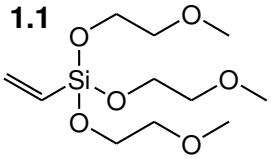
# Anhang

## Strukturformeln der untersuchten siliziumorganischen Substanzen

**1.1**



1067-53-4

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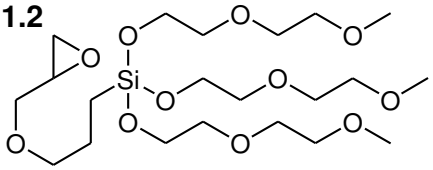

88127-84-8

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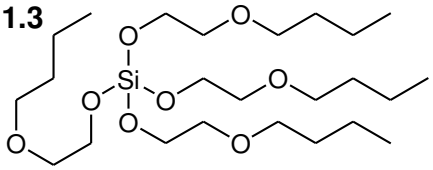
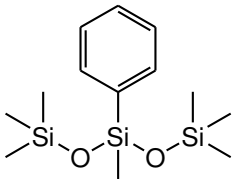


18765-38-3

**2.1**



546-44-1

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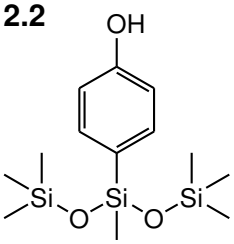
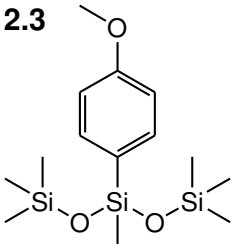


946153-01-1

**2.3**



946152-98-3

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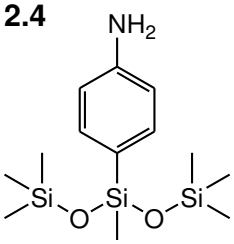

946153-02-2

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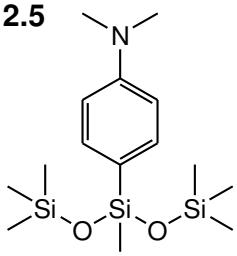

1583286-06-9

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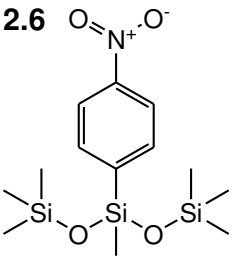

946153-07-7

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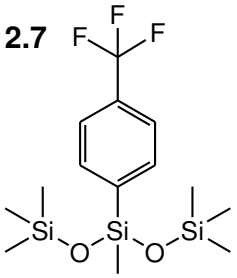

946153-06-6

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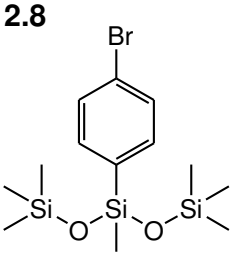

27628-22-4

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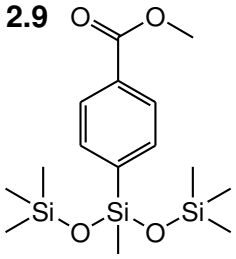
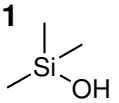


**3.1**



1066-40-6

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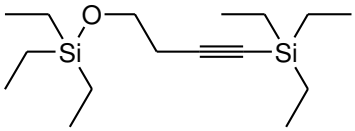

160194-28-5

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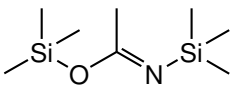

10416-59-8

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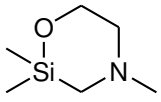

10196-49-3

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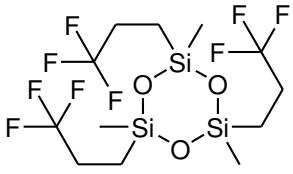

2374-14-3

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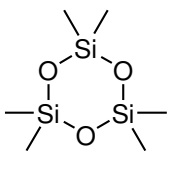

541-05-9

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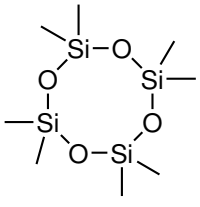

556-67-2

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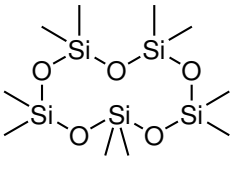

541-02-6

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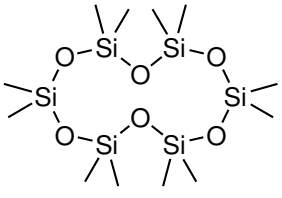

540-97-6

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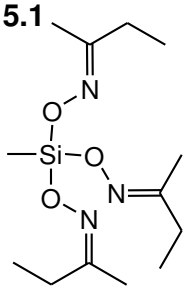

22984-54-9

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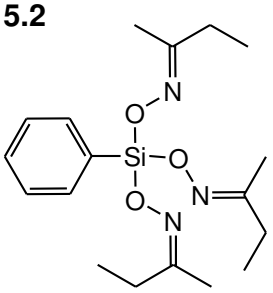

34036-80-1

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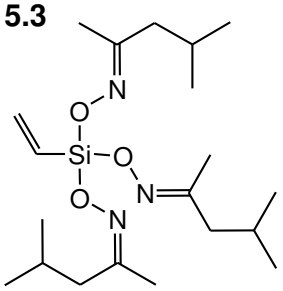

156145-64-1

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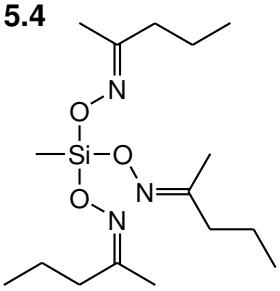
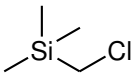


37859-55-5

**6.1**

75-76-3

**6.2**



2344-80-1

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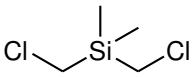

2917-46-6

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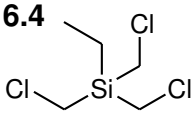

1858250-64-2

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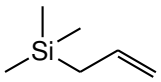

762-72-1

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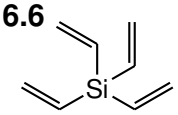

1112-55-6

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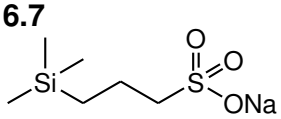

2039-96-5

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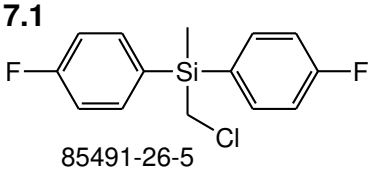

85491-26-5

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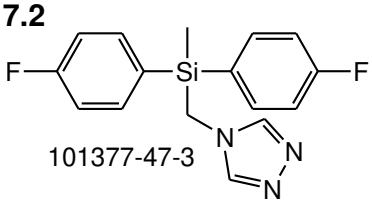

101377-47-3

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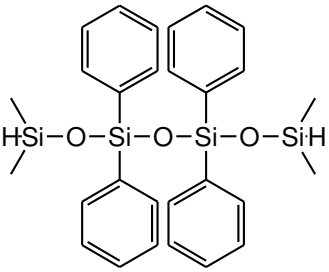

70940-00-0

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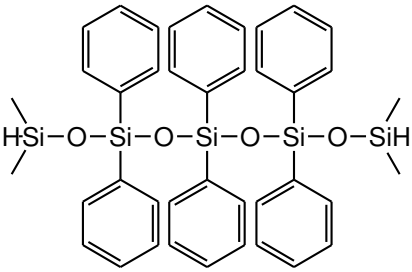

180073-46-5

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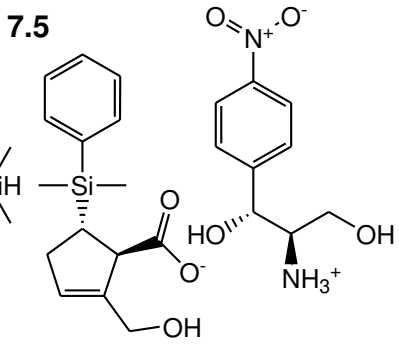

649761-22-8

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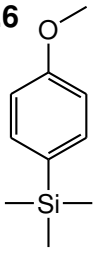

877-68-9

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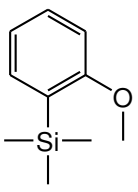

704-43-8

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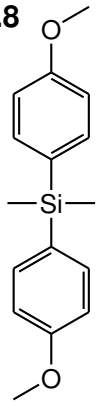

69983-36-4

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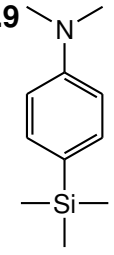

16087-24-4

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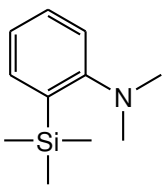

17961-92-1

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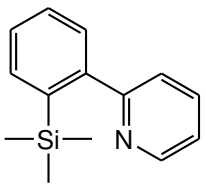

1170176-75-6

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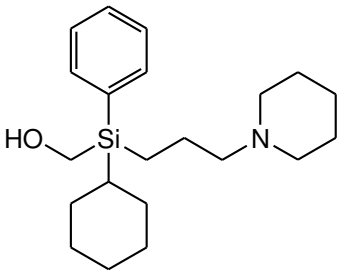

180613-38-1

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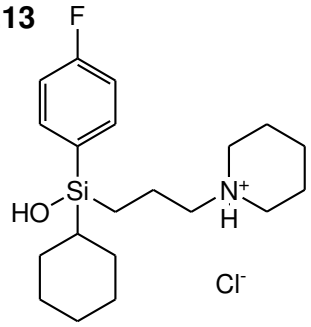
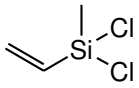


175615-76-6

**8.1**

75-77-4

**8.2**



124-70-9

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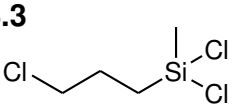

7787-93-1

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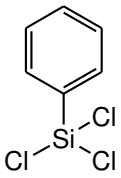

98-13-5

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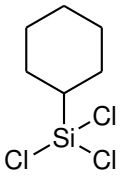

98-12-4

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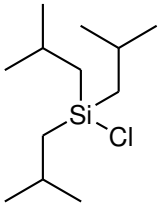

13154-25-1

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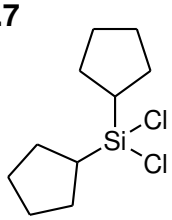

139147-73-2

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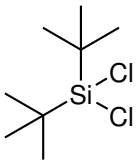

18395-90-9

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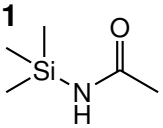

13435-12-6

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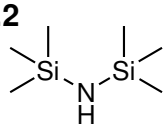
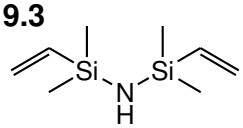


999-97-3

**9.3**



7691-02-3

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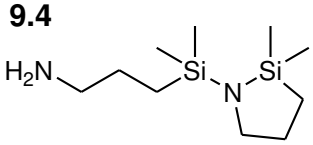

388606-32-4

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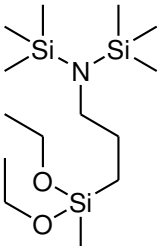

201290-01-9

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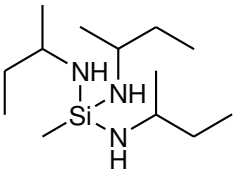

37697-65-7

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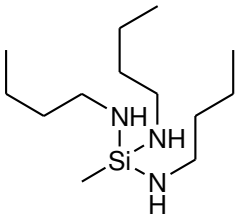

16411-33-9

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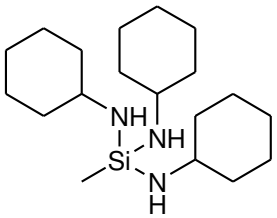

15901-40-3

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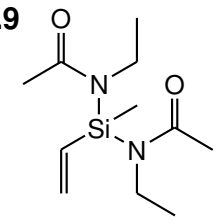
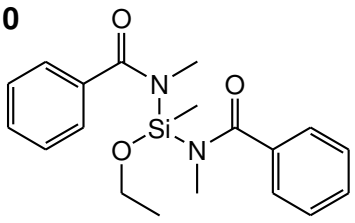


87855-59-2

**9.10**



16230-35-6

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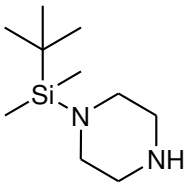

138938-64-4

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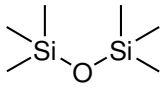

107-46-0

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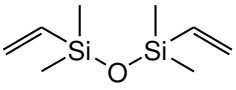

2627-95-4

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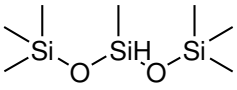

1873-88-7

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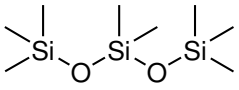

107-51-7

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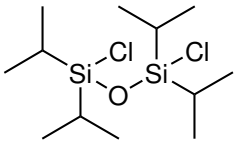

69304-37-6

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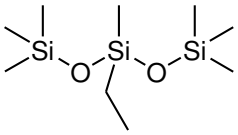

17861-60-8

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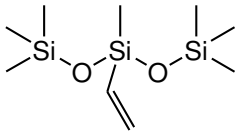

5356-85-4

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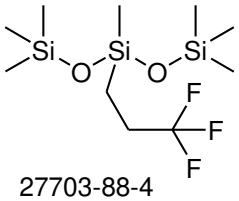

27703-88-4

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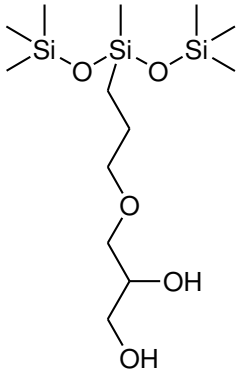

70280-68-1

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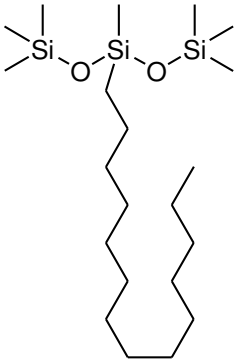

286938-65-6

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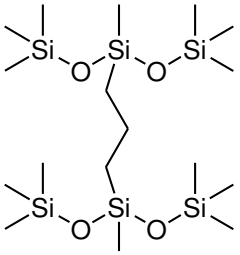

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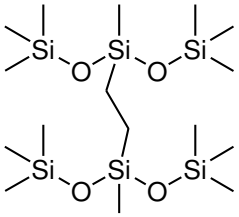

52337-35-6

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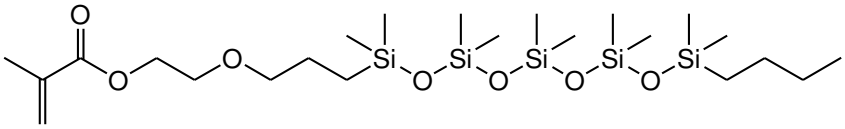

1052075-57-6

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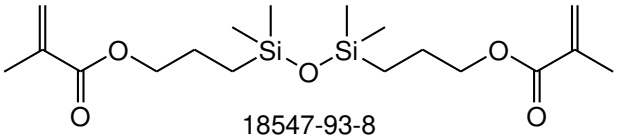

18547-93-8

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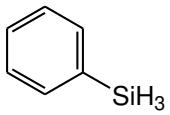

694-53-1

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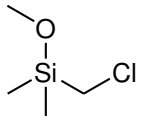

18143-33-4

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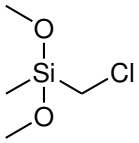

2212-11-5

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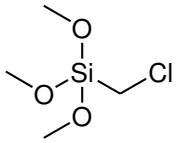

5926-26-1

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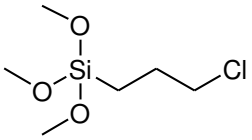

2530-87-2

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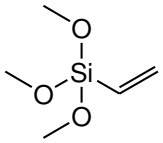

2768-02-7

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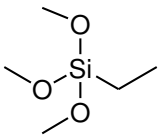

5314-55-6

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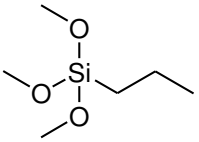

1067-25-0

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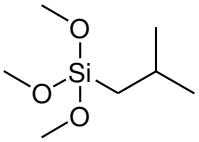

18395-30-7

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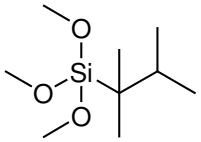

142877-45-0

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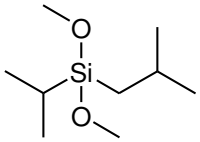

111439-76-0

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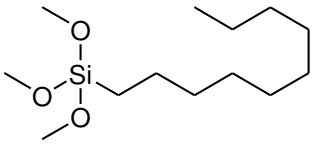

5575-48-4

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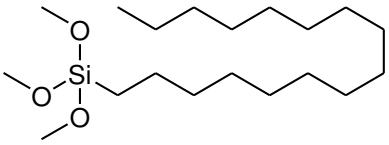

16415-12-6

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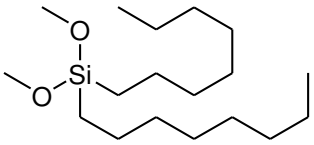

947155-81-9

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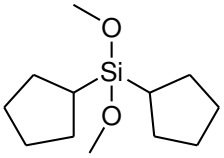

126990-35-0

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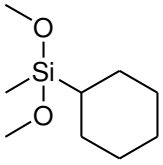

17865-32-6

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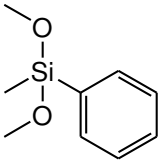

3027-21-2

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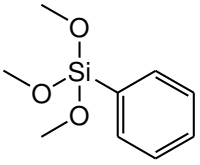

2996-92-1

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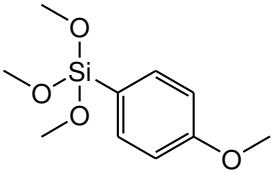

35692-27-4

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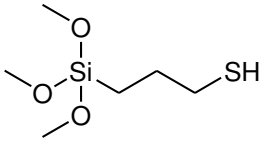

4420-74-0

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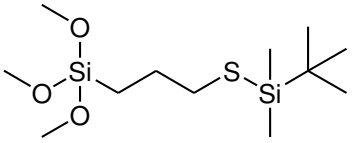

1128026-41-4

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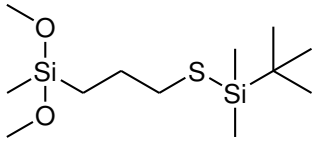

927395-20-8

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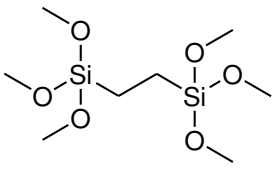

18406-41-2

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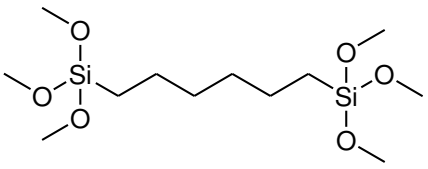

87135-01-1

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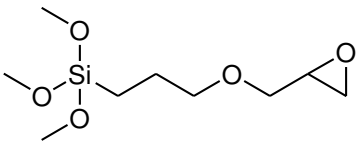

2530-83-8

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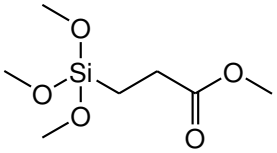

76301-03-6

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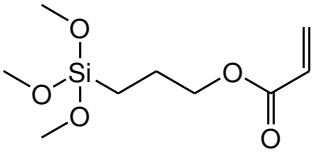

4369-14-6

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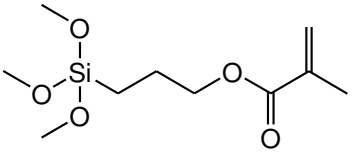

2530-85-0

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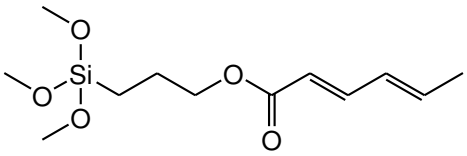

163802-53-7

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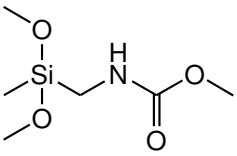

23432-65-7

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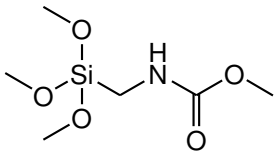

23432-64-6

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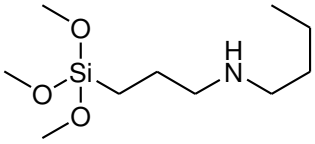

31024-56-3

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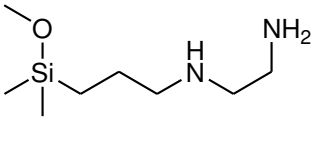

3069-33-8

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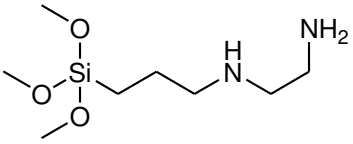

1760-24-3

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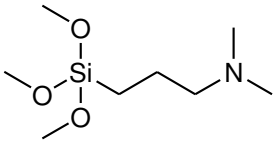

2530-86-1

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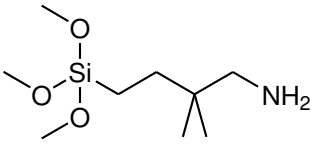

157923-74-5

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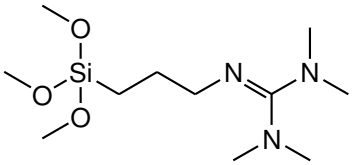

69709-01-9

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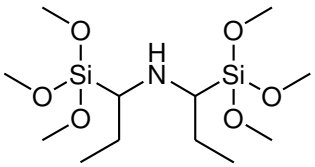

82985-35-1

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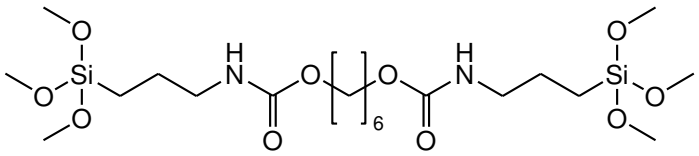
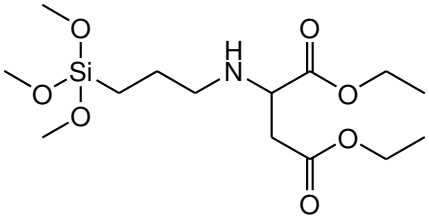


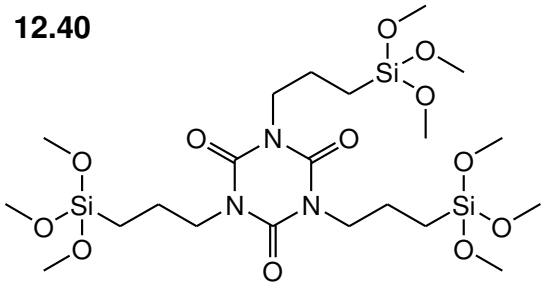
501925-98-0

**12.39**



192389-48-3

**12.40**



26115-70-8

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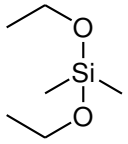
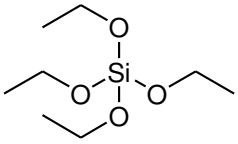


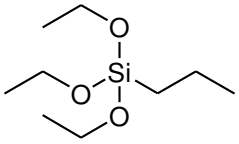
78-62-6

**13.2**



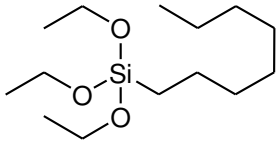
78-10-4

**13.3**



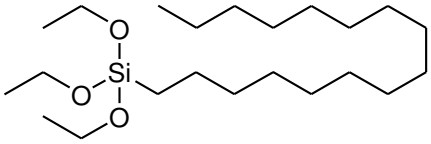
2550-02-9

**13.4**



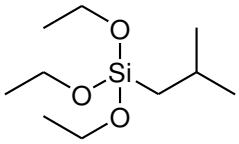
2943-75-1

**13.5**



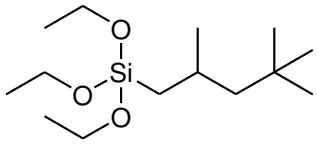
16415-13-7

**13.6**



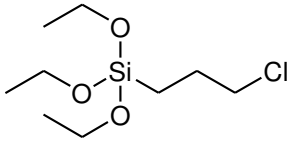
17980-47-1

**13.7**



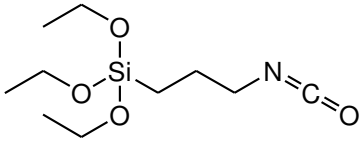
35435-21-3

**13.8**



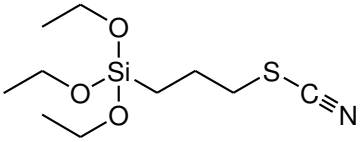
5089-70-3

**13.9**



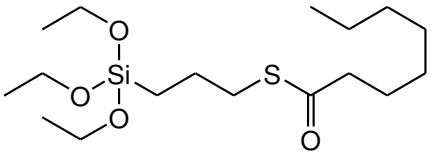
24801-88-5

**13.10**



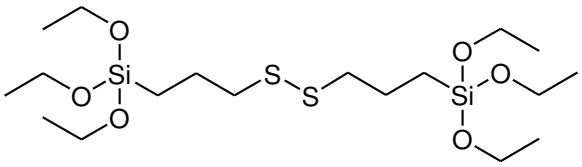
34708-08-2

**13.11**



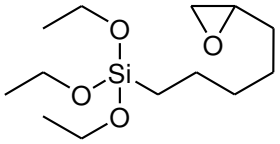
220727-26-4

**13.12**



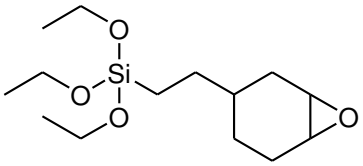
56706-10-6

**13.13**



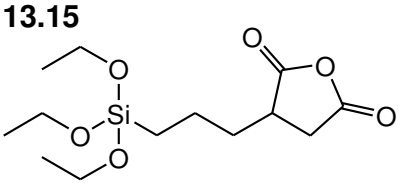
2602-34-8

**13.14**



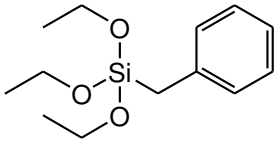
10217-34-2

**13.15**



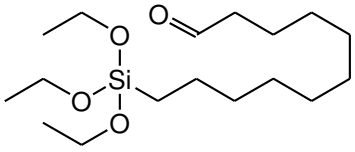
93642-68-3

**13.16**



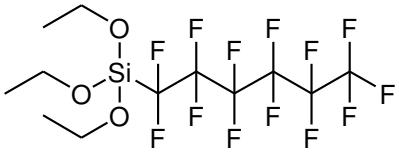
2549-99-7

**13.17**



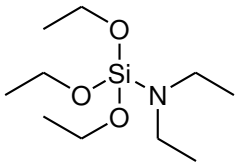
116047-42-8

**13.18**



51851-37-7

**13.19**



35077-00-0

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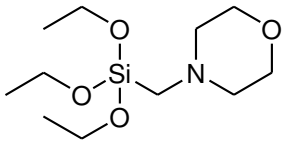

21743-27-1

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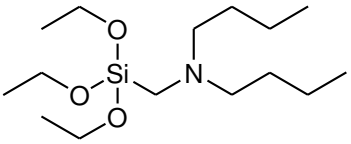
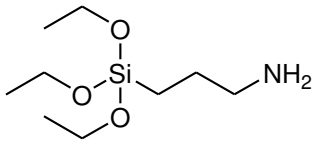


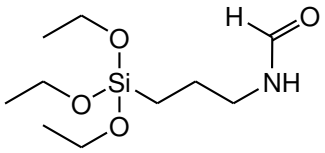
35501-23-6

**13.22**



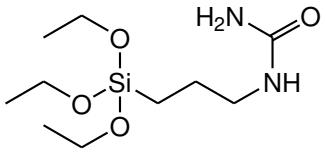
919-30-2

**13.23**



76524-94-2

**13.24**



23779-32-0

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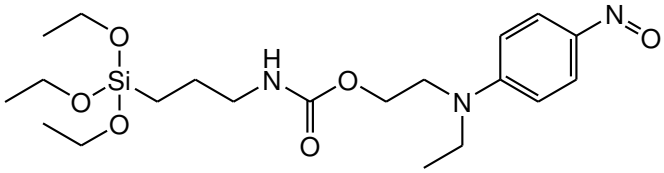
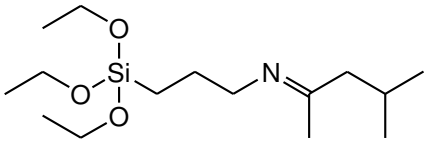


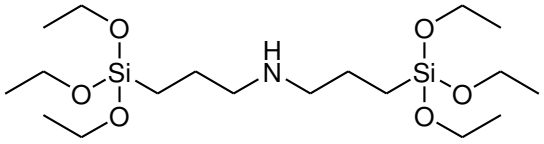
1195231-94-7

**13.26**



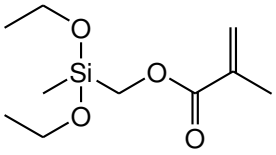
116229-43-7

**13.27**



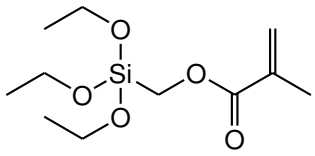
13497-18-2

**13.28**



3978-58-3

**13.29**



5577-72-0

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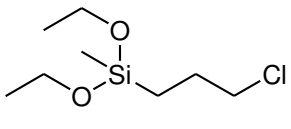
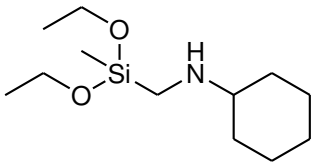


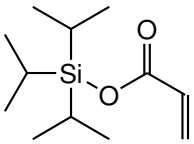
13501-76-3

**13.31**



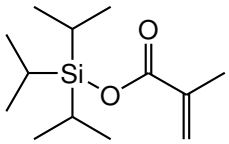
27445-54-1

**14.1**



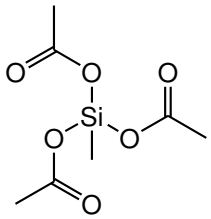
157859-20-6

**14.2**



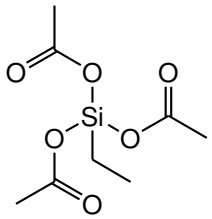
134652-60-1

**14.3**



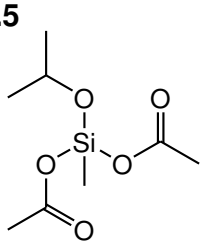
4253-34-3

**14.4**



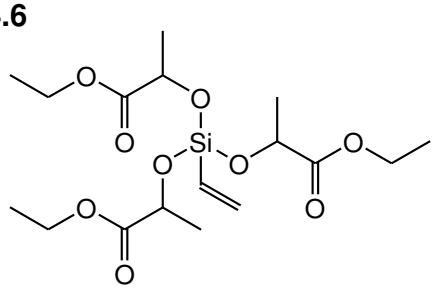
17689-77-9

**14.5**



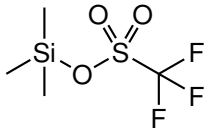
329039-38-5

**14.6**



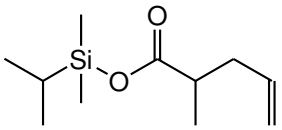
1124196-01-5

**14.7**

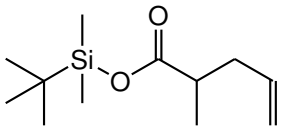


27607-77-8

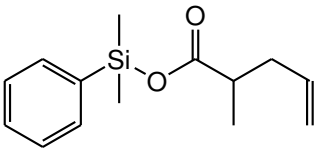
**14.8**



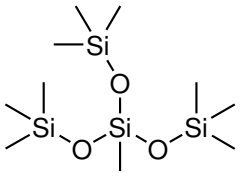
**14.9**



**14.10**

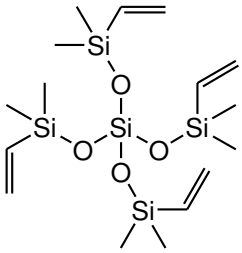


**15.1**



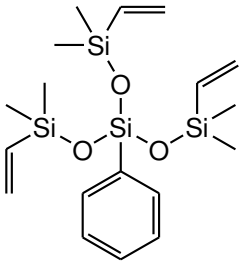
17928-28-8

**15.2**



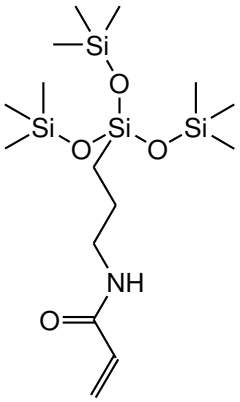
60111-54-8

**15.3**



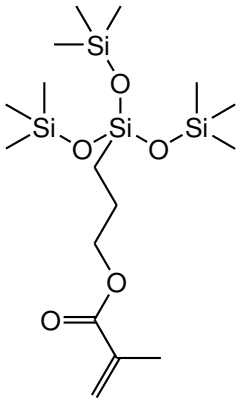
60111-47-9

**15.4**



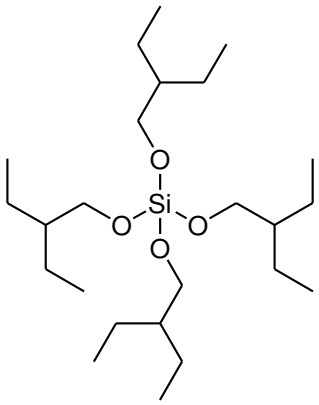
115258-10-1

**15.5**



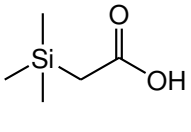
17096-07-0

**15.6**



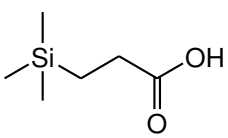
78-13-7

**16.1**



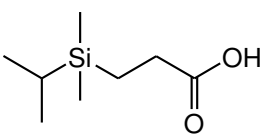
2345-38-2

**16.2**

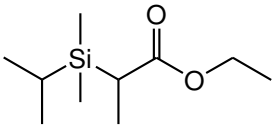


5683-30-7

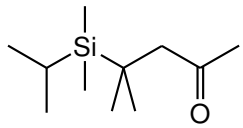
**16.3**



**16.4**

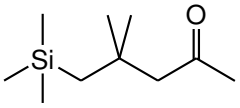


**16.5**



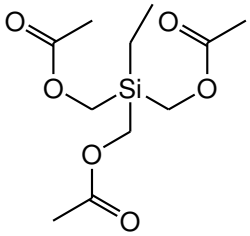
1858241-43-6

**16.6**



947169-99-5

**16.7**



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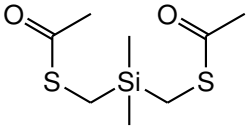

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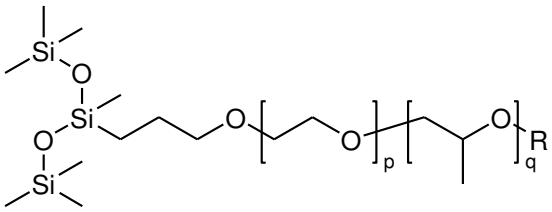

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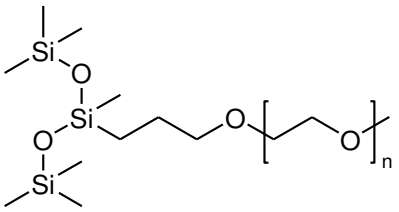

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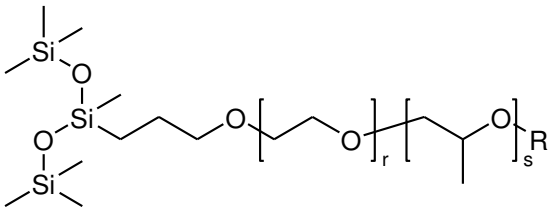

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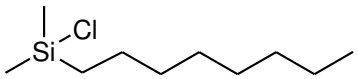

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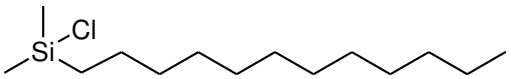

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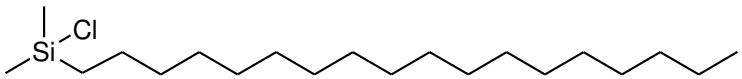

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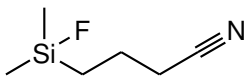

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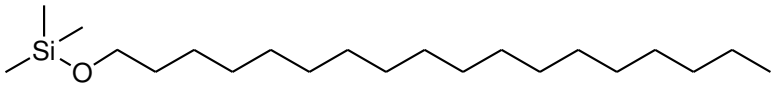

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# Publikationen zur kumulativen Dissertation

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# Publikation 1

## Abiotic and biotic degradation of five aromatic organosilicon compounds in aqueous media – Structure degradability relationships

Elisa Grabitz; Oliver Olsson; Ann-Kathrin Amsel; Britta Rummel; Norbert W. Mitzel; Klaus Kümmerer

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# Abiotic and biotic degradation of five aromatic organosilicon compounds in aqueous media—Structure degradability relationships

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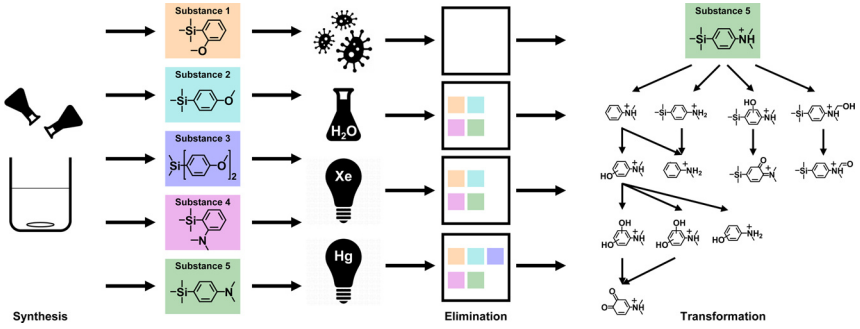
## GRAPHICAL ABSTRACT

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## ABSTRACT

Silicones have many applications and are produced in large quantities. Despite their potential toxicity, information on their environmental mineralisation is scarce. Therefore, we investigated a group of five organosilicon compounds (*o*-$MeOC_6H_4SiMe_3$ (**1**), *p*-$MeOC_6H_4SiMe_3$ (**2**), $(p\text{-}MeOC_6H_4)_2SiMe_2$ (**3**), *o*-$Me_2NC_6H_4SiMe_3$ (**4**) and *p*-$Me_2NC_6H_4SiMe_3$ (**5**)), recently developed to be 'benign by design' based on their readily degradable core structure. Five different degradability tests were performed, one assessing hydrolytic and two analysing biological and photolytic stability, respectively.

All substances, except $(p\text{-}MeOC_6H_4)_2SiMe_2$ (**3**), hydrolysed within 24 h to 50% indicating that this is one of the major pathways of their primary elimination. In agreement with previous research, none of the substances was readily biodegradable. In contrast, 100% of *p*-$Me_2NC_6H_4SiMe_3$ (**5**) was primarily eliminated by photolytic and hydrolytic processes. The elimination rates of the other substances ranged from 7% to 64%. Irradiation at shorter wavelengths increased both the extent and speed of photodegradation.

Eleven transformation products of *p*-$Me_2NC_6H_4SiMe_3$ (**5**) were detected, all of which were completely eliminated within 64 min of irradiation with a Hg lamp (200–400 nm). The insertion of an electron-donating group on the benzene ring like in *p*-$Me_2NC_6H_4SiMe_3$ (**5**) clearly enhanced photolytic degradability but further research is necessary to achieve truly biodegradable silicones.

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## 1. Introduction

Silicones are characterised by chains of alternating silicon and oxygen atoms, with organic side chains bound to silicon ($R_3Si–O–(SiR_2–O)_n–SiR_3$). Historically the name originates from the idea of describing sila-analogues of ketones, however, silicones do typically not exist as Si=O double bounded monomers but rather in the form of polymeric chains or rings. Smaller molecules with alternating silicon and oxygen atoms are named siloxanes. Other compounds without the silicon-oxygen backbones will in the following be mentioned as organosilicon compounds. They are characterised by Si–C bonds. Silicones encompass e.g. polydimethylsiloxanes (PDMS), polyethermethylsiloxanes (PEMS), and volatile methylsiloxanes (VMS) and other siloxanes with silicon-oxygen backbones ($SiR_2–O)_n$ (Rücker and Kümmerer, 2015). These bonds are man-made and not naturally occurring (Hirner et al., 2003). Silicones are usually designed to be very stable in the products and applications. However, when they enter the environment, this originally intended chemical stability inhibits abiotic and biotic degradation and enables the dispersal of the persistent compounds.

Silicones are renowned for the high diversity in chemical properties. They found a wide range of applications in many products including numerous uses in our daily lives, i.e. they are ubiquitous. They are used as defoamers and foam stabilising agents, lubricants, surfactants, in adhesives, in coatings, for construction, in sealants, as flexible polymers, medical materials and many more (Benkeser and Krysiak, 1953). In 2016, the global siloxanes production was 1.7 million metric tonnes (QYResearch, 2017) and it is still increasing.

Few organosilicon compounds are classified as emerging contaminants, which are partially suspected to be persistent, bioaccumulative, and toxic (PBT) (ECHA, 2018; Lefèvre-Brevart, 2019). Some are known to be substances of very high concern (Feng et al., 2019).

As siloxanes are also surfactants or ingredients of personal care products, they will be released to the environment after their intended use. Others are released during washing e.g. compounds used for softening textiles. There is many data about the occurrence of siloxanes in different compartments. Desideri et al. (1991) have detected less than 81 ng $L^{-1}$ of octamethylcyclotetrasiloxane ($D_4$) in sea water in the Antarctica. Sparham et al. (2008) have found 10–29 ng $L^{-1}$ of decamethylcyclopentasiloxane ($D_5$) in the river Great Ouse in UK (Sparham et al., 2008). In wastewater treatment plants influent and effluent, a study has shown 9–11 µg $L^{-1}$ of $D_5$ and 3.0–4.5 µg $L^{-1}$ of dodecamethylcyclohexasiloxane ($D_6$) (influent) and 0.31–0.35 µg $L^{-1}$ of $D_5$ and 0.07–0.12 µg $L^{-1}$ of $D_6$ (effluent) (van Egmond et al., 2013).

However, data about the abiotic or biotic degradation of siloxanes in the environment is very scarce. Mostly only hydrolysis is taken into account. Michel et al. (2014) have shown that Silwet L77, a commercial PEMS, hydrolysed faster at pH 9 than at pH 7. They figured out that Silwet L77 has a half-life of several weeks under environmental conditions (12 °C, pH 7). Hydrolysis of PDMS fluids was reported under extreme chemical conditions (pH 2–4 and 9–12), but was very slow at pH 6 (Ducom et al., 2013). Xu (1999) demonstrated in his study that some cyclic volatile methylsiloxanes including $D_4$, $D_5$, and $D_6$ were completely degraded in soil environments via volatilisation, biodegradation and multistep hydrolysis. For example, $D_4$ was directly hydrolysed via ring-opening to the tetramer diol ($HO–[Si(CH_3)_2O]_4–H$). This product hydrolysed to smaller diols and finally to dimethylsilanediol (Xu, 1999). Xu et al. (2013) concluded from their study on the degradability of cyclic volatile methylsiloxanes that biocatalysed hydrolysis was the main degradation pathway of $D_4$ and $D_5$ besides volatilisation and adsorption. They also reported that the hydrolysis rate decreased with an increasing chain length attributed to steric hindrance. Often silicones are not biodegradable in sewage treatment (Hobbs et al., 1975). Since, siloxanes are owning a stable bond between silicon and carbon and oxygen atoms, there is the perception that no microorganisms can cleave these bonds in nature (Hirner et al., 2003). Bletsou et al. (2013) argued that the high amounts of different linear oligo siloxanes in effluents of waste water treatment plants belong to biodegradation of polydimethylsiloxanes. However, this conclusion was neither proofed by biodegradation tests nor represented by the given results. Further studies used specific microorganisms (*Pseudomonas Aeruginosa* S240 (Li et al., 2014) *Methylibium sp*. (Boada et al., 2020)) to predict biodegradation in biogas plants, which will be normally displaced by faster growing microorganisms in the environment (Rücker and Kümmerer, 2015).

Photochemical cleavage of Si–C bonds has been reported (Kira et al., 1985). They investigated benzyltrimethylsilane and substituted benzyltrimethylsilanes with UV irradiation of 254 nm and demonstrated the cleavage of a $Si–C_{benzyl}$ bond. Drake et al. (2003) have concluded that oxidation caused by UV light increased as the energy of the UV light raised with shorter wavelengths (123 and 147 nm (Skurat and Dorofeev, 1994), 147 nm (Vasilets et al., 1994), 193 and 248 nm (Joubert et al., 1991), 313 nm (Imakoma et al., 1994) and < 300 nm (Israëli et al., 1992)).

The above-mentioned studies demonstrate that there is a lack of data for a better understanding of degradation processes including the formation of products of incomplete mineralisation (transformation products, TPs) that could also enable a design of better degradable silicones under environmental conditions. Hitherto, only non-specific photolysis products (e.g. methane, ethane, and benzene) of silicon rubbers are taken into account (Skurat and Dorofeev, 1994). Except this, FT-IR spectra of silicon rubber samples were measured to compare virgin and aged rubbers (Imakoma et al., 1994), but determination of TPs was not their focus.

The key to improve environmental mineralisation of chemicals is a better understanding of the relationship between the structure of molecules and their (bio)degradability. However, there is no such knowledge for silicones. As conventional siloxanes are persistent in the environment, we designed five organosilicon substances inspired by structurally similar but better degradable compounds anisole and *N,N*-dimethylaniline as core structures (Chemicals Inspection and Testing Institute, 1992). The hypothesis was that these new organosilicon compounds are better biodegradable and/or photodegradable (benign by design concept (Kümmerer et al., 2018)). The resulting substances *o*-$MeOC_6H_4SiMe_3$ (**1**), *p*-$MeOC_6H_4SiMe_3$ (**2**), (*p*-$MeOC_6H_4)_2SiMe_2$ (**3**), *o*-$Me_2NC_6H_4SiMe_3$ (**4**), *p*-$Me_2NC_6H_4SiMe_3$ (**5**) (Table 1) were then introduced to the OECD tests for hydrolysis (OECD 111), biodegradation (OECD 301D & F) and photodegradation (xenon and medium pressure mercury lamp). Primary elimination was determined by HPLC-UV/vis and possible generated TPs were detected by LC-$MS^n$ analysis. If they turn out to be better degradable, silicones based on the structural units of the selected compounds could be envisioned, expecting them to contain defined breaking points, which allow designing new and better degradable silicones for a wide range of applicability.

## 2. Materials and methods

### 2.1. Design of test substances

One strategy to improve bio- and photodegradability of organosilicon compounds could be the use of bio- and/or photodegradable molecules as base structures. Organosilicon groups could be inserted into these structures and then tested in various degradation tests. Therefore, anisole ($–C_6H_4–OCH_3$) and *N,N*-dimethylaniline ($–C_6H_4–N(CH_3)_2$) units are potential candidates for substituents of better degradable siloxanes. Anisole is reported to be 56% biodegradable in the

MITI-I-test (OECD 301 C) within 14 d (Chemicals Inspection and Testing Institute, 1992) and 10% degradable within 60 min via photolysis with a low pressure mercury lamp (Juretic et al., 2013). Data about *N,N*-dimethylaniline are inconclusive. In the ECHA data base it is mentioned to be readily biodegradable, but test systems are not compliant to the OECD guidelines. According to J-Check, a database for biodegradation rates, *N,N*-dimethylaniline is only biodegradable to 1.9% (J-Check, 2019). Phototransformation in water of *N,N*-dimethylaniline was not yet reported, but seems promising due to its structure. Phenyl substituents were chosen as base structures with the aim of better photodegradability because they absorb UV light. Benzene rings functionalised with +M groups shift the absorption maximum to longer wavelengths (Hallas, 1979) and thus improve UV absorption of the compound by a better overlap with the lamp emission spectrum. Methoxy (–$OCH_3$) and substituted amino groups (–$NR_2$) are known to be auxochromic groups (Sidney et al., 1958).

### 2.2. Chemicals

The designed substances *o*-$MeOC_6H_4SiMe_3$ (**1**), *p*-$MeOC_6H_4SiMe_3$ (**2**), $(p\text{-}MeOC_6H_4)_2SiMe_2$ (**3**), *o*-$Me_2NC_6H_4SiMe_3$ (**4**), *p*-$Me_2NC_6H_4SiMe_3$ (**5**) were synthesised at Bielefeld University. The synthetic procedures were generally based on a protocol described by Cren et al. (2009) and are provided in the supplementary material (Text S1). The purity of the substances was proven by $^1$HNMR (supplementary material, Figure S2–S6). The reference substances anisole (< 99%) and *N,N*-dimethylaniline (99%) were purchased at TCI (Eschborn, Germany) and Sigma Aldrich (Steinheim, Germany), respectively. Acetonitrile and methanol (HiPerSolv CHROMANORM® for LC-MS) were purchased from VWR International GmbH (Darmstadt, Germany) and formic acid (98–100%) from Merck (Darmstadt, Germany). 2-Propanol (ROTISOLV HPLC) was obtained from Roth (Karlsruhe, Germany). Dimethyl sulfoxide (≥ 99%) was purchased from Alfa Aesar (Karlsruhe, Germany). All aqueous solutions were prepared with ultrapure water.

### 2.3. Aerobic biodegradation testing

Closed bottle test (CBT, OECD 301D) and Manometric respirometry test (MRT, OECD 301 F) were performed according to OECD guidelines (OECD, 1992). The pass levels of ready biodegradability are 60% removal of theoretical oxygen demand (ThOD) within a 10-d window within the 28-d period after 10% of ThOD has been reached (OECD, 1992). Other validation criteria are: Differences of the duplicate bottles should not be higher than 20% at the end of the test, the ThOD of blind control should not exceed 1.5 mg $L^{-1}$, the degradation rate of the toxicity control must be higher than 25% on day 14, the oxygen concentration in the bottles with test substance must be higher than 0.5 mg $L^{-1}$ at the end of the test, and the degradation rate of the positive control has to be min. 60% on day 14 (OECD, 1992).

For both tests, a blind control without any substance, a positive control with sodium acetate, a toxicity control with both sodium acetate and test compound, and the test compound itself were included. In MRT a sterile control, containing sodium azide was used to identify abiotic elimination. Both tests were conducted over a period 28 d in the dark at a temperature of 20 ± 1 °C. Duplicates were performed during both tests.

#### 2.3.1. Closed bottle test

The CBT was performed with a fibre optic oxygen meter (Fibox 3) as described earlier (Friedrich et al., 2013). Two drops of effluent of a municipal wastewater treatment plant (AGL Lüneburg, Germany) were used as inoculum per litre of test solution. The test was conducted with a low content of mineral medium and a theoretical oxygen demand (ThOD) of 5 mg $L^{-1}$ for each test substance (OECD, 1992). To increase water solubility of the test compounds, 1% v/v dimethyl sulfoxide (DMSO) was added. DMSO was found to be not biodegradable in the test. Total depletion of oxygen of DMSO was low (range of 0.6–2.2 mg $L^{-1}$) and consistent.

#### 2.3.2. Manometric respirometry test

This biodegradation test was conducted with a respirometric OxiTop® measuring system, which determines the oxygen depletion, by the pressure decrease of carbon dioxide formed and adsorbed on sodium hydroxide. The substance was incubated with a ThOD of 30 mg $L^{-1}$ and a low content of mineral medium (OECD, 1992). As inoculum 80 mL of effluent of a waste water treatment plant was used per litre of test solution. Because of the low solubility substances 1% v/v DMSO was added.

### 2.4. Abiotic degradation

#### 2.4.1. Hydrolysis

The tests were performed for all compounds at three different pH values. The selected buffer systems were acetate (pH 4, 5.9 mmol $L^{-1}$), phosphate (pH 7, 5.0 mmol $L^{-1}$) and carbonate (pH 9, 10.0 mmol $L^{-1}$). As the focus of the hydrolysis experiment was not on the simulation of environmental conditions, but on generating a knowledge of reactions of organosilicon compounds in water, the experiment were carried out with 10 mg $L^{-1}$ substance in buffer and 1% v/v acetonitrile (5% v/v acetonitrile for $(p\text{-}MeOC_6H_4)_2SiMe_2$) as a co-solvent to improve the handling of these compounds. In preliminary tests, we have shown that there is no reaction with the co-solvents. The tests were performed at a temperature of 25 ± 1 °C in the dark according to the OECD guideline 111 (OECD, 2004). Before use, all buffer solutions were sterile filtered to prevent biodegradation. Samples for HPLC analysis were taken each day within the first 5 d and subsequently on day 7, 14, 21 and 28. The test ended after 28 d or after an elimination rate of 90%.

#### 2.4.2. Photodegradation using a xenon and a mercury lamp

The tests simulating sun light with a xenon (Xe) lamp were operated in a SUNTEST CPS + device (Atlas Material Testing Technology GmbH, Linsengericht, Germany). An optical cut off filter was applied that only wavelengths between 300 and 800 nm could pass. The intensity was set to 500 W $m^{-2}$. Each substance (10 mg $L^{-1}$) was dissolved in ultrapure water with 1% v/v of the co-solvent (5% v/v for $(p\text{-}MeOC_6H_4)_2SiMe_2$). Acetonitrile, 2-propanol and a mixture of both were used as cosolvents. Another test was conducted with 100% acetonitrile to exclude the effect of water. This solution (25 mL) was filled into the test vessel covered with an irradiation permeable plate made of quartz glass as protection against evaporation. Similar samples were filled into beakers, sealed with parafilm and covered with aluminium foil to exclude irradiation (non-irradiated reference sample). Every 2 h samples were taken and directly analysed with HPLC-UV/vis.

The second experiment was conducted in addition to the irradiation with a Xe lamp. The elimination should be assessed to determine the impact of increased irradiation energy and different emitted wavelength. The test was performed in a photo reactor with a start volume of 800 mL (Jentzsch et al., 2016). The used medium pressure mercury (Hg) lamp (TQ 150, UV Consulting Peschl, Mainz, Germany) emitted wavelengths between 200 and 400 nm. Temperature (20 ± 2 °C) and pH value were continuously monitored. The initial concentration of each test compound was 10 mg $L^{-1}$ with 1% v/v of the co-solvent acetonitrile (5% v/v for $(p\text{-}MeOC_6H_4)_2SiMe_2$) in water. Samples for analysis were taken at 0, 2, 4, 8, 16, 32, 64, 128, and 256 min. Samples of the non-irradiated reference vessels were taken only at 0, 128, and 256 min because it was expected that there are less effects than in irradiated vessels.

The two different lamps were chosen to cover a broader range of emitted wavelengths. Additionally, conclusions can be drawn on the compounds behaviour in surface water under sunlight and during UV

treatment of wastewater or drinking water for disinfection.

Peroxide test stripes (MQuant®, Merck KGaA, Darmstadt, Germany) were used to determine the generation of reactive oxygen species (ROS) in both irradiation tests to identify direct photolysis and because acetonitrile and 2-propanol are known to be radical scavengers (Faraggi et al., 1984; Newton and Milligan, 2006). Acetonitrile is an appropriated co-solvent because it does not react during irradiation (Jentzsch et al., 2016).

### 2.5. Chemical analysis

#### 2.5.1. Primary elimination of model compounds

All measurements for primary elimination were performed with a Shimadzu Prominence 20 HPLC system (Duisburg, Germany) equipped with an UV/vis-detector. Separation of compounds were done on a RP-phenyl-hexyl column (EC 125/3 NUCLEODUR® 3 µm, Macherey-Nagel, Düren, Germany) with a binary mobile phase consisting of water (eluent A) and acetonitrile (eluent B) at a flow rate of 0.4 mL $min^{-1}$. Analysis of hydrolysis and photo reactor samples were performed with a precolumn (EC 4/3 NUCLEODUR® 3 µm, Macherey-Nagel, Düren, Germany). Oven temperature was set at 45 °C. The concentration was determined using the following gradient: Start with 45% eluent B for 1 min, increase eluent B to 80% until minute 4. Then increase it slowly to 90% until minute 6 and hold it for 3 min. After this eluent B was decreased to 45% in 2 min and hold 45% for further 4 min. The injected sample volume was 10 µL. The detector was set to a wavelength of 227 nm for substance **1** (*o*-$MeOC_6H_4SiMe_3$), 228 nm for substance **2** (*p*-$MeOC_6H_4SiMe_3$), 236 nm for substance **3** ($(p\text{-}MeOC_6H_4)_2SiMe_2$), 256 nm for substance **4** (*o*-$Me_2NC_6H_4SiMe_3$) and 264 nm for substance **5** (*p*-$Me_2NC_6H_4SiMe_3$). Wavelengths of maximum absorption were determined before by measurements with a photo-diode array detector in 1% acetonitrile (substance **3** in 5% acetonitrile).

#### 2.5.2. Structure elucidation of transformation products with LC-MS/MS

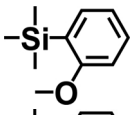
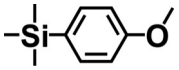
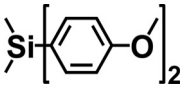
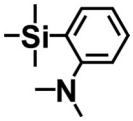
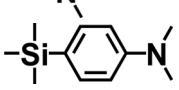
LC-$MS^n$ analysis was performed on a Dionex Ultimate 3000 UHPLC system (Dionex, Idstein, Germany) coupled with an LTQ Orbitrap-XL high-resolution mass spectrometer with H-ESI source (Thermo Scientific, Bremen, Germany). Compounds were separated with a pentafluorophenyl (PFP) column (Kinetex® 1.7 µm 100 Å, 100 × 2.1 mm, Phenomenex LTD, Aschaffenburg, Germany) coupled with a SecurityGuard™ ULTRA 2.1 mm precolumn. The binary mobile phase consisted of 0.1% formic acid (eluent A) and methanol (eluent B). The following binary gradient was used: Start with 5% eluent B for 0.5 min, increase eluent B to 85% until 10 min and hold it for 4 min. Then decrease eluent B to 5% within 0.5 min and hold it for further 5.5 min. The flow rate, oven temperature, and injection volume was set at 0.1 mL $min^{-1}$, 30 °C, and 10 µL, respectively. Other parameters of the MS analysis are in the supplementary material (Table S1). Samples of the irradiation tests (Xe and Hg lamp) and the CBT were measured with this method. Non-irradiated samples, which were made at the same time like the irradiated samples, were used to determine TPs generated via hydrolysis. The initial concentration of the parent compound (**5**) was 10 mg $L^{-1}$, which allows to find possible TPs in detectable quantities. However, this analytical method cannot represent all generated TPs as they may have different ionisation properties. The peak area A of the occurring TPs was related to the initial peak area of substance **5**. The area A gives no indication of the real concentration of unknown transformation products because their ionisation rate is also unknown. A calibration with a standard must be carried out in order to determine the concentration.

## 3. Results and discussion

### 3.1. Designed test substances

The synthesised compounds are presented in Table 1. The process of substance development followed the concept of "benign by design". *Ortho*- and *para*-substituted compounds were synthesised to get more information about the behaviour of different isomers in degradation tests. Benzene as a base structure has its absorption maximum at 200 nm (Doub and Vandenbelt, 1947). The absorption maxima of the designed substances are at 227, 228, 236, 256, and 264 nm, respectively. Therefore, insertion of auxochromic groups like methoxy and substituted amino groups resulted in an absorption in a longer wavelength range compared to the base molecule benzene. Hallas (1979) observed the same phenomenon and reported that $–NMe_2$ had a marked bathochromic shift of 43 nm, which is in correlation to our measured absorption maxima of 256 and 264 nm of substances **4** and **5**, respectively. Methoxy groups had also effects on the absorption maxima, but it was smaller than the effect of the substituted amino group according to a smaller +M effect compared to amino functionalities.

**Table 1**
Specification of the selected substances including number, term, structure and InChI.

| No | Formula | Structure | InChI |
|---|---|---|---|
| 1 | *o*-$MeOC_6H_4SiMe_3$ |  | InChI = 1S/C10H16OSi/c1-11-9-7-5-6-8-10(9)12(2,3)4/h5-8H,1-4H3 |
| 2 | *p*-$MeOC_6H_4SiMe_3$ |  | InChI = 1S/C10H16OSi/c1-11-9-5-7-10(8-6-9)12(2,3)4/h5-8H,1-4H3 |
| 3 | $(p\text{-}MeOC_6H_4)_2SiMe_2$ |  | InChI = 1S/C16H20O2Si/c1-17-13-5-9-15(10-6-13)19(3,4)16-11-7-14(18-2)8-12-16/h5-12H,1-4H3 |
| 4 | *o*-$Me_2NC_6H_4SiMe_3$ |  | InChI = 1S/C11H19NSi/c1-12(2)10-8-6-7-9-11(10)13(3,4)5/h6-9H,1-5H3 |
| 5 | *p*-$Me_2NC_6H_4SiMe_3$ |  | InChI = 1S/C11H19NSi/c1-12(2)10-6-8-11(9-7-10)13(3,4)5/h6-9H,1-5H3 |

### 3.2. Biodegradation

All CBT experiments were valid according to the OECD guidelines (OECD, 1992). An example curve of substance **1** is shown in Fig. 1 (1 – CBT, 2 – MRT), which is representative for all tested compounds. ThOD of blind control with 1% v/v DMSO exceeded 1.5 mg $L^{-1}$ because DMSO consumed around 1.5 mg $L^{-1}$ of oxygen, but compared to the amount of DMSO, it is negligible. Furthermore, the blind control was subtracted from the result of the tested substances. In some cases, negative values of biodegradation resulted from this calculation (e.g. Fig. 1 (1)). This means that no degradation was observed. The pH showed no significant change in all test vessels.

During the CBT and MRT, values of about −10–8% of biodegradation was calculated for the five tested compounds (Table 2). Negative values can be interpreted as no degradation. This means that these substances are not readily biodegradable (OECD, 1992). This can be confirmed by available data of other organosilicon substances (Hirner et al., 2003; Michel et al., 2014; Rücker and Kümmerer, 2015). This was the first time of biodegradation testing of these five substances. Comparable data on biodegradability was not available for these compounds.

The structurally related substances anisole and *N,N*-dimethylaniline were investigated in the CBT to improve the comparability of our results and because of inconsistent data in databases. Degradation rates of 92% and 8% were reached, respectively, which confirm the data for anisole from the biodegradation test OECD 301C and the data for *N,N*-dimethylaniline obtained by the MITI-I-test. The poor biodegradation

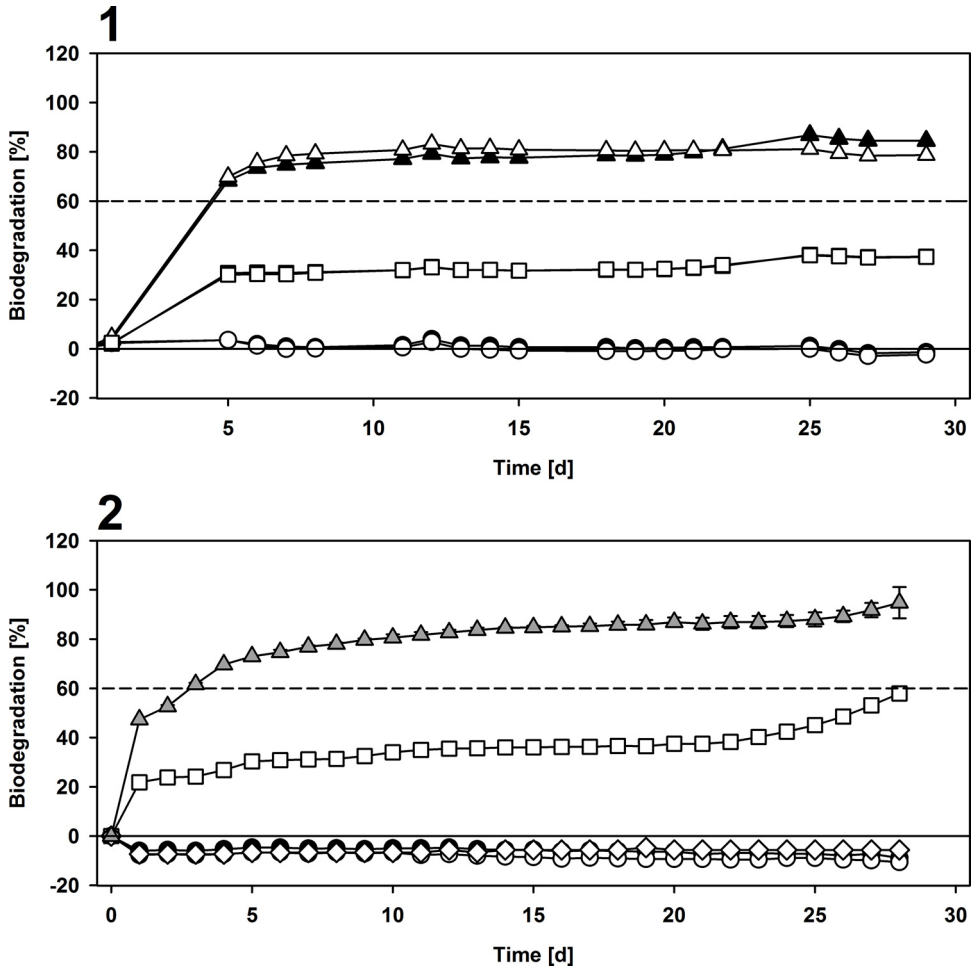



**Fig. 1.** Example curves of the CBT (1) and MRT (2) of substance **1**. The threshold of at least 60% means readily biodegradable. The tested substance **1** is displayed as black and white circles ($n = 2$), toxicity control as squares (CBT $n = 2$, MRT $n = 1$), sterile control as diamonds (MRT $n = 1$) and the positive control sodium acetate as triangles (CBT $n = 2$, MRT $n = 3$, means ± SD).

**Table 2**
Overview of the endpoints of the biodegradation results of the tested substances (**1**–**5**). CBT and MRT were performed for 28 days with mineral medium, inoculum, 1% v/v DMSO at 20 ± 1 °C in the dark ($n = 2$).

| Test Compound no | CBT | MRT |
|---|---|---|
| | Biodegradation [%] | |
| **1** | −2 | −10 |
| **2** | 3 | −7 |
| **3** | 0 | 8 |
| **4** | −2 | −3 |
| **5** | −2 | −4 |

rate of compounds **1** and **2** is attributable to the presence of the trimethylsilyl group, because anisole differs only by this group. *N,N*-Dimethylaniline did not show ready biodegradability in CBT as substances **4** and **5** did. The *N,N*-dimethylamino group seemed also to have a negative effect on the biodegradability as aniline itself is readily biodegradable and often used as a reference substance for ready biodegradability (Nyholm, 1991). In this study, the use of readily biodegradable base structures coupled to organosilicon units did not result in better biodegradable organosilicon compounds because the typical silicone structure inhibited the degradation through microorganisms.

### 3.3. Abiotic degradation

#### 3.3.1. Hydrolysis

Experiments were conducted until 90% of hydrolysis was observed or for 28 d (OECD, 2004). In Fig. 2, the hydrolysis of the five tested compounds (diagrams 1–5) is presented in dependence of time and pH. The results showed that substance **1** and **2** hydrolysed below 10% of initial concentration of 10 mg $L^{-1}$ after two and three days, respectively. The disappearance times ($DT_{50}$), where the parent compound is reduced by 50%, were 0.5 and 0.7 d for all pH values and showed no dependence of hydrolysis on pH. After 28 d, more than 10% of substance **3** was detected at all pH values. At pH 4, the $DT_{50}$ value is 7.5 d, at pH 7 it is 58.7 d, and at pH 9 it is 169.1 d. The elimination rate of the substance at pH 4, 7 and 9 was 83%, 30% and 10%, respectively. Substances **4** and **5** behaved similar in water. At lower pH, they hydrolysed very fast ($DT_{50}$ = 0.7 and 0.3 d, respectively). At pH 7 and 9 it took around 1 day to hydrolyse half of the initial concentration of the two substances. The concentration of substance **4** was less than 10% of the initial concentration after three days at all pH. Substance **5** hydrolysed to less than 10% of the start concentration after one day at pH 4 whereas at pH 7 and 9 around four days were needed to hydrolyse to less than 10%. Hence, hydrolysis of substance **3** showed the highest dependence on pH but the slowest hydrolysis rate of these five

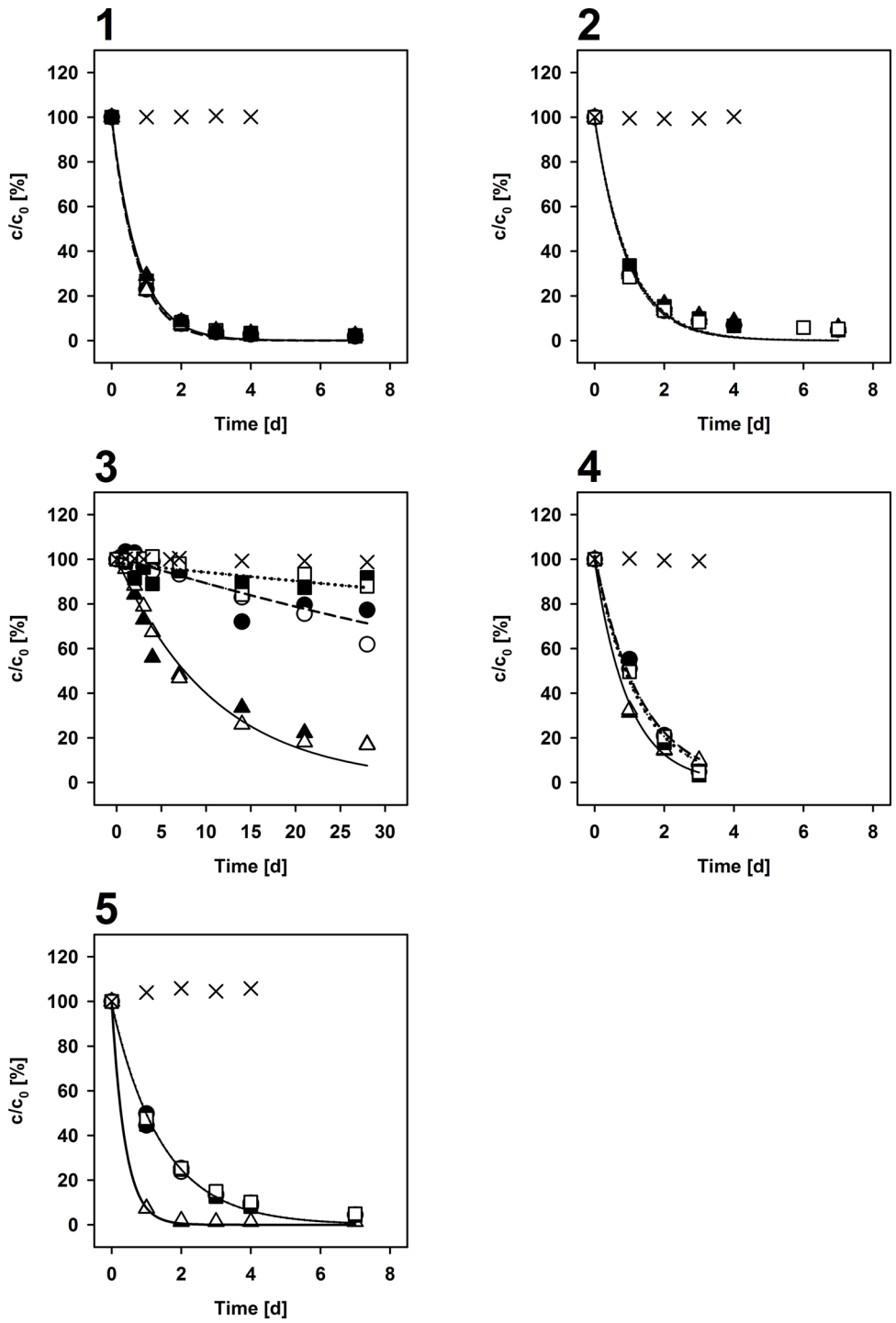



**Fig. 2.** Elimination of the five tested compounds (**1–5**) via hydrolysis at different pH values (pH 4 = triangles, pH 7 = circles, pH 9 = squares, $n$ = 2). For each substance two experiments were conducted, which were represented by black and white symbols. Crosses (×) show the results of an anhydrous experiment in 100% acetonitrile ($n$ = 1).

compounds.

Fig. 2 (diagrams 1–5) shows results from anhydrous studies. These experiments in 100% acetonitrile were conducted to demonstrate that the elimination is only caused by the presence of water. As the concentration of the substances remained at 100% during test in acetonitrile, it can be concluded that the elimination is caused by hydrolysis.

The results obtained from the hydrolysis experiments showed that the five tested compounds had different behaviour in water, but if the substances reacted differently at tested pH, lower pH increased the hydrolysis rate. Therefore, it is likely that hydrolysis is acid catalysed for these substances. Substance **3** was hydrolytically more stable than the other four substances. Reason for this could be the obstruction of the access of water molecules due to steric shielding by the two benzene rings (Bruice et al., 2011; Xu et al., 2013). These findings support the idea of "directed hydrolysis" (Rücker and Kümmerer, 2013). This means that molecules are designed to degrade in a specific time (e.g. ester). They should degrade slowly enough for their application but fast enough after they are entering the environment by using protection groups or groups with different sizes (Gitto and Wooley, 1995). The hydrolysis results of substances **4** and **5** confirmed the data of the ECHA

database (ECHA, 2019). *N,N*-Dimethylaniline, a structural analogue of the tested substances without the trimethylsilyl group, hydrolysed well at pH 5. At pH 7 and 9, *para*-substituted compounds hydrolysed slightly slower than their *ortho*-substituted analogues. This is supported by the study of Jindra et al. (1973). They described the hydrolysis of aromatic carbamates in pig liver homogenates at pH 7.4 and 8.8 and found *para*-substituted compounds hydrolyse slower than their *ortho*-analogues (Jindra et al., 1973). At lower pH values (pH 4), there is no clear relation between the position of the substituent and the hydrolysis rate. Michel et al. (2014) investigated the trisiloxane surfactant Silwet L-77 ($\{Me[O(CH_2)_2]_nCH_2\}(Me_3SiO)_2SiMe$) in a test for hydrolysis (OECD 111) and found out that the surfactant hydrolysed faster at pH 9 than at pH 7. This is in contrast to the results presented in this study. However, the long polyether chain of Silwet L-77 results in properties different to those of the five tested compounds **1**–**5**. Also, the silicon atoms in Silwet L-77 are embedded in a trisiloxane unit, whereas the silicon atoms in the tested compounds are bonded to three methyl groups and an aromatic ring, i.e. they have only Si–C bonds of low polarity and no highly

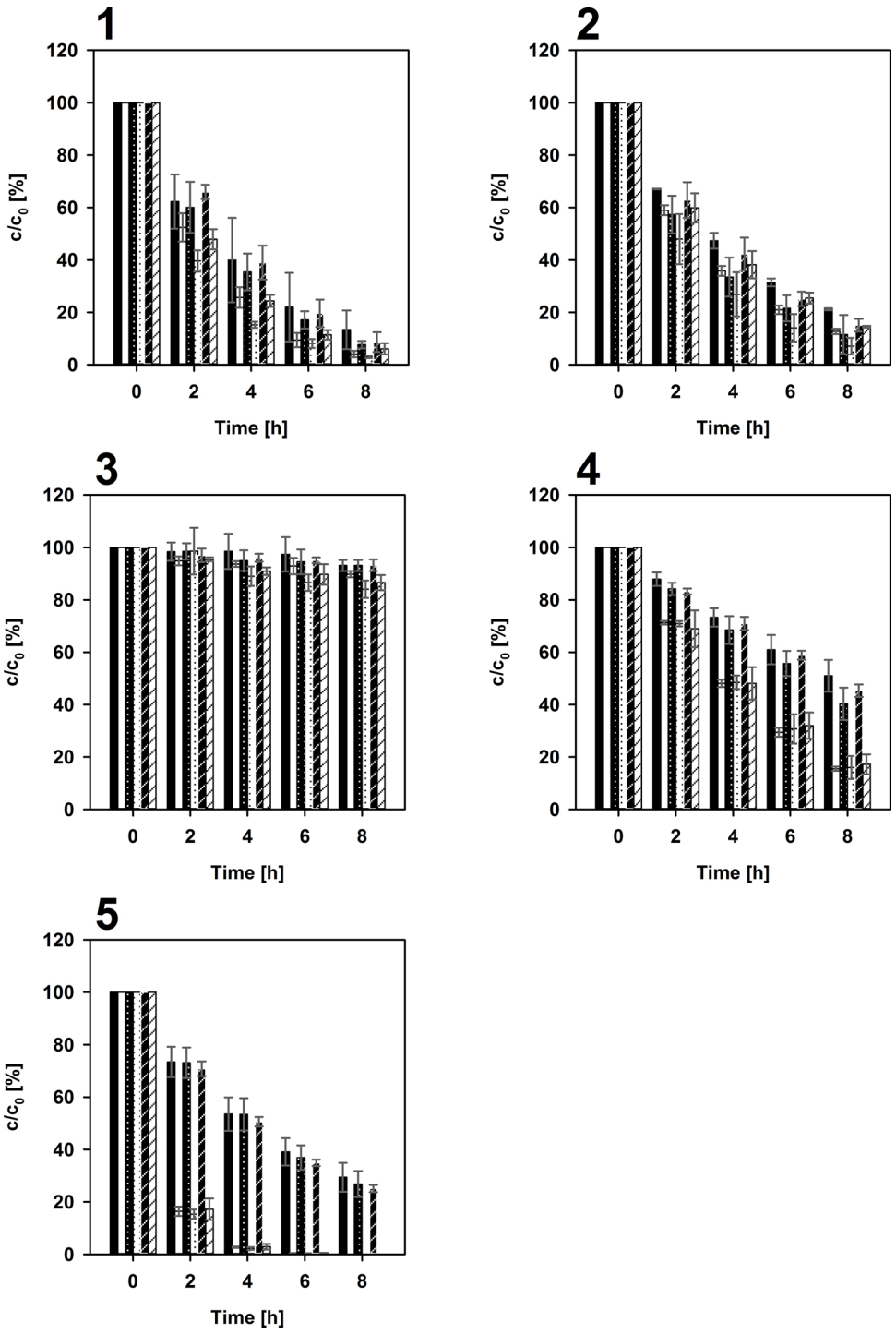



**Fig. 3.** Comparison of the effects of different co-solvents on the photolytic degradation by a Xe lamp (300–800 nm) of the five tested compounds (**1**–**5**) during a period of 8 h. Black columns represent samples without irradiation and white columns show irradiated samples. Acetonitrile (pattern-free), 2-propanol (spotted), and a mixture of both (striped) were used as radical scavengers and to increase the water solubility. Initial mass concentration was 10 mg $L^{-1}$. Reaction volume was set to 25 mL. Values represent the mean ± SD ($n$ = 3).

polar Si–O bond. This results in different electronic and steric effects and affects in particular their lability towards hydrolysis.

*3.3.2. Photodegradation by Xe lamp in the presence of different co-solvents*

The results of the photolysis experiments employing a Xe lamp are presented in Fig. 3. Diagrams 1–5 show the concentration of the test substance in relation to the start concentration in percent as a function of time in dependence of the co-solvents acetonitrile, 2-propanol and a mixture of both. Substances **1–5** showed elimination rates of around 96%, 88%, 13%, 84%, and 100%, respectively, after 8 h of irradiation for all tested co-solvents. Obtaining the relative elimination rate caused by irradiation, the quotient of elimination rates of irradiated and non-irradiated samples was calculated. When irradiated in water, substances **1–4** showed constantly slightly faster degradation rates compared to the reactions without exposure to light. Only substance **5** (diagram 5) showed a strong, non-constant deviation from the reaction in the dark. Substance **3** was the least efficiently eliminated one (diagram 3). After 8 h, only 7% were primarily eliminated during irradiation. Substance **5** displayed the highest degradation rate (diagram 5). After 6 h, 99% of the parent compound was eliminated. Two hours later, the parent

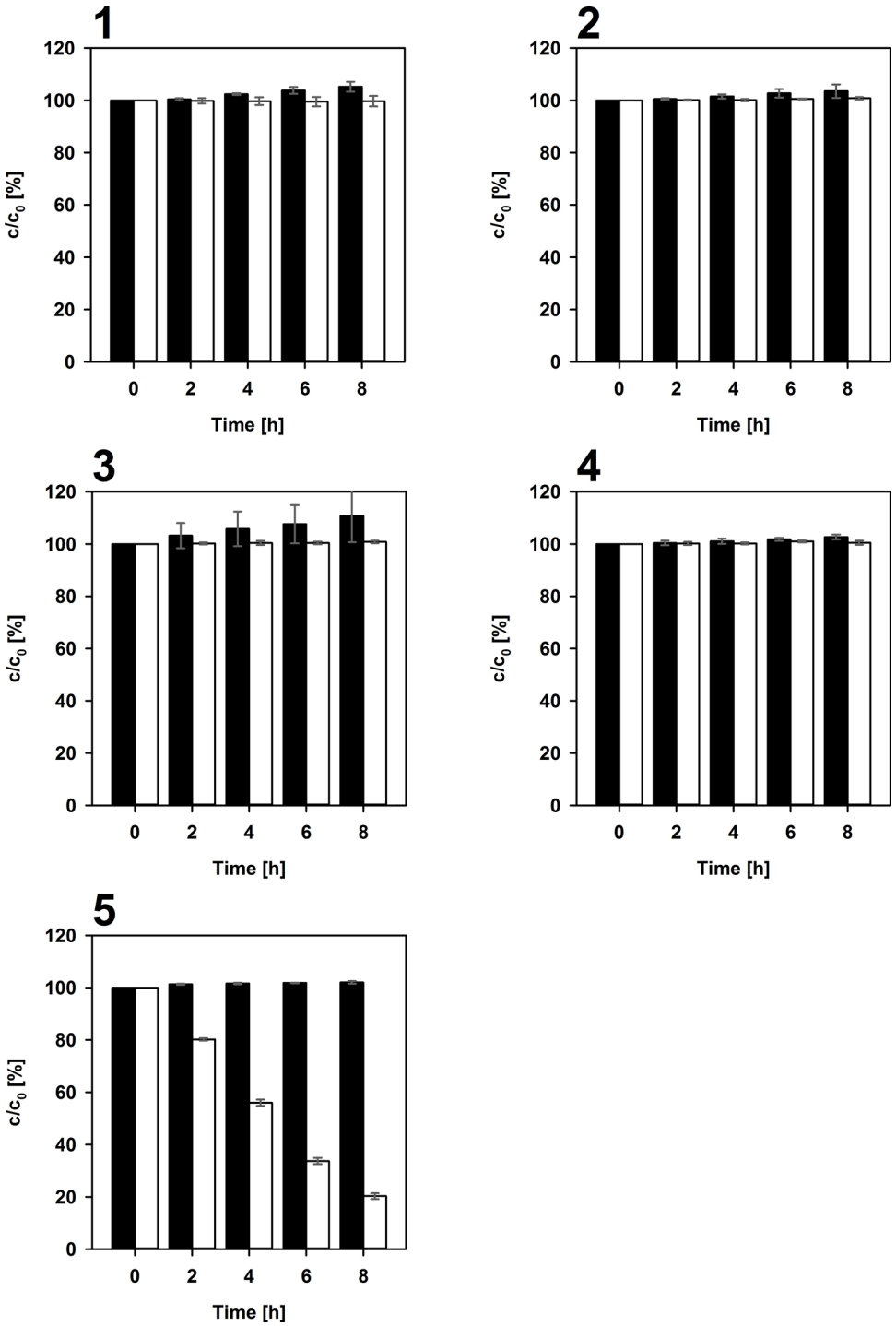



**Fig. 4.** Elimination of the five tested substances **1–5** during 8 h of irradiation with a Xe lamp (white column) compared to a sample of the same substance in the dark (black column) in 100% acetonitrile to show degradation without the influence of hydrolysis. Initial mass concentration was 10 mg $L^{-1}$. Reaction volume was set to 25 mL. Values represent the mean ± SD ($n$ = 3).

compound was completely eliminated. Substances **1**, **2**, and **4** showed relative elimination rates of around 56%, 23% and 64%, respectively, after 8 h. No major differences were observed for experiments with various co-solvents acetonitrile, 2-propanol and the mixture of both acetonitrile and 2-propanol. A special effect of one of the co-solvents can be excluded based on these results. Small amounts of ROS (0.5 mg $L^{-1}$) could be detected via peroxide test stripes in all irradiated samples after 2 h. The non-irradiated samples showed 90%, 85%, 7%, 54%, and 73% of elimination, respectively. As already in the hydrolysis experiments, water has a high impact on the primary elimination of these five compounds. The hydrolysis rates of the non-irradiated samples during the tests with the Xe lamp confirmed the data generated by the hydrolysis experiments at pH 4 and showed the same tendency as for the impact of the position of the substituent at the aromatic ring. The pH in the photolysis experiment was relatively low (pH 6) and comparable with the hydrolysis experiment (pH 4). Irradiation of water causes a decrease in pH (Huang, 1989).

Consequently, during the irradiation experiment with the Xe lamp, the substances were eliminated by both photolysis as well as non-photo-induced hydrolysis.

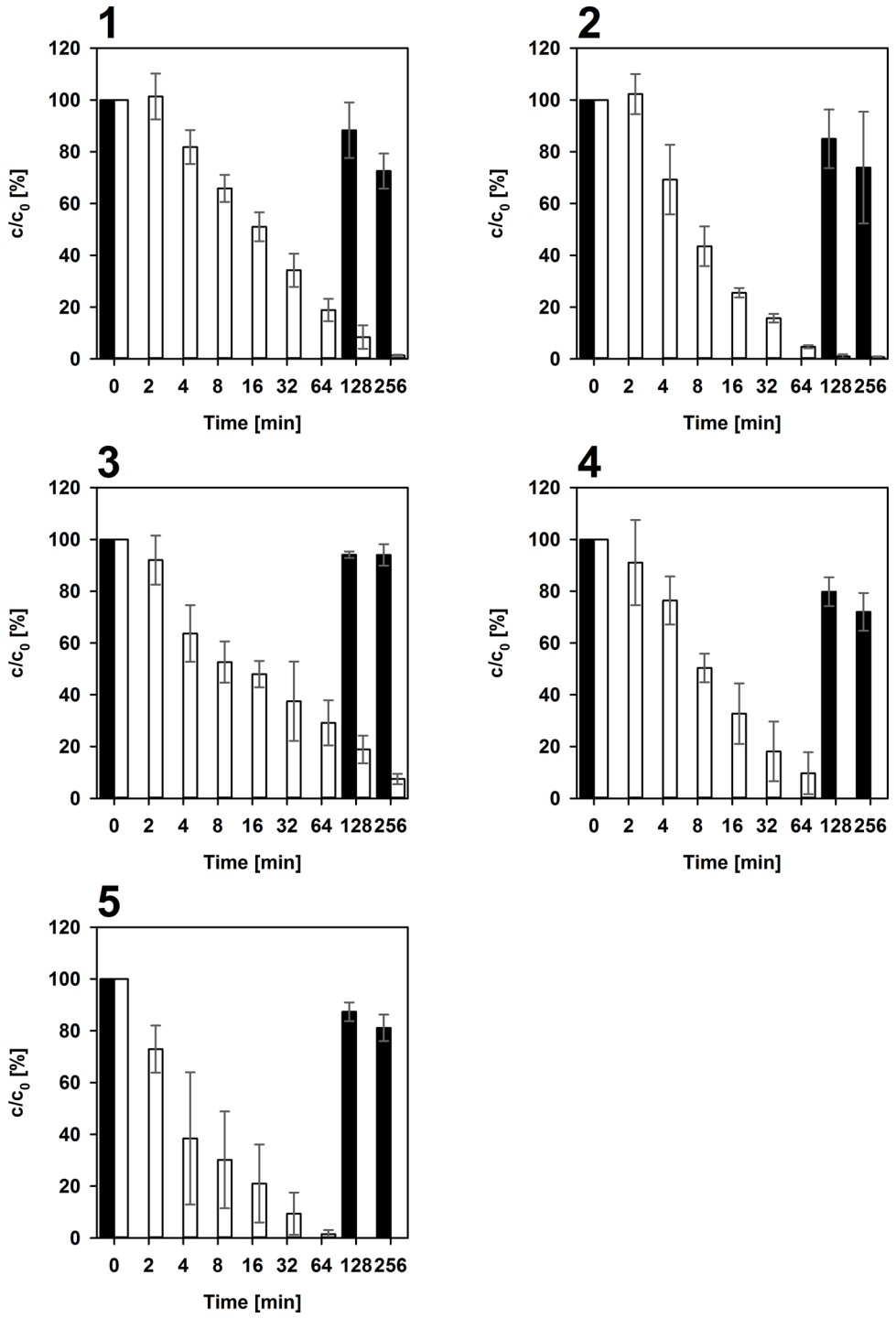



**Fig. 5.** Elimination of the five tested compounds (**1**–**5**) in the photo reactor (white columns). Irradiation was done with a Hg lamp (200–400 nm) in water with 1% acetonitrile (5% acetonitrile for substance **3**) as a co-solvent over a period of 256 min. Non-irradiated samples of the tested compounds during the photodegradation experiment are shown as black columns. Initial mass concentration was 10 mg $L^{-1}$. Reaction volume was set to 800 mL. Values represent the means ± SD ($n$ = 3).

Photolysis is only relevant for substances **4** and **5** because of distinct differences in the elimination rate of irradiated and non-irradiated samples (30% points and 27% points, respectively). Fig. 3 shows that only photolysis of substance **5** was fast. Between 0 and 2 h of irradiation was a strong decrease of the concentration of substance **5**. Therefore, photolysis was found to be faster than hydrolysis during the irradiation experiment and can be explained by the better overlap of the substance absorption with the lamp emission spectrum (supplementary material, Figure S1). This could give a hint to direct photolysis of substance **5**.

Irradiation experiments under anhydrous conditions in pure acetonitrile were performed to support the thesis of high hydrolysis rates and to determine the type of photolysis process (direct or indirect photolysis). The results of the experiments in pure acetonitrile are shown in dependence of time in Fig. 4. The comparison of irradiated and non-irradiated samples illustrates the effect of irradiation. Both, the irradiated and non-irradiated samples of the tested substances (**1–4**) showed approximately 100% of the initial concentration after 8 h of irradiation. This means that there is no photodegradation. Substance **5** showed a primary elimination of 80% in the irradiation experiment and no changes of concentration in the non-irradiated solution. The determined rate constant $k$ of substance **5** was 0.174 $h^{-1}$ at an initial mass concentration of 10 mg $L^{-1}$. Substance **5** has an absorption maximum at 364 nm (1% acetonitrile, supplementary material, Figure S1). Of all substances, it had the absorption maximum at the longest wavelength range. The absorption maximum of substance **5** overlapped with the emission spectrum of the Xe lamp. The energy of the irradiation was high enough to split bonds. Si−C, C−H and Si−O bonds can be homolytically cleaved by high energy radiation (Noll, 1968). Thus, substance **5** could be directly eliminated by irradiation without the involvement of ROS, which are formed in irradiated water. Accordingly, indirect photolysis and hydrolysis played a subordinated role in this case. Electron-donating groups like the amino group in substance **5** enrich the aromatic system with electrons (+M effect) and shift the absorption maximum towards longer wavelengths (bathochromic effect) (Pohorecki et al., 2010).

The small differences between irradiated and non-irradiated samples of substances **1–4** and therefore low elimination rates during the irradiation experiment in aqueous solution with 1% acetonitrile could only be due to the formation of hydroxyl radicals (ROS) by irradiation (Jager de et al., 2017). Small amounts of ROS (0.5 mg $L^{-1}$) were detected by peroxide test stripes during the experiment in irradiated samples but not in non-irradiated samples. The test stripes displayed the presence of ROS during irradiation via a generated blue oxidation product (Jentzsch et al., 2016). The blue colour of the test stripe was visually compared with a colour scale of the producer (Merck KGaA). Peroxide test stripes were used in all irradiation tests for all substances to control the generation of ROS. This hypothesis that the low rate of elimination during irradiation belongs to the formation of ROS was supported by irradiation experiments in 100% acetonitrile. There was no elimination observed for substances **1–4** due to the absence of ROS and the poor overlapping of the absorption spectra of substances **1–4** and emission spectrum of the Xe lamp (supplementary material, Figure S1). It can be concluded that substances **1–4** were indirectly photolysed, i.e. modified by the reaction with formed ROS resulting in more polar compounds. Indirect photolysis is relatively independent from substance properties because ROS react by any collision with other molecules (Freinbichler et al., 2011). This means that the concentration of 1% v/v of co-solvent (5% v/v for substance **3**) was not high enough to intercept the generated ROS. Faraggi et al. (1984) used about 5.4% v/v of the co-solvent to minimise ROS.

### 3.3.3. Photodegradation by Hg lamp

Fig. 5 shows the results of the photodegradation experiments with Hg lamp irradiation of the five tested compounds compared to their corresponding samples in the dark. The non-irradiated samples of the substances **1–5** showed primary elimination of 27%, 26%, 6%, 28%, and 19%, respectively, after 256 min. With irradiation, elimination of 99%, 99%, 92%, 100%, and 100%, respectively, was observed after 256 min. Although some of the substances were almost completely degraded, different rate constants were observed. Substance **3** degraded slower compared to the other ones. After 256 min, substance **3** was the only one that was still detectable at a level higher than 7% after 256 min. At an initial mass concentration of 10 mg $L^{-1}$ the rate constant $k$ was 0.024 $min^{-1}$. Substance **5** was degraded most rapidly and was not detectable after 64 min anymore ($k$ = 0.158 $min^{-1}$). The related *ortho*-compound (substance **4**) was more slowly degraded. A rate constant $k$ of 0.068 $min^{-1}$ was calculated. In contrast, substance **4** was not detectable anymore after 128 min. The same phenomenon could be observed for substances **1** and **2**. They were primary eliminated within 256 min whereby the *ortho*-compound (substance **1**, $k$ = 0.035 $min^{-1}$) was degraded slower than the *para*-compound (substance **2**, $k$ = 0.089 $min^{-1}$). In conclusion, it was found that in the photo reactor using UV-C irradiation the *para*-substituted substances were better photodegradable than the related *ortho*-substituted compounds. In contrast, in the test with the Xe lamp, no differences between *para*- and *ortho*-derivatives were observed.

Hydrolysis played a bigger role in the elimination process with the Xe lamp because the latter one was slower according to the lower energy level of irradiation. With the Hg lamp, the irradiation was more intensive because of the UV doses so that hydrolysis played a less important role. In addition, the elimination rate using the Hg lamp was higher than the hydrolysis rate and higher than using the Xe lamp.

In summary, the two lamps cover different ranges of the emission spectrum (Xe lamp 300–800 nm, Hg lamp 200–400 nm) and allowed testing and discussing general photodegradability of the selected substances in relation to their structures and absorption spectra. First insights can also be obtained concerning the behaviour of substances in surface water under sunlight and during UV treatment of water for disinfection. In surface water, it is probable that substance **5** would be photodegraded, while the other substances would hydrolyse to a certain degree. With UV treatment of potable water or effluent of a wastewater treatment plant all substances should be primary eliminated within at least approximately four hours, but matrix effects should not be underestimated.

It was found that the five model substances show different behaviour in abiotic degradation tests related to their structure. Substance **3** proved to be very stable in hydrolysis and photolysis tests, but showed the highest dependence on pH during hydrolysis. This was ascribed to the second aromatic ring, which is the only difference to substances **1** and **2**. In contrast, substance **5** showed the fastest elimination rates in all abiotic degradation tests. Photolysis experiments under anhydrous conditions with a Xe lamp showed that substance **5** was directly photolysed via irradiation. The other substances (**1–4**) were only degraded with the presence of water and probably the formation of ROS. The better photolysis of substance **5** can be related to the electron donating amino group in *para*-position at the aromatic ring (+M effect). This fulfilled our expectations, based on the better degradable core structures. Insertion of such groups into PDMS could thus improve the ability to photolyse after their usage.

It was also shown that increasing the energy of irradiation (Hg lamp) resulted in degradation of all parent compounds. Therefore, it can be concluded that only intense irradiation degraded all selected organosilicon compounds within hours.

In general, no clear statements can be made regarding the position of the substituent at the aromatic ring in relation to the degradability. The experiment with Hg lamp irradiation showed that photolysis of the *para*-substituted compound was faster than that of the *ortho*-compound, but hydrolysis was faster for the *ortho*-substituted compound. However, no consistent results could be achieved for Xe lamp irradiation. Once, hydrolysis and photolysis were faster with *ortho*- and once with *para*-substituents. However, during the hydrolysis experiments *ortho*-substituted compounds were hydrolysed slightly faster at higher pH than

their related *para*-substituted compounds. Comparable literature is not available.

### 3.4. Transformation products of substance **5**

#### 3.4.1. Occurrence of transformation products

Substance **5** was selected for analysing possible TPs because it shows the fastest degradation rate of primary elimination in all irradiation experiments according to its absorption spectrum. It was the only substance that was degradable in pure acetonitrile, indicating direct photolysis. Thus, substance **5** seemed to be a good candidate as a base unit for polymers. However, primary elimination is no evidence for complete mineralisation, which is favoured. Therefore, high-resolution MS measurements were performed to get an idea of the generated products and the degradation pathway via different processes (hydrolysis, direct or indirect photolysis). The LC-MS total and extracted ion chromatograms were checked for samples of substance **5** irradiated by the Xe and Hg lamps and non-irradiated samples (hydrolysis and biodegradation). In sum, 11 TPs were observed and their chemical structure could be assigned, respectively. All the observed TPs had not been observed in any earlier studies. The detected TPs were more polar than substance **5** (reduced retention time). There are silicon-containing TPs identified by their characteristic isotope pattern of silicon, TPs only generated in the presence of water and irradiation, and TPs formed via hydrolysis (Table 3). Experiments in pure acetonitrile were used to identify direct photolysis products and hydrolysis products because they were not formed in acetonitrile.

The irradiation of substance **5** with a Hg lamp in 1% acetonitrile resulted in a mixture of all detected TPs with the following *m/z* ratio: 124.0757, 154.0863, 152.0706, 154.0863, 138.0913, 122.0964, 208.1152, 210.1309, and 180.1203 (Table 3, column 4). TPs with masses of 154.0863, 208.1152, and 210.1309 were detected at two different retention times, respectively. These were structural isomers and were labelled in the following with a and b. All TPs were named after their *m/z* ratio. In the related non-irradiated samples (Table 3, column 5), all silicon containing TPs (TP 208a, TP 210a, TP 210b, TP 180, and TP 208b) and TP 122 could be found, but not the TPs with a retention time shorter than 9 min. The same results were observed for the experiment with the Xe lamp in 1% acetonitrile, whereas the experiment in 100% acetonitrile showed no TPs from 0 to 9 min (retention time) and all TPs from 9 to 17 min (TP 122, TP 208a, TP 210a, TP 210b, TP 180, and TP 208b) whether with or without irradiation. It can be concluded that TP 124, TP 154a, TP 152, TP 154b, and TP 138 are only formed in an irradiated and water containing surrounding. This confirms the studies of Mahmoud et al. (2013). They found that most of the TPs were generated by hydroxylation, which is only possible in the presence of water and results in more polar TPs. Table 3 also indicates the TPs detected at the end of the CBT. TP 122, TP 180, and substance **5** occurred during the test (Table 3, column 10). TPs from 0 to 9 min (retention time) did not occur in CBT samples because they were typically formed in aqueous irradiated samples. The reason that not all TPs typically formed via hydrolysis could be detected, relates to the lower concentration of substance **5** in the biodegradation test. The mass concentration of substance **5** was 1.9 mg $L^{-1}$ at the beginning of the test, which corresponds to 5 mg $L^{-1}$ of ThOD. Therefore, the concentration of TPs was lower than the limit of detection. Detected TPs in CBT samples were attributed to hydrolysis because there was no measured oxygen demand.

In standard samples, one product (TP 122) was observed at the beginning of all tests. It is assumed that this TP was formed within a long time of storage of substance **5** caused by exposition to air and humidity. It was identified as *N,N*-dimethylaniline via the accurate mass (*m/z* 122.0964) and the specific retention time of 9.19 min. *N,N*-dimethylaniline was also irradiated with UV light to better understand the degradation pathway. During irradiation with the Hg lamp all TPs with a retention time lower than 9 min were detected (Table 3, column 13). This means that these TPs were formed from TP 122 and they were more polar than this. TP 138 was also detected in non-irradiated samples of TP 122, which could refer to aging and hydrolysis. Expectedly, no silicon containing TPs were found in these samples.

The formation of TPs of substance **5** during different irradiation experiments is demonstrated in Fig. 6. The diagrams (1–6) show the process of TP formation and elimination in dependence of the source of irradiation (Xe and Hg lamp), the solvent (1% and 100% acetonitrile), and time. Diagrams 1 (irradiated with Xe lamp) and 2 (non-irradiated) show the behaviour of substance **5** and its TPs in 1% acetonitrile within 8 h. TP 122 was detected in all samples at the beginning of the tests in amounts between 30% and 80% ($A/A_0$). With irradiation some TPs were formed (TP 124, TP 138, TP 122, TP 208a, and TP 180) and then decreased over time, but in the end of this experiment some TPs were

**Table 3**

Occurrence (X) and absence (O) of substance **5** and its transformation products in chronologic order according to retention time $t_R$ during LC analysis in dependence of the used test and the amount of the co-solvent (ACN – acetonitrile, DMSO – dimethyl sulfoxide), detected accurate mass and the highest observed value for $A/A_0$ with A being equal to the peak area of the transformation product and $A_0$ is the peak area of substance **5** at 0 min. Transformation products were named with their *m/z* value. Letters a and b are assigned for multiple occurrences of one mass (isomers). The irradiation tests were started with 10 mg $L^{-1}$. CBT was started with an initial mass concentration of 1.9 mg $L^{-1}$. (For interpretation of the reference to colour in the Table 3, the reader is referred to the web version of this article).

| Name | $t_R$ [min] | Detected mass [m/z] | Occurrence of transformation products | | | | | | | Highest observed $A/A_0$ [%] | Test with highest observed $A/A_0$ | TP 122 | TP 122 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Hg 1% ACN | dark 1% ACN | Xe 1% ACN | dark 1% ACN | Xe 100% ACN | dark 100% ACN | CBT 1% DMSO | | | Hg 1% ACN | dark 1% ACN |
| TP 124 | 4.70 | 124.0757 | X | O | X | O | O | O | O | 5.00 | Hg 1% ACN | X | O |
| TP 154a | 5.05 | 154.0863 | X | O | X | O | O | O | O | 0.02 | Hg 1% ACN | X | O |
| TP 152 | 6.55 | 152.0706 | X | O | X | O | O | O | O | 0.54 | Hg 1% ACN | X | O |
| TP 154b | 6.61 | 154.0863 | X | O | X | O | O | O | O | 0.02 | Hg 1% ACN | X | O |
| TP 138 | 8.81 | 138.0913 | X | O | X | O | O | O | O | 3.54 | Hg 1% ACN | X | X |
| TP 122 | 9.19 | 122.0964 | X | X | X | X | X | X | X | 93.63 | Hg 1% ACN | X | X |
| TP 208a | 13.08 | 208.1152 | X | X | X | X | X | X | O | 1.34 | Xe 100% ACN | O | O |
| TP 210a | 13.33 | 210.1309 | X | X | X | X | X | X | O | 0.95 | dark 1%ACN | O | O |
| TP 210b | 14.95 | 210.1309 | X | X | X | X | X | X | O | 3.86 | dark 1%ACN | O | O |
| TP 180 | 15.31 | 180.1203 | X | X | X | X | X | X | X | 12.22 | Xe 100% ACN | O | O |
| TP 208b | 16.12 | 208.1152 | X | X | X | X | X | X | O | 0.31 | Xe 1% ACN | O | O |
| Substance 5 | 16.23 | 194.1359 | X | X | X | X | X | X | X | 100 | | O | O |

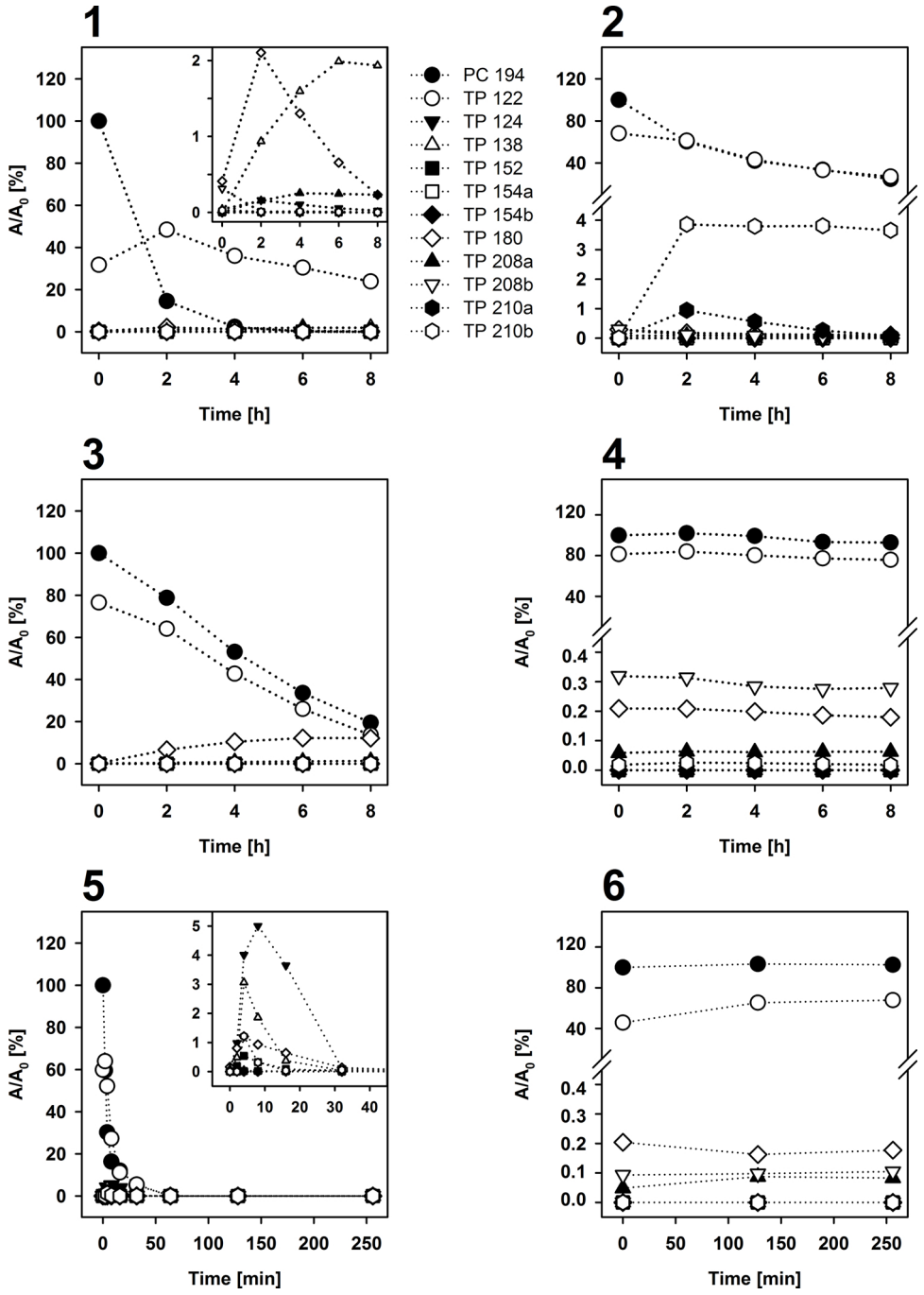



**Fig. 6.** Generation of transformation products of substance **5** (PC 194) during irradiation with the Xe lamp in 1% acetonitrile (1 – irradiated, 2 – non-irradiated), 100% acetonitrile (3 – irradiated, 4 – non-irradiated), and with the Hg lamp in 1% acetonitrile (5 – irradiated, 6 – non-irradiated). A is the peak area of the transformation product at a specific time and $A_0$ is the peak area of substance **5** at 0 h.

still detectable. Without irradiation TP 210b was formed and the amount stay nearly constantly. TP 210a was formed until 2 h and then it diminished. Diagrams 3 (irradiated with Xe lamp) and 4 (non-irradiated) show the experiments in pure acetonitrile in a time period of 8 h. The amount of TP 180 increased steadily while substance **5** and TP 122 decreasing. In 100% acetonitrile and without irradiation concentrations of all substances stayed constantly at the same level. Diagrams 5 and 6 show experiments in 1% acetonitrile with and without irradiation (Hg lamp). TP 124 was preferably formed by Hg lamp irradiation besides the generation of TP 138 and TP 180. After 64 min, none of the substances were detected anymore. In the dark, the concentration of TP 122 and TP 208a rose while the concentrations of the other substances stayed nearly constantly. The kinetic investigations during irradiation of TP 122 can be found in the supplementary material (Figure S11). TP 124 and TP 138 were mainly formed during irradiation.

In general, we demonstrated that the use of different lamps does not influence the formation of TPs itself. Only the concentration and the rate of formation was affected by differences in the source of irradiation. Some TPs were preferably formed by using the Xe lamp and others by using the Hg lamp. However, in the end TPs could still be detected in the experiment with the Xe lamp, but not in the experiment with the Hg lamp. This means that irradiation with UV light eliminated all detected TPs.

*3.4.2. Structural elucidation of transformation products*

The degradation pathway of substance **5** can be derived from the experiments described above. TPs containing silicon (TP 208a, TP 210a, TP 210b, TP 180, and TP 208b), were more or less directly formed from the parent compound via different processes (hydrolysis, direct and indirect photolysis). The irradiation of the major degradation product (TP 122) showed the derived TPs (TP 124, TP 154a, TP 152, TP 154b, and TP 138). Hydrolysis products were identified via tests with and without water. With all these information, a scheme of transformation can be proposed (Fig. 7). Molecular formulas of the generated TPs can be calculated from the accurate mass. Structural formulas can be developed based on these and the according $MS^n$ spectra. Fragments analysed with high resolution mass spectrometry (LTQ Orbitrap-XL) were measured in positive mode and therefore positively charged. Furthermore, chemical knowledge on reactivity and reaction pathways starting with the parent compound was taken into consideration.

Structural elucidation was performed for all generated TPs. TP 122 ($C_8H_{12}N^+$) was identified as *N,N*-dimethylaniline through the exact mass, the retention time based on a standard compound, and the MS spectrum. This substance was probably formed by hydrolysis of substance **5**, i.e. the bond between $C_{benzyl}$ and Si was cleaved. This cleavage was also observed for a photolytic cleavage by Kira et al. (1985). The first appearing TP according to the retention time was TP 124. It was probably formed via photolysis in water by irradiating with a Hg lamp and during the irradiation of TP 122. The accurate mass of 124.0757 resulted in the chemical formula $C_7H_{10}NO^+$. This leads to the assumption that one methyl group has been cleaved from the amino group and that the aromatic ring was hydroxylated. Therefore, 2-(methylamino)phenol and 4-(methylamino)phenol sulphate were analysed using the same analytical method. The retention time of TP 124 from the photolytic mixture and 4-(methylamino)phenol differed by 35 s. In a measurement combining both samples (photolytic mixture and 4-(methylamino)phenol), two narrow signals could be observed, but the fragment patterns of both substances were almost identical. TP 154a and b were formed in water-containing irradiated surroundings and also from TP 122. The chemical formula $C_8H_{12}NO_2^+$ can be derived from the *m/z* ratio 154.0863. The difference to TP 122 are two oxygen atoms. Thus, it is assumed that the aromatic ring was twofold hydroxylated. The isomers a and b could be formed by hydroxylating different positions at the ring. TP 152 was generated during all irradiation experiments in water. The accurate mass of 152.0706 led to the formula $C_8H_{10}NO_2^+$. This substance could be an oxidation product of TP 154 because only two hydrogen atoms were abstracted. TP 138 was formed via photolysis in water. The chemical formula is $C_8H_{12}NO^+$, which possibly leads to a hydroxylated TP 122. The possible TPs 2-(dimethylamino)phenol, 3-(dimethylamino)phenol, and 4-(dimethylamino)phenol were analysed with the same analytical method. 2-(Dimethylamino)phenol had a retention time of 8.22 min, differing by 41 s from the TP formed in the photolytic mixture. Hydroxylation through ROS was the major degradation pathway during irradiation in water because oxygen was often added to the molecular formula. This is confirmed by photolysis studies of Rastogi et al. (2015). They found out that hydroxyl groups were often attached to the aromatic ring, which often results in ring-opening, too. TP 210a and b were mainly formed in non-irradiated aqueous samples. Their chemical formula is $C_{11}H_{20}NOSi^+$. It is assumed that these TPs were generated via hydroxylation of substance **5** at different positions. This group could have been added to the aromatic ring or a methyl group, which results in a hemi aminal, likely to be unstable. Another possible structure is that of an *N*-oxide. TP 208a and b were mostly detected in the irradiation experiment in 1% and 100% acetonitrile (Xe lamp). The chemical formula is $C_{11}H_{18}NOSi^+$. TP 208a and b could be oxidation products of TP 210a and b because their mass differed by only two hydrogen atoms. TP 180 is predominantly formed during irradiation in 100% acetonitrile. This means that this product is directly formed by photolysis from substance **5** without the involvement of ROS. The chemical formula of $C_{10}H_{18}NSi^+$ shows that only one methyl group was abstracted. The used methods have shown that different processes were involved while substance **5** was degraded. Mostly hydroxylation causes modifications in the molecule.

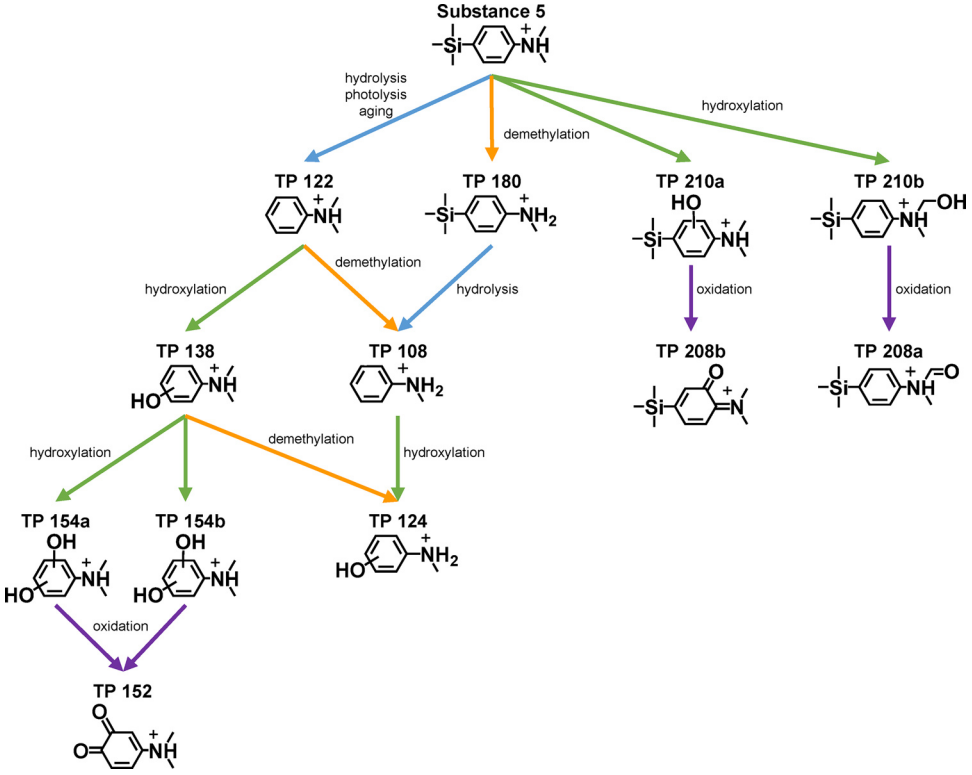



**Fig. 7.** Proposed degradation pathway of substance **5** with all detected TPs during irradiation with a Hg and a Xe lamp and hydrolysis in different solvents (1% and 100% acetonitrile). Different colours symbolise different degradation pathways. Blue arrows show hydrolysis, photolysis, and aging processes. The yellow arrows symbolise demethylation and the green arrows show hydroxylation (indirect photolysis). Oxidised TPs are symbolised by violet arrows. Presented structural formulas were only proposed structures. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

## 4. Conclusion

In this study, first insights on the degradation behaviour of five newly synthesised organosilicon compounds were achieved. It extends the knowledge on biotic degradation, hydrolysis and photolysis and provides an integrative method to analyse generated TPs of *p*-$Me_2NC_6H_4SiMe_3$ (substance **5**). The obtained results showed that none of the five tested substances was readily biodegradable. Moreover, it was shown that the use of a better biodegradable basic structure did not result in a better biodegradability of the corresponding organosilicon compound. The trimethylsilyl group has a pronounced negative influence on biodegradability as demonstrated by comparison with the related anisole. Hydrolysis is one of the major pathways of primary elimination for all tested organosilicon compounds. Hydrolysis and photolysis with the Xe lamp resulted in an incomplete elimination. The elimination rate using the Hg lamp irradiation was for all tested substances higher than with the Xe lamp irradiation. In general, photolysis was most successful for *p*-$Me_2NC_6H_4SiMe_3$. The substance was photodegradable within 6 h by irradiation with a Xe lamp and within 64 min by irradiation with a Hg lamp in 1% acetonitrile. During these experiments, eleven more polar TPs compared to their respective parent compound were detected. They were formed via different processes like hydrolysis, direct and indirect photolysis and were also eliminated within 64 min of irradiation with the Hg lamp. The main degradation pathway of *p*-$Me_2NC_6H_4SiMe_3$ is hydroxylation via photolysis. Therefore, it can be assumed that the tested compounds were not completely mineralisable in the environment. High intensities of irradiation were necessary to eliminate these substances and their TPs.

Since waste water treatment cannot eliminate all micropollutants, complete mineralisable substances are required. This study demonstrates that changes in the structure of organosilicon substances are a possible way to address the problem of persistent silicones. It also shows in particular that many more reliable data on the degradation of organosilicon compounds are needed for an improved assessment of the influence of different substituents on the degradation behaviour of their organosilicon derivatives. Overall, this is a promising start into the direction of a development of better degradable silicones.

## Declaration of Competing Interest

There is no conflict of interests.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2020.122429.

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# Supplementary material

## Abiotic and biotic degradation of organosilicon compounds in aqueous media – structure degradability relationships

**Keywords**: Closed bottle test (OECD 301D), Manometric respirometry test (OECD 301F), Hydrolysis (OECD 111), Photolysis, Transformation product

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## S.1 Synthesis procedures of model compounds

**_o_-$MeOC_6H_4SiMe_3$ (1)**

7.5 g (40 mmol) of 2-bromoanisole were dissolved in 120 mL of tetrahydrofurane (THF). The mixture was cooled to 0 °C. 8.8 g of trimethylchlorosilane (81 mmol) and 50 mL (81 mmol) of a 1.6 M n-butyllithium solution in hexane were added. The reaction mixture was stirred for 1 h at room temperature. 150 mL of water were added. The phases were separated and the aqueous phase was extracted 3 times with 150 mL of diethyl ether each. The combined organic phases were dried with sodium sulphate, filtered and the filtrate concentrated under reduced pressure at 100 Torr. The raw product was distilled at 10 Torr and 85 °C. Spectroscopic data were consistent to those reported (Freeburger and Spialter, 1971), (Effenberger and Haebich, 1979).

**_p_-$MeOC_6H_4SiMe_3$ (2)**

9.4 g (50 mmol) 4-bromoanisole was dissolved in 200 mL of THF and cooled to 0 °C. 11.1 g trimethylchlorosilane (102 mmol) were added and then 63 mL (101 mmol) of a 1.6 M *n*-butyllithium solution in hexane were added dropwise. The reaction mixture was stirred for 1 h at room temperature. Then 150 mL of water were added. The phases were separated and the aqueous phase extracted 3 times with 150 mL diethyl ether each. The combined organic phases were dried with sodium sulphate, filtered and the filtrate concentrated under reduced pressure at 100 Torr. The raw product was distilled at 20 Torr and 109 °C. Spectroscopic data were consistent to those reported (Angelelli et al., 1970).

**($p$-$MeOC_6H_4)_2SiMe_2$ (3)**

7.6 g (39 mmol) 4-bromoanisole were dissolved in 120 mL of THF and cooled to −78 °C. At this temperature 25 mL (39 mmol) of a 1.6 M n-butyl lithium solution in hexane was added. The mixture was stirred for 1 h. 2.5 g (19 mmol) of dimethyldichlorosilane were added. The reaction mixture is stirred overnight at room temperature. The solvent was removed under vacuum and the residue was dissolved in 50 mL of dichloromethane. 50 mL distilled water was added and the mixture was stirred. The phases were separated and the turbid organic phase was collected. The aqueous phase was extracted again with 20 mL of dichloromethane. The combined dichloromethane phases were concentrated under vacuum. After addition of 25 mL of hexane, the slightly brownish sediment was separated as product. Spectroscopic data were consistent to those reported (van der Vlugt et al., 2003, Hengge and Eberhardt, 1979).

**_o_-$Me_2NC_6H_4SiMe_3$ (4)**

5.0 g (25 mmol) 2-bromo-*N,N*-dimethylaniline were dissolved in 120 mL of THF. The mixture was cooled to 0 °C. Then 5.4 g trimethylchlorosilane (50 mmol) and 32 mL (50.1 mmol) of a 1.6 M n-butyllithium solution in hexane were added. The reaction mixture was stirred for 1 h at room temperature. 120 mL of water were added. The phases were separated and the aqueous phase was extracted 3 times with 120 mL of diethyl ether. The combined organic phases were

dried over sodium sulphate, filtered and the filtrate was concentrated under reduced pressure at 100 Torr. The raw product was distilled at 8 Torr and 96 °C. Spectroscopic data were consistent to those reported (Jung and Jones, 1975).

***p*-$Me_2NC_6H_4SiMe_3$ (5)**

8.0 g (40 mmol) of 4-bromo-*N,N*-dimethylaniline were dissolved in 120 mL of THF and cooled to 0 °C. 8.7 g of trimethylchlorosilane (80 mmol) and 50 mL (80 mmol) of a 1.6 M n-butyllithium solution in hexane were added. The reaction mixture was stirred overnight at room temperature. 150 mL of water were added. The phases were separated and the aqueous phase was extracted 3 times with 150 mL of diethyl ether each. The combined organic phases were dried with sodium sulphate, filtered and the filtrate concentrated under reduced pressure at 100 Torr. The raw product was distilled at 10 Torr and 127 °C. Spectroscopic data were consistent to those reported (Benkeser and Krysiak, 1953).

## S.2 Absorption spectra of tested compounds and emission spectra of employed irradiation sources

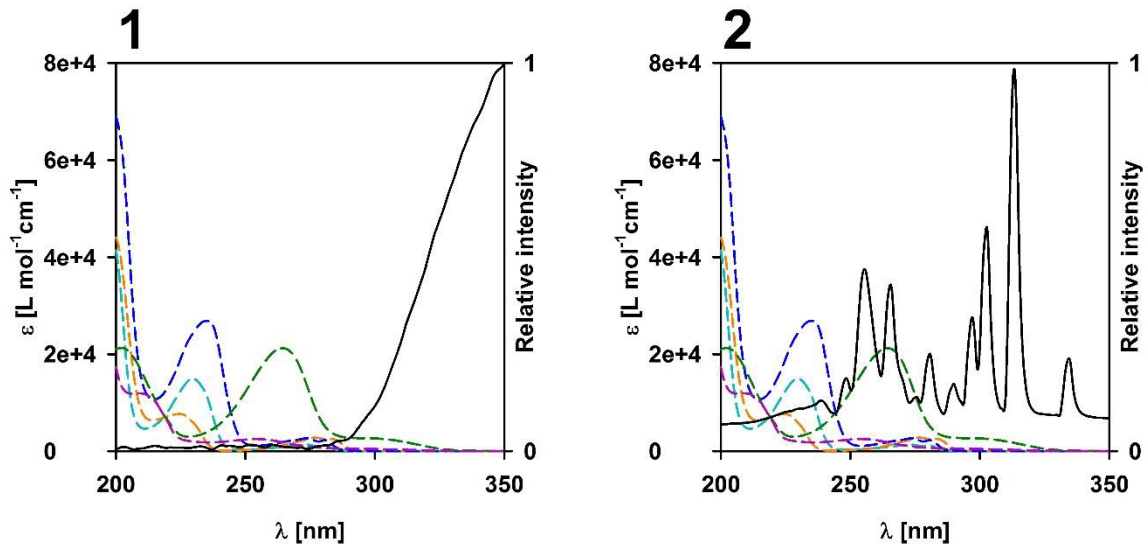


**Figure S1: Absorption spectra of the five tested compounds (1 – orange, 2 – turquoise, 3 – blue, 4 – magenta, 5 – green) in 1% acetonitrile (substance 3 in 5% acetonitrile) compared to the emission spectrum of the Xe lamp (diagram 1, black line) and to the emission spectrum of the Hg lamp (diagram 2, black line).**

## S.3 Additional information

In nearly all samples in 100% acetonitrile, a small increase of the substance concentration could be observed. The increase (max. 10%) is due to evaporation of acetonitrile during the treatment. Parts of the solvent evaporated during time and while taking the samples. The covered test vessels had to be opened for this process.

## S.4 $^1$H NMR-spectra of tested substances

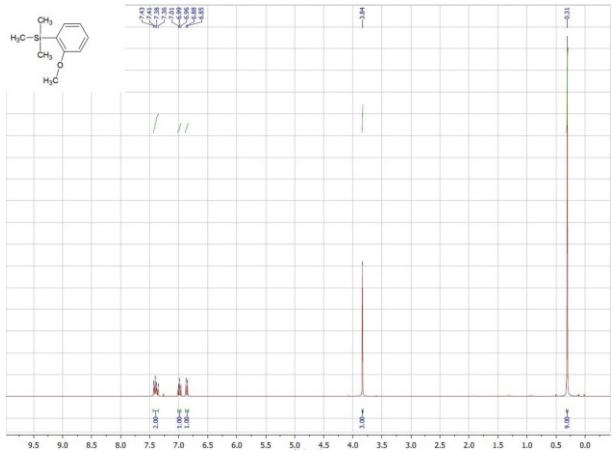

Figure S2: $^1$H NMR-spectrum of *o*-$MeOC_6H_4SiMe_3$ (1)

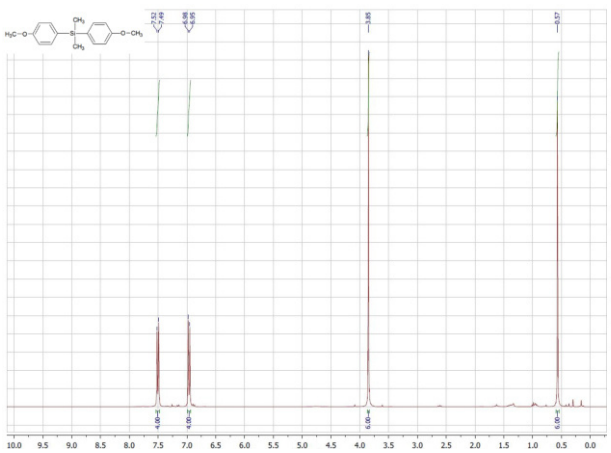

Figure S3: $^1$H NMR-spectrum of *p*-$MeOC_6H_4SiMe_3$ (2)

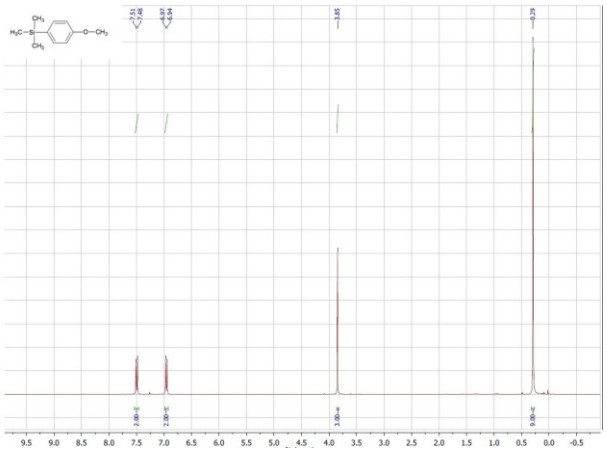

Figure S4: $^1$H NMR-spectrum of $(p\text{-}MeOC_6H_4)_2SiMe_2$ (3)

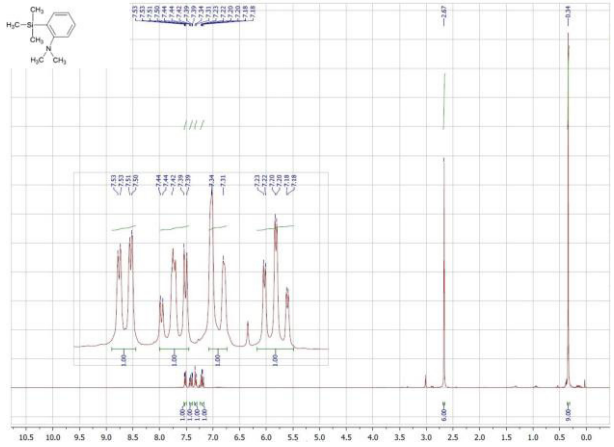

Figure S5: $^1$H NMR spectrum of *o*-$Me_2NC_6H_4SiMe_3$ (4)

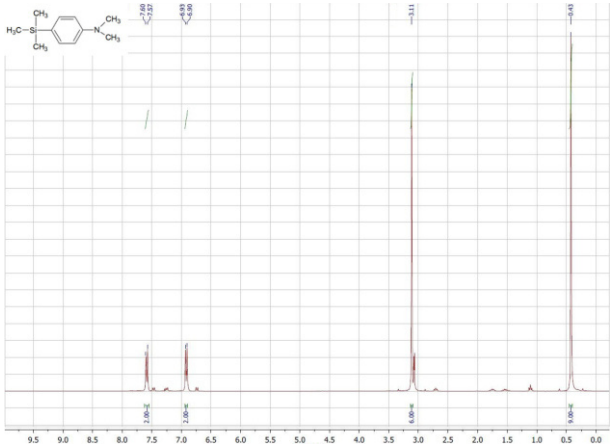

Figure S6: $^1$H NMR spectrum of *p*-$Me_2NC_6H_4SiMe_3$ (5)

## S.5 Tuning parameters of high resolution mass spectrometry

**Table S1: Tuning parameters of the LTQ Orbitrap-XL high resolution mass spectrometer**

| | | | | | |
|---|---|---|---|---|---|
| Source Type: | HESI | | | | |
| Capillary Temp (C): | 275.00 | | | | |
| APCI Vaporizer Temp (C): | | 50.00 | | | |
| Sheath Gas Flow (): | 20.00 | | | | |
| Aux Gas Flow (): | 5.00 | | | | |
| Sweep Gas Flow (): | 0.00 | | | | |
| Injection Waveforms: | Off | | | | |
| Ion Trap Zoom AGC Target: | | 3000.00 | | | |
| Ion Trap Full AGC Target: | | 30000.00 | | | |
| Ion Trap SIM AGC Target: | | 10000.00 | | | |
| Ion Trap MSn AGC Target: | | 10000.00 | | | |
| FTMS Injection Waveforms: | | Off | | | |
| FTMS Full AGC Target: | | 200000.00 | | | |
| FTMS SIM AGC Target: | | 100000.00 | | | |
| FTMS MSn AGC Target: | | 100000.00 | | | |
| POSITIVE POLARITY | | | | NEGATIVE POLARITY | |
| Source Voltage (kV): | 3.80 | | | Source Voltage (kV): | 4.00 |
| Source Current (uA): | 100.00 | | | Source Current (uA): | 100.00 |
| Capillary Voltage (V): | 10.00 | | | Capillary Voltage (V): | 10.00 |
| Tube Lens (V): | 69.00 | | | Tube Lens (V): | -100.00 |
| Skimmer Offset (V): | 0.00 | | | Skimmer Offset (V): | 0.00 |
| Multipole RF Amplifier (Vp-p): | | 660.00 | | Multipole RF Amplifier (Vp-p): | 400.00 |
| Multipole 00 Offset (V): | | -5.00 | | Multipole 00 Offset (V): | 4.00 |
| Lens 0 Voltage (V): | -5.40 | | | Lens 0 Voltage (V): | 4.20 |
| Multipole 0 Offset (V): | -6.90 | | | Multipole 0 Offset (V): | 4.50 |
| Lens 1 Voltage (V): | -9.00 | | | Lens 1 Voltage (V): | 15.00 |
| Gate Lens Offset (V): | -46.00 | | | Gate Lens Offset (V): | 35.00 |
| Multipole 1 Offset (V): | -9.00 | | | Multipole 1 Offset (V): | 8.00 |
| Front Lens (V): | -8.00 | | | Front Lens (V): | 5.25 |
| Ion Trap Zoom Micro Scans: | | 1 | | Ion Trap Zoom Micro Scans: | 1 |
| Ion Trap Zoom Max Ion Time (ms): | | | 50.00 | Ion Trap Zoom Max Ion Time (ms): | 50.00 |
| Ion Trap Full Micro Scans: | | 1 | | Ion Trap Full Micro Scans: | 1 |
| Ion Trap Full Max Ion Time (ms): | | 10.00 | | Ion Trap Full Max Ion Time (ms): | 10.00 |
| Ion Trap SIM Micro Scans: | | 1 | | Ion Trap SIM Micro Scans: | 1 |
| Ion Trap SIM Max Ion Time (ms): | | 50.00 | | Ion Trap SIM Max Ion Time (ms): | 50.00 |
| Ion Trap MSn Micro Scans: | | 3 | | Ion Trap MSn Micro Scans: | 1 |
| Ion Trap MSn Max Ion Time (ms): | | 100.00 | | Ion Trap MSn Max Ion Time (ms): | 100.00 |
| FTMS Full Micro Scans: | | 1 | | FTMS Full Micro Scans: | 1 |
| FTMS Full Max Ion Time (ms): | | 500.00 | | FTMS Full Max Ion Time (ms): | 10.00 |
| FTMS SIM Micro Scans: | | 1 | | FTMS SIM Micro Scans: | 1 |
| FTMS SIM Max Ion Time (ms): | | 50.00 | | FTMS SIM Max Ion Time (ms): | 50.00 |
| FTMS MSn Micro Scans: | | 1 | | FTMS MSn Micro Scans: | 1 |
| FTMS MSn Max Ion Time (ms): | | 100.00 | | FTMS MSn Max Ion Time (ms): | 100.00 |

## S.6 Determination of transformation products during biodegradation of substance 5

Figure S7 shows the elimination of substance 5 (PC 194) and the generation of some transformation products (TPs) during the CBT. TP 122 and TP 180 were detected during the CBT. TP 122 decreased from 37% to 32% within 28 d. TP 180 was formed in this time (ca. 2%) from PC 194. Other TPs could not be detected.

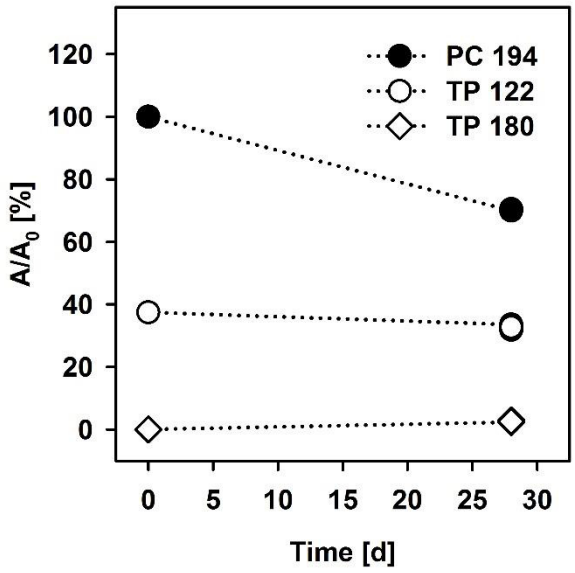


**Figure S7: Generation of transformation products of substance 5 during 28 d of Closed Bottle test (CBT). 1% DMSO was used as a co-solvent. A is the peak area of the transformation product at a specific time and $A_0$ is the peak area of substance 5 at day 0. The initial concentration of substance 5 was 1.9 mg $L^{-1}$ and is equal to 5 mg $L^{-1}$ of theoretical oxygen demand (ThOD).**

**Table S2: Name and molecular formula of the detected transformation products of substance 5.**

| Name | Molecular formula | Difference to PC 194 [u] |
|---|---|---|
| TP 124 | $C_7H_{10}NO^+$ | −70 |
| TP 154a/b | $C_8H_{12}NO_2^+$ | −40 |
| TP 152 | $C_8H_{10}NO_2^+$ | −42 |
| TP 138 | $C_8H_{12}NO^+$ | −56 |
| TP 122 | $C_8H_{12}N^+$ | −72 |
| TP 208a/b | $C_{11}H_{18}NOSi^+$ | +14 |
| TP 210a/b | $C_{11}H_{20}NOSi^+$ | +16 |
| TP 180 | $C_{10}H_{18}NSi^+$ | −14 |
| PC 194 | $C_{11}H_{20}NSi^+$ | ±0 |

## S.7 Chromatograms of potential TPs of substance 5

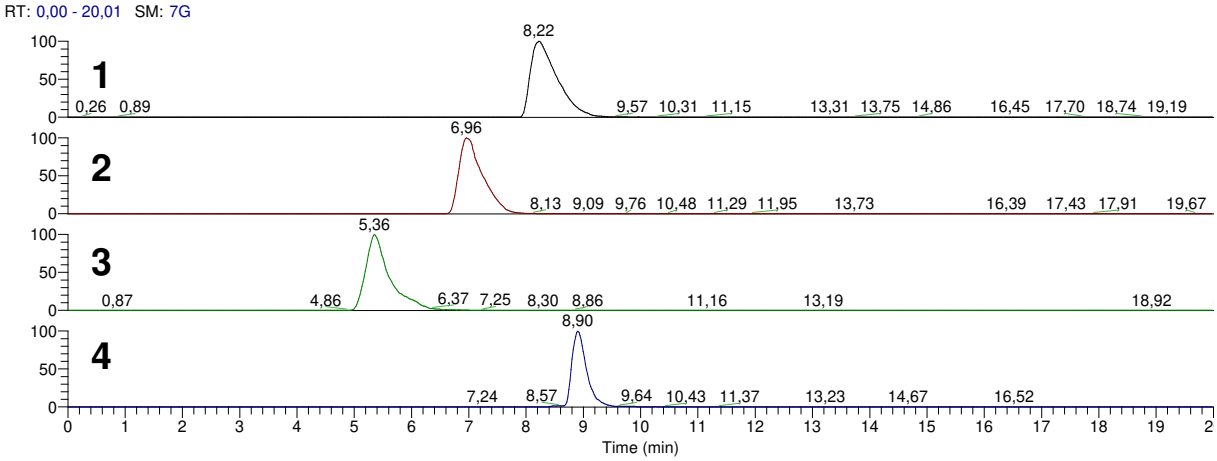


**Figure S8: Chromatograms of potential TPs with the accurate mass of 138.0913, 2-(dimethylamino)phenol (1), 3-(dimethylamino)phenol (2), and 4-(dimethylamino)phenol (3) compared to the photolytic mixture of substance 5 at 4 min (4).**

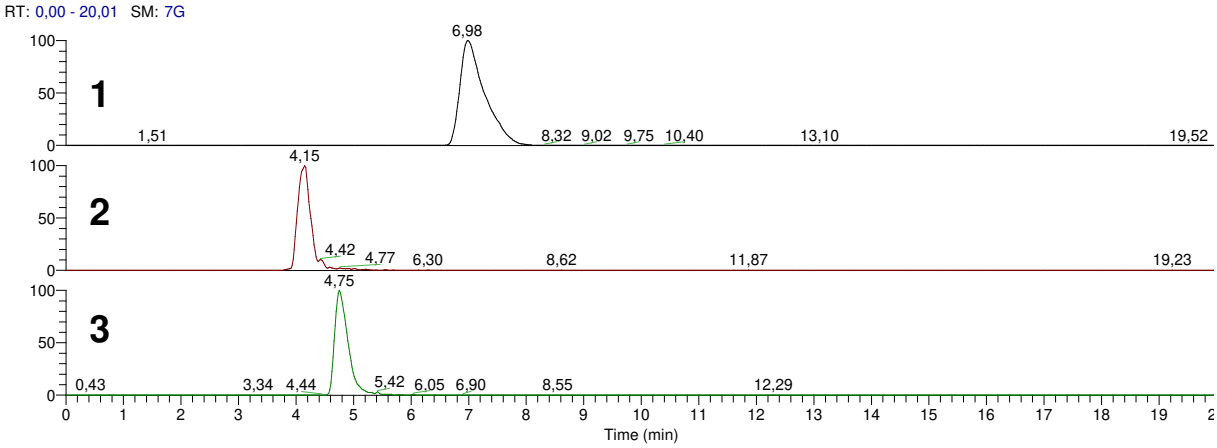


**Figure S9: Chromatograms of potential TPs with the accurate mass of 124.0757, 2-(methylamino)phenol (1) and 4-(methylamino)phenol (2) compared to the photolytic mixture of substance 5 at 4 min (3).**

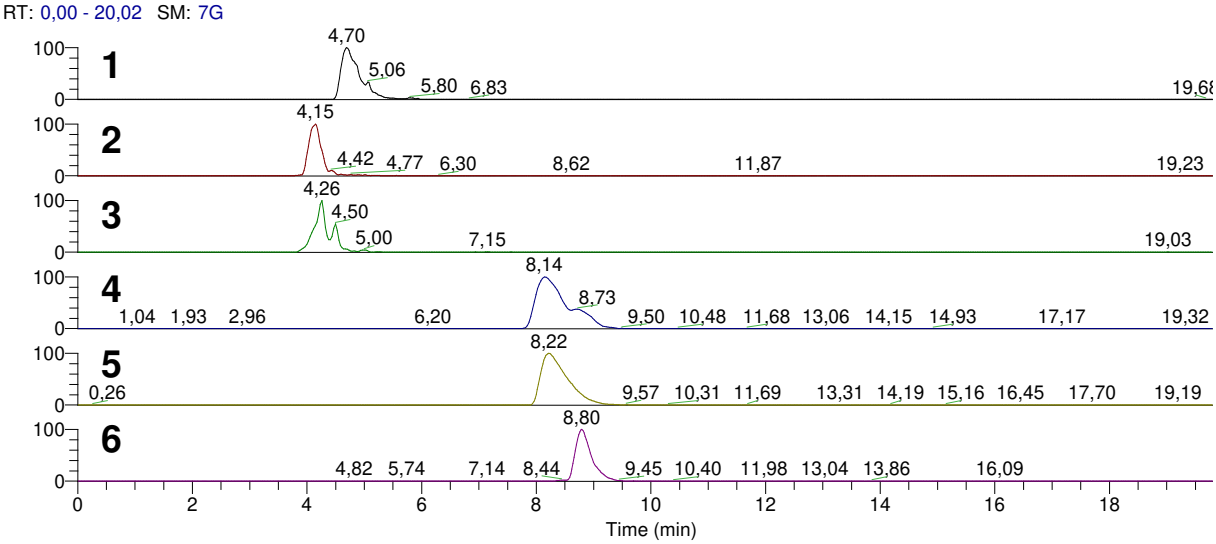


**Figure S10: Chromatograms of potential TPs 4-(methylamino)phenol (*m/z* 124.0757) and 2-(dimethylamino)phenol (*m/z* 138.0913) compared to the photolytic mixture of substance 5 at 4 min and a mixture of all three samples together. 1 – photolytic mixture at 4 min (*m/z* 124.0757), 2 – 4-(methylamino)phenol (*m/z* 124.0757), 3 – mixture of potential TPs and the photolytic mixture (*m/z* 124.0757), 4 – mixture of potential TPs and the photolytic mixture (*m/z* 138.0913), 5 – 2-(dimethylamino)phenol (*m/z* 138.0913), 6 – photolytic mixture at 4 min (*m/z* 138.0913).**

## S.8 Irradiation of TP 122 (*N,N*-dimethylaniline) with a Hg lamp

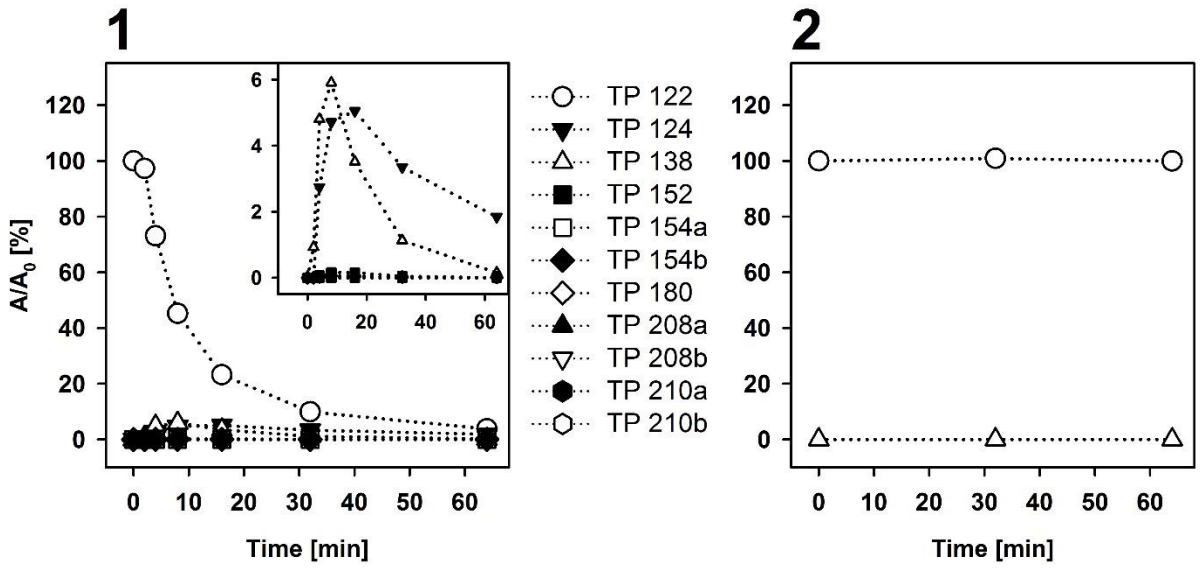


**Figure S11: Generation of transformation products of *N,N*-dimethylaniline (TP 122) during irradiation with a Hg lamp in 1% acetonitrile (1 - irradiated, 2 - non-irradiated). A is the peak area of the transformation product at a specific time and $A_0$ is the peak area of *N,N*-dimethylaniline at 0 min.**

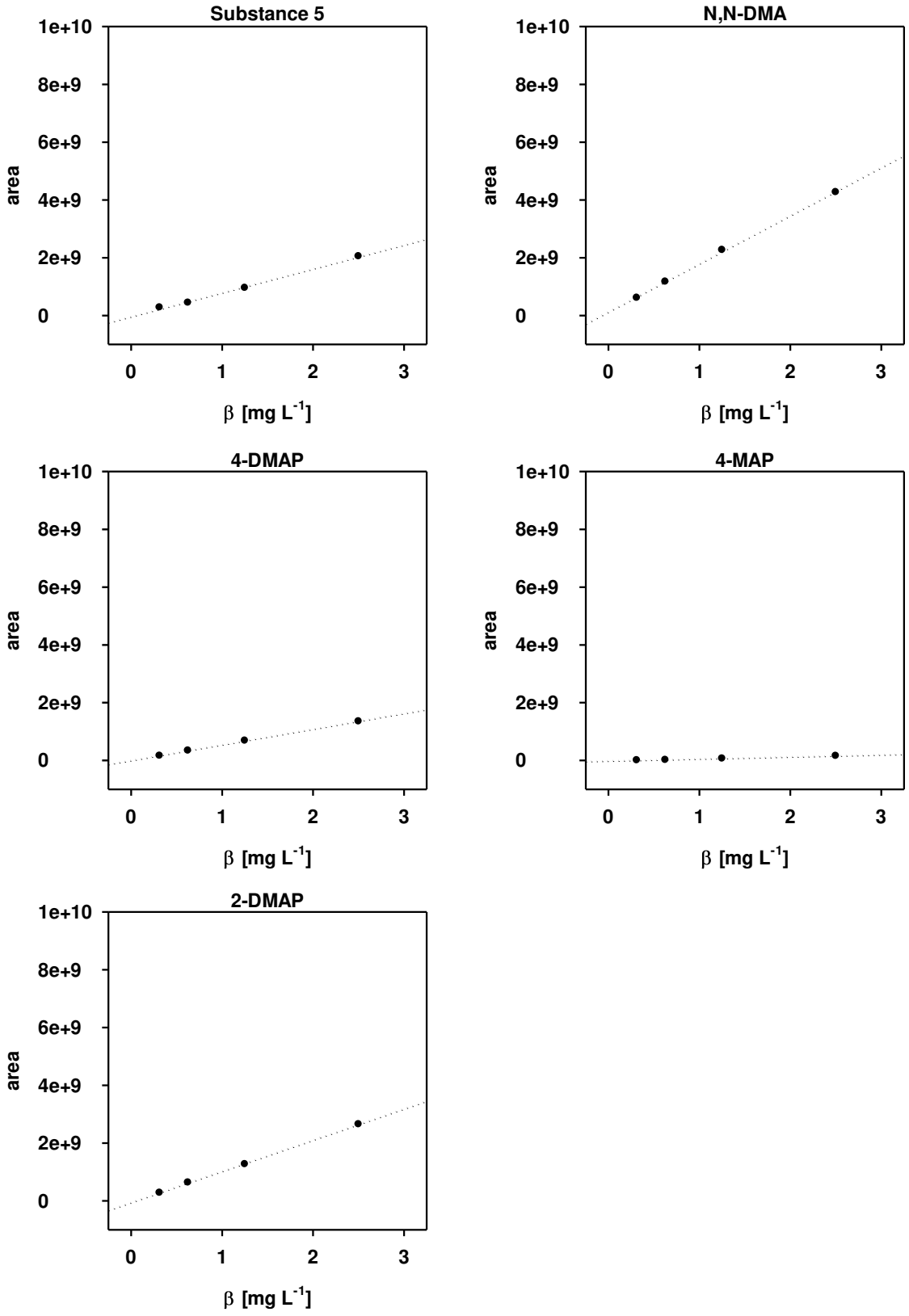


**Figure S12: Calibration curves of substance 5, TP 122 (*N,N*-dimethylaniline (*N,N*-DMA), and possible TPs for masses 124 (4-(methylamino)phenol (4-MAP)) and 138 (4-(dimethylamino)phenol (4-DMAP) and 2-(dimethylamino)phenol (2-DMAP))**

# Publikation 2

Using structure biodegradability relationships for environmentally benign design of organosilicons – An experimental comparison of organosilicons and their carbon analogues

Elisa Grabitz; Marco Reich; Oliver Olsson; Klaus Kümmerer

2020

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# Using structure biodegradability relationships for environmentally benign design of organosilicons – An experimental comparison of organosilicons and their carbon analogues

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Extraction
Gas chromatography
Heteroatom
Hydrolysis

ABSTRACT

Organosilicon substances are ubiquitous in the environment due to their stability and numerous applications in consumer products. Therefore, it is desirable to reduce their environmental persistency. Our study aimed to better understand the impact of silicon atoms in organic compounds on their environmental biodegradability as a contribution to sustainable chemistry. Accordingly, we investigated the biodegradability of organosilicon compounds and their carbon analogues. OECD 301D test was used to assess ready biodegradability. In addition, GC-MS analyses were performed to study the fate of the compounds in the test. Three out of five carbon compounds and no organosilicon compound were found readily biodegradable. In all but one case, higher biodegradation degrees could be observed for the carbon compounds. Hydrolysis was identified as a mandatory step prior to the biodegradation of organosilicon substances. The silicon-free product of hydrolysis determined the rate of biodegradation. The silicon-containing reaction products of hydrolysis were not biodegradable. The high biodegradability of one organosilicon compound can be attributed to faster hydrolysis due to an easily hydrolysable Si–N bond and a high biodegradation rate of the resulting silicon-free hydrolysis product. Insertion of such heteroatoms or functional groups into polysiloxane chains may be a promising approach to benign organosilicon compounds.

## 1. Introduction

In 2018, 2.8 million tons of siloxanes were produced globally (imarc group, 2019). For decades, siloxanes and organosilicon compounds were increasingly used in various fields of application, e.g., industry, agriculture, and personal care products (Andriot et al., 2007; Knoche, 1994; Knoche, 1994; O'Lenick & O'Lenick, 2014; O'Lenick & O'Lenick, 2014). They are currently used in drugs, odorants or reagents, as they extend the physical properties of carbon-based compounds, e.g., by influencing the size, shape, conformational flexibility, and polarity of the molecule (Bains and Tacke, 2003). Due to their high production volume, increased use in personal care and other consumer products and their limited elimination in wastewater treatment plants, siloxanes occur ubiquitously in the environment (Rücker and Kümmerer, 2015). Even advanced effluent treatment cannot solve the issue (Kümmerer et al., 2018, 2019). Furthermore, only 20% of effluents are treated at all (UNESCO World Water Assessment Programme, 2017). Therefore, in order to reduce the environmental burden of such compounds, measures at the source are urgently needed. An essential approach in this context is the targeted design of chemicals for environmental mineralization after they enter the environment. This is also a principle of green chemistry – design for degradation.

The lowered electron density at the carbon atoms, which are bonded to silicon, can explain the persistence of siloxanes and their stability against biodegradation (Heinonen et al., 1996). In the case of polydimethylsiloxanes (PDMS) a steric shielding effect of the methyl groups is also of importance. Several studies confirmed these findings and showed that siloxanes are not readily biodegradable (Büttner et al., 2007). For example, $(CH_3)_2Si(OCH_2CH_3)_2$ (**2-Si**) and $C_6H_5Si(OCH_3)_3$ (**5-Si**) (Table 1) were listed as 0% biodegradable in the ECHA database, but these results were obtained via read-across of existing biodegradation data of the structure analogues, trimethyl silanol and

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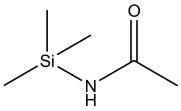
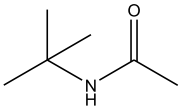
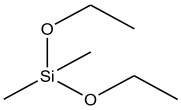
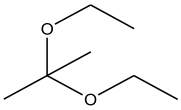
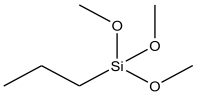
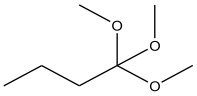
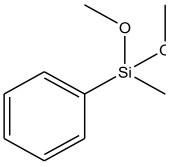
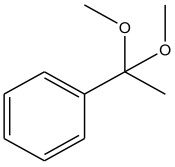
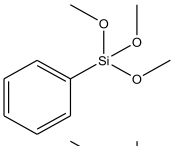
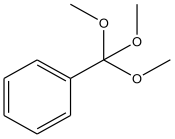
trichlorophenyl silane, respectively (Organisation for Economic Co-operation and Development guideline 310 (OECD 310), European Chemicals Agency (ECHA), 2008b). However, in contrast to that, $CH_3(CH_2)_2Si(OCH_3)_3$ (**3-Si**) was tested according to OECD 301A and was degraded by 54% after 28 d (ECHA, 1994). In these studies, different and not the most critical tests were used to determine biodegradability. By applying the read-across approach, which means that relevant information on analogues is used to predict the properties of a target substance, a tendency can be derived from how a substance behaves in the biodegradation test. However, this approach cannot replace a precise result from a laboratory experiment. Furthermore, Rücker and Kümmerer observed for these three and two additional substances ($CH_3CONHSi(CH_3)_3$ (**1-Si**) and $C_6H_5Si(OCH_3)_2CH_3$ (**4-Si**)) biodegradation from 18% to 35% in OECD 301D and for substances **1-Si**, **2-Si**, **3-Si** 19%–52% in OECD 301F (Rücker and Kümmerer, 2013). However, none of the available studies investigated the preferably biodegradable basic structure nor the influence of special functional groups regarding biodegradability.

Additionally, $CH_3CONHSi(CH_3)_3$ (**1-Si**) is known to be very unstable in water. This information is presented in the safety data sheet of this compound (Sigma-Aldrich, 2019). For siloxanes, it is also known that Si–O bonds are prone to hydrolysis (Bains and Tacke, 2003). Hence, hydrolysis and subsequent biodegradation of some hydrolysis products should also be considered because biodegradation tests are performed in an aqueous medium.

In the past, the effects of a switch between carbon and silicon atoms in organic compounds were already investigated on many substance properties for important substance classes like pharmaceuticals, odorants, and amino acids (Büttner et al., 2007; Tacke et al., 2000; Wannagat et al., 1988). For pharmaceuticals, it was found that some silicon analogues showed higher selectivity to the receptor than their related carbon compounds (Lambrecht et al., 1989). Büttner et al. measured higher $K_{OW}$ values for odorant silicon analogues compared to the carbon compounds (Büttner et al., 2007). Against the authors' expectations,

**Table 1**
Specification of the tested compounds including number, linear formula, structure and InChI.

| No | Linear formula | Structure | InChI |
|---|---|---|---|
| **1-Si** | $CH_3CONHSi(CH_3)_3$ |  | InChI = 1S/C5H13NOSi/c1-5(7)6–8(2,3)4/h1-4H3,(H,6,7) |
| **1-C** | $CH_3CONHC(CH_3)_3$ |  | InChI = 1S/C6H13NO/c1-5(8)7–6(2,3)4/h1-4H3,(H,7,8) |
| **2-Si** | $(CH_3)_2Si(OCH_2CH_3)_2$ |  | InChI = 1S/C6H16O2Si/c1-5-7-9(3,4)8-6-2/h5-6H2,1–4H3 |
| **2-C** | $(CH_3)_2C(OCH_2CH_3)_2$ |  | InChI = 1S/C7H16O2/c1-5-8-7(3,4)9-6-2/h5-6H2,1–4H3 |
| **3-Si** | $CH_3(CH_2)_2Si(OCH_3)_3$ |  | InChI = 1S/C6H16O3Si/c1-5-6-10(7–2,8-3)9–4/h5-6H2,1–4H3 |
| **3-C** | $CH_3(CH_2)_2C(OCH_3)_3$ |  | InChI = 1S/C7H16O3/c1-5-6-7(8–2,9-3)10–4/h5-6H2,1–4H3 |
| **4-Si** | $C_6H_5Si(OCH_3)_2CH_3$ |  | InChI = 1S/C9H14O2Si/c1-10-12 (3,11–2)9-7-5-4-6-8-9/h4-8H,1–3H3 |
| **4-C** | $C_6H_5C(OCH_3)_2CH_3$ |  | InChI = 1S/C10H14O2/c1-10(11–2,12-3)9-7-5-4-6-8-9/h4-8H,1–3H3 |
| **5-Si** | $C_6H_5Si(OCH_3)_3$ |  | InChI = 1S/C9H14O3Si/c1-10-13(11–2,12-3)9-7-5-4-6-8-9/h4-8H,1–3H3 |
| **5-C** | $C_6H_5C(OCH_3)_3$ |  | InChI = 1S/C10H14O3/c1-11-10(12–2,13-3)9-7-5-4-6-8-9/h4-8H,1–3H3 |

they found out that an increase of bond polarization compared to their carbon analogues resulted in increased lipophilicity and, therefore, in a worse bioavailability than the carbon analogues. However, in these studies, environmental degradation was mostly not considered. If it was investigated, both the carbon and the silicon compound were not readily biodegradable (OECD 301F, Büttner et al., 2007).

The carbon analogues to the above-introduced siloxanes (**1-Si**, **2-Si**, **3-Si**, **4-Si**, and **5-Si**) were not investigated in biodegradation tests, so far. $(CH_3)_2C(OCH_2CH_3)_2$ (**2-C**), as carbon analogue to substance **2-Si**, was predicted as not readily biodegradable (Danish QSAR database, ECHA, 2018).

The studies described above demonstrate that there is a lack of environmental biodegradation data of siloxanes, especially on their ready biodegradability in water. The comparison of biodegradation behavior of siloxanes and their carbon analogues seem to be promising to gain more insights on structural effects. In this case, it could also allow to utilize the knowledge about organic compounds to understand environmental biodegradation of silicon analogues and their targeted design to improve environmental biodegradation of organosilicon compounds, including siloxanes. Therefore, the main objective of this study is to assess when carbon compounds are better biodegradable than their structural analogue organosilicon compounds. The influence of functional groups regarding stability in water and resistance to biodegradability was studied in a test for ready biodegradability (closed bottle test, CBT, OECD 301D). This test uses the sum parameter oxygen consumption (measured as dissolved oxygen) for the monitoring of biodegradation. Biodegradation test samples were analyzed using gas chromatography coupled with mass spectrometry (GC-MS) to get additional insights into the fate of the test compounds in the biodegradation test. The selected compounds (**1-Si**, **1-C**, **2-Si**, **2-C**, **3-Si**, **3-C**, **4-Si**, **4-C**, **5-Si**, **5-C** (Table 1)) were investigated.

## 2. Materials and methods

### 2.1. Chemicals

The ten tested substances (**1-Si**, **1-C**, **2-Si**, **2-C**, **3-Si**, **3-C**, **4-Si**, **4-C**, **5-Si**, **5-C** (Table 1)) were purchased from ABCR GmbH (Karlsruhe, Germany) with the highest available purity (≥95%). Dimethyl sulfoxide (DMSO, ≥ 99%) was obtained from Alfa Aesar (Karlsruhe, Germany). All compounds used for mineral medium in the biodegradation test had a purity of at least 98.5%. Aqueous solutions were prepared with ultrapure water (18.2 MΩ cm). Solvents used for extraction and GC analyses (hexane, ≥ 98.0%, chloroform, 99.8%, methanol, 99.9%) had MS grade and were obtained from Merck (Darmstadt, Germany), VWR (Darmstadt, Germany), and Acros Organics (Darmstadt, Germany), respectively.

### 2.2. Aerobic biodegradation testing

The CBT was based on the OECD 301D guideline with slight modifications (Friedrich et al., 2013). The pass levels of ready biodegradability were 60% removal of theoretical oxygen demand (ThOD) within a 10-d window within the 28-d period after 10% of ThOD has been reached (OECD, 1992). Other validation criteria were defined in these guidelines. A blind control without any substance, a positive control with sodium acetate, a toxicity control with both sodium acetate and the test compound, and the test compound itself were included. The test lasted 28 d and was performed in the dark at a temperature of 20 ± 1 °C. As a source of bacteria, two drops of the effluent of a municipal wastewater treatment plant (AGL Lüneburg, Germany) were used per liter of test solution. The test was performed with a low content of mineral medium and a ThOD of 5 mg $L^{-1}$ for each test substance (OECD, 1992). In modification of the standard OECD 301D, DMSO was added as a co-solvent (1% v/v) to increase water solubility of the organosilicon compounds. DMSO was proved to be very resistant to biological degradation under test conditions so that the depletion of oxygen was low, consistent, and in the range of blind control (0.6–2.2 mg $L^{-1}$). Duplicates were executed per substance. Oxygen concentration during the test was read out on a daily basis (five days per week, 4 weeks). Samples for chemical analysis were taken at the beginning (day 0, n = 1) and the end of the test (day 28, n = 2) and stored at −80 °C until further analysis.

### 2.3. Sample preparation for GC-MS analysis

The aqueous samples from the CBT were prepared to be analyzed by GC-MS. Liquid-liquid extraction was successfully applied for substances **1-C**, **3-Si**, **4-Si**, **4-C**, **5-Si**, and **5-C** (Table 2, Fig. S1+S2, supplementary material). Substances **4-Si** and **5-Si** were extracted employing HR-X cartridges (Fig. S3, supplementary material). The substances **1-Si**, **2-Si**, **2-C**, and **3-C** could not be extracted from aqueous solutions with the available methods.

For liquid-liquid extraction, 1 mL of the test solution was mixed with 2 mL of extracting agent chloroform and methanol (2:1 v/v) (Folch et al., 1957). After phase separation, 1.2 mL of the chloroform phase were transferred into a glass tube and reduced to dryness under gentle nitrogen flow.

Solid phase extraction (SPE) was conducted with HR-X cartridges (6 mL/200 mg, Macherey Nagel, Düren, Germany). Conditioning of cartridges was done with 10 mL methanol and 10 mL water. After this, 1 mL of the sample was sucked through to the cartridges. The cartridges were dried under vacuum for 20 min. The analyte was eluted with 5 mL of chloroform/methanol (1:1) and reduced to dryness under gentle nitrogen flow. As for both extraction procedures, the residue was dissolved in 100 μL hexane and transferred to a screw neck vial with an insert and analyzed via GC-MS.

### 2.4. GC-MS analysis

GC-MS was chosen as analytical method because the analytes are relatively small and of low polarity. Therefore, they are easy to vaporize on the one hand and, on the other hand, difficult to analyze via liquid chromatography coupled with electrospray ionization. GC coupled with electron impact ionization was performed with a Thermo Scientific Trace 1310 gas chromatograph with ISQ single quadrupole mass spectrometer. The samples were injected with a Thermo Scientific TriPlus RSH autosampler. Inlet and transfer line temperatures were set to 260 °C. A VF-5ms column (30 m × 0.25 mm, 0.25 μm, 10 m EZ-guard, Agilent Technologies, Middelburg, Netherlands) was used for compound separation. Helium was used as carrier gas with a constant flow of 1.5 mL $min^{-1}$. The temperature profile started at 35 °C (hold time 5 min), including a solvent delay of 3 min and increased to 70 °C with a ramp rate of 10 °C $min^{-1}$. The oven temperature was increased with a heat rate of 30 °C $min^{-1}$ until 260 °C was reached and held for 1 min (Fig. S5, supplementary material). The electron energy was 70 eV, and the ion source temperature was set to 270 °C. The other GC-MS settings

**Table 2**
Overview of the applied extraction methods. LLE – liquid-liquid extraction, SPE – solid phase extraction, O – not performed, ✓ – successful, X – not successful.

| No | LLE | SPE | Final method |
|---|---|---|---|
| **1-Si** | X | O | none |
| **1-C** | ✓ | O | LLE |
| **2-Si** | X | X | none |
| **2-C** | X | X | none |
| **3-Si** | ✓ | X | LLE |
| **3-C** | X | X | none |
| **4-Si** | ✓ | ✓ | SPE |
| **4-C** | ✓ | O | LLE |
| **5-Si** | ✓ | ✓ | SPE |
| **5-C** | ✓ | O | LLE |

**Table 3**
Retention time ($t_R$) and selected masses for the SIM mode of the tested compounds.

| No | $t_R$ [min] | Main masses [amu] |
|---|---|---|
| **1-Si** | 9.21 | 131; 116 |
| **1-C** | 9.21 | 115; 100 |
| **2-Si** | 5.48 | 148; 133 |
| **2-C** | 5.66 | 132; 117 |
| **3-Si** | 8.98 | 164; 121 |
| **3-C** | 9.30 | 148; 117 |
| **4-Si** | 11.55 | 182; 167 |
| **4-C** | 11.53 | 166; 151 |
| **5-Si** | 11.93 | 198; 120 |
| **5-C** | 12.05 | 182; 151 |

are listed in the supplementary material (Table S1). Each sample (1 μL) was measured in full scan (*m/z* 40–206, dwell time 0.2 s) and selected ion monitoring (SIM) mode (masses are shown in Table 3). Masses were chosen based on reference spectra of target compounds from the NIST database. The mass spectrum of substance **4-C** was not available in the database and therefore calculated with the "competitive fragmentation modeling for metabolite identification" software (http://cfmid.wishartlab.com/predict). The interpretation of the generated MS spectra was based on this information.

The standard solutions used for the method development (GC-MS) consisted of the tested substance dissolved in hexane with 1% DMSO reaching a final mass concentration of 2 mg $L^{-1}$. Here, DMSO was used for the highly concentrated stock solution, which was diluted with hexane to the final concentration. These solutions were also used as quality controls. All selected substances were detectable with this method (Fig. S4, supplementary material). The retention times of the tested substances are listed in Table 3. It is noticeable that the retention times of the respective analogue pairs are very similar, indicating similar physical-chemical properties such as polarity and boiling point.

## 3. Results and discussion

### 3.1. Degradation of the tested compounds

The pH value at the beginning of the CBT was in the range of 7.48–7.61. After 28 d, the pH value was in the range of 6.95–7.52. All performed tests were valid according to the OECD guideline 301D. The toxicity controls showed expected behavior in the CBT (Fig. S7, supplementary material), which means that their oxygen demand formed the average of the positive control (sodium acetate) and the tested substance (Fig. S6, supplementary material). The biodegradation in percent was calculated by using the measured oxygen consumption, but hydrolysis could not be determined via this method. The CBT progress of biodegradation over 28 d is presented in Fig. 1 (**1**–**5**). It rose during the first days (except substance **1-C**) until it reached a plateau after at least 10 d. A dashed line marks the threshold of 60% required for a substance to be classified as readily biodegradable. The results show that none of the silicon-containing substances (**1-Si**, **2-Si**, **3-Si**, **4-Si**, and **5-Si**), but

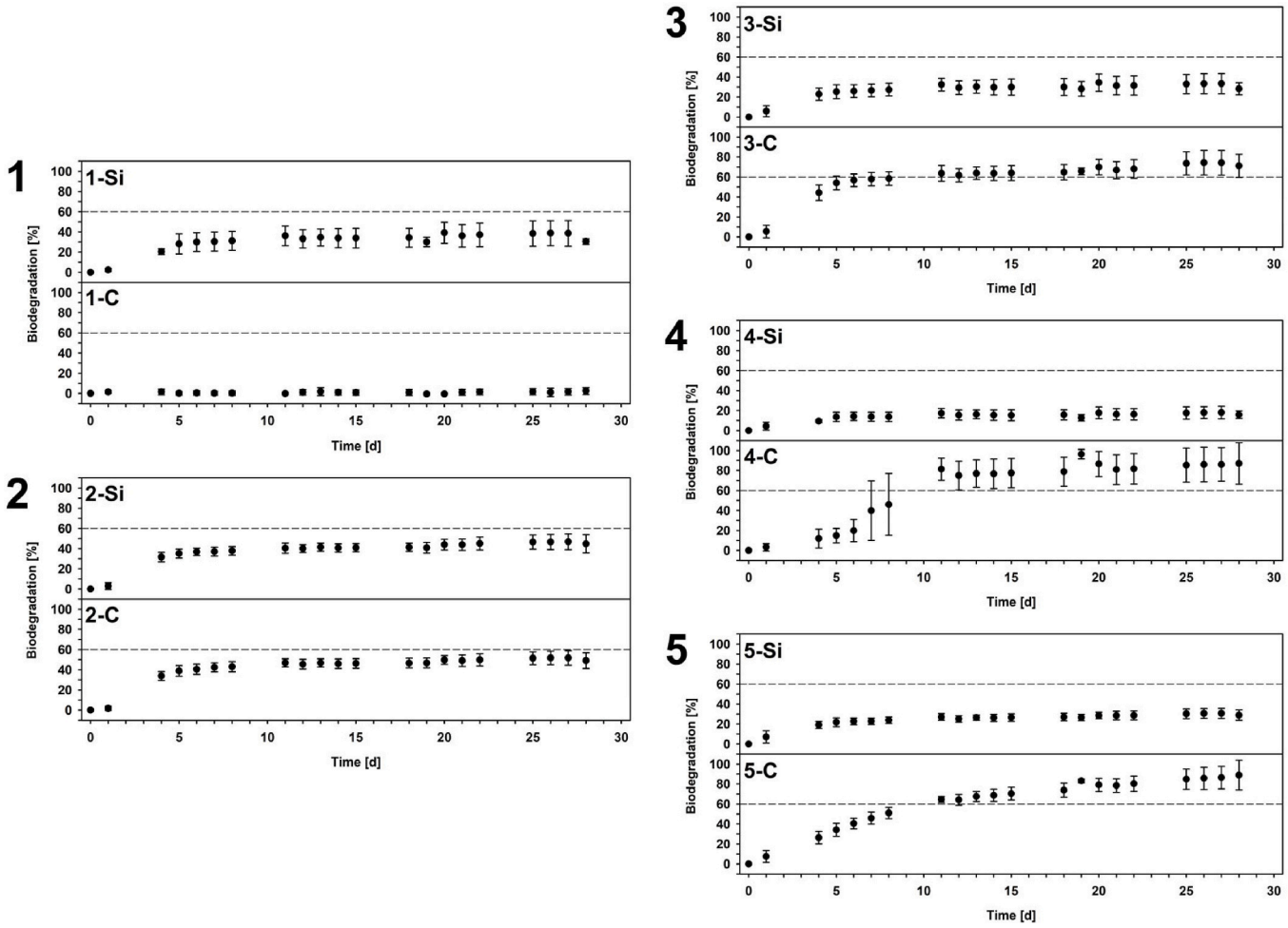



**Fig. 1.** Biodegradation of the ten tested compounds in the CBT (**1** – **1-Si**, **1-C**; **2** – **2-Si**, **2-C**; **3** – **3-Si**, **3-C**; **4** – **4-Si**, **4-C**; **5** – **5-Si**, **5-C**). The biodegradation in percent is displayed as a function of time (black dots). Removal of ≥60% ThOD within a 10-d window within the 28-d period after 10% of ThOD allows classifying a test compound as "readily biodegradable" (dashed line). The test was performed three times in duplicates, respectively. Values represent the means ± SD ($n = 6$).

three out of five carbon analogues (**3-C**, **4-C**, and **5-C**) were readily biodegradable according to the OECD guidelines. Even if the biodegradation was below 60%, further findings could be derived from the results and discussed for each substance, respectively. Partial degradation could be possible and hydrolytic processes have to be considered during the CBT.

In previous studies, substances **1-Si**, **2-Si**, **3-Si**, **4-Si**, and **5-Si** were tested in CBT (OECD 301D) and substances **1-Si**, **2-Si**, and **3-Si** in OECD 301F, but without the co-solvent DMSO (Rücker and Kümmerer, 2013). Results obtained in this study differ from around 1–20% (CBT). These differences are within the threshold for errors in biodegradation tests and could be caused by seasonal changes in the composition of bacteria (OECD, 1992). Findings from the manometric respirometry test (MRT, OECD 301F) were, except for one result of substance **2-Si** (19%), higher than the biodegradation achieved with the CBT. The higher and/or faster degradation in MRT is due to a higher bacterial density and diversity and, therefore, a higher possibility that the effluent contains degrading bacteria. Even if the degradation was higher in MRT, none of the substances were readily biodegradable according to the criteria and under consideration of validity. However, there was no indication of a Si–C bond split (Rücker and Kümmerer, 2013). These findings confirm that the DMSO used within this study did not influence the degree of degradation, but it simplifies the processes significantly and reduces handling errors by avoiding to weigh small quantities of substances.

The extraction processes, GC-MS measurements, and CBT results of the analytical study are summarized in Table 4. Despite successful extraction from aqueous samples, substances **3-Si** and **5-Si** could not be found in CBT samples of day 0. Too much time may have passed between introducing the substances to the test vessels, sampling, and freezing, so the substance probably has been hydrolyzed before freezing and during storage.

The results of the oxygen consumption from CBT extended the analytical studies with GC-MS and provided information even for substances that were difficult to analyze or to extract from aqueous samples.

### 3.1.1. *Substances **1-Si** and **1-C***

Substance **1-Si** showed biodegradation of 39%. This value is below the threshold of 60%, indicating no ready biodegradability, but partial biodegradation by microorganisms. Substance **1-Si** was not extractable and not detectable from aqueous CBT samples as it was primarily eliminated after exposure to water and air. The instability is ascribed to the reaction with water because hydrolysis of the Si–N bond is very fast (Rücker and Kümmerer, 2013). In this case, the expected reaction products of hydrolysis are trimethyl silanol and acetamide (Fessenden and Fessenden, 1961; Yamamoto and Kimura, 1976). Trimethyl silanol was indirectly tested in a CBT as a fast generated hydrolysis product of trimethylsilyl chloride (Rücker and Kümmerer, 2013). This compound hydrolyzed to its silanol and hydrochloric acid (ECHA, 2008a). Trimethylsilyl chloride was tested twice, and both tests showed no biodegradation (ECHA, 2008a; Rücker and Kümmerer, 2013). The second product of hydrolysis of substance **1-Si** is acetamide, which is readily biodegradable (ECHA, 2014). This explains the test result of substance **1-Si** in the performed CBT. It can be argued that the parent compound hydrolyzed into two compounds, and at least one of the hydrolysis products was readily biodegradable.

The carbon analogue of this compound, substance **1-C**, was not readily biodegradable. The performed GC-MS analysis of substance **1-C** in CBT samples, showing 100% on day 0 and 98% at day 28, also demonstrates no biodegradation and no formation of hydrolysis products (Fig. 2). On the one hand, microorganisms did not degrade the parent compound, and on the other hand, it is improbably that substance **1-C** hydrolyzed within 28 d. A possible hydrolysis product, acetamide, would be readily biodegradable as it was shown with substance **1-Si** and according to literature (ECHA, 2014). The voluminous *tert*-butyl group prevents the hydrolysis of the $C_{quarternary}$–N bond by steric obstruction (Bruice et al., 2011). It is also improbable that the amide bond will be cleaved because acidic or basic conditions or enzyme catalysis are necessary to split this bond, whereas the CBT was run close to pH 7 (Bruice et al., 2011).

Hydrolysis, as an essential step for the subsequent biodegradation, was only observed for substance **1-Si**, which was the only one with an easily hydrolyzable Si–N bond. The different sizes and electronic properties of silicon and carbon and thus the different polarity of the bonds resulted in the described hydrolysis and biodegradation behavior.

### 3.1.2. *Substances **2-Si** and **2-C***

Substance **2-Si** showed degradation of 47% within 28 d, therefore, it cannot be classified as readily biodegradable. The biodegradation value of 47% could be caused by partial biodegradation of hydrolysis products. This could be explained by the fact that substance **2-Si** could be cleaved into dimethyl silanediol and two molecules of ethanol by fast hydrolysis of Si–O bonds, and ethanol is known to be readily biodegradable (Bains and Tacke, 2003; Birch and Fletcher, 1991; Rücker and Kümmerer, 2015). Substance **2-Si** was also classified as not readily biodegradable via read-across of the analogue substance trimethyl silanol (OECD, 2014). In contrast to substance **2-Si**, during the biodegradation of trimethyl silanol, no readily biodegradable substances such as ethanol could be released by hydrolysis.

The observed biodegradation of substance **2-C** in the CBT was 52%. Thus, substance **2-C**, a ketal, is not readily biodegradable. The substance was not investigated in a biodegradation test in previous studies but was predicted to be not readily biodegradable (Danish QSAR database, ECHA, 2018). The partial biodegradation is attributable to incomplete biodegradation of hydrolysis products. In this case, acetone and two molecules of ethanol were formed via hydrolysis, and it is known that ketals hydrolyze easily (Cordes and Bull, 1974; Deslongchamps et al.,

**Table 4**
Summary of the extraction and analysis results of the tested substances. The analysis with GC-MS was successful for all substances. The columns with CBT day 0 and CBT day 28 represent the measurement results with GC-MS of the CBT samples after extraction. If the substance was detected on day 0, but not on day 28, the substance was degraded during the test. The last column indicates whether the substance is readily biodegradable or not. * Ready biodegradability could only be achieved by hydrolysis of the parent compound and complete biodegradation of the hydrolysis products. ° No persistent transformation products (TP) could be detected, but the parent compound was persistent. LLE – liquid-liquid extraction; SPE – solid phase extraction; ✓ – successful; X – not successful.

| No | Extraction | GC-MS | CBT day 0 | CBT day 28 | Persistent TPs | Readily biodegradable |
|---|---|---|---|---|---|---|
| **1-Si** | none | ✓ | X | X | yes | no |
| **1-C** | LLE | ✓ | ✓ | ✓ | no° | no |
| **2-Si** | none | ✓ | X | X | yes | no |
| **2-C** | none | ✓ | X | X | no | no |
| **3-Si** | LLE | ✓ | X | X | yes | no |
| **3-C** | none | ✓ | X | X | no | yes* |
| **4-Si** | SPE | ✓ | ✓ | ✓ | yes | no |
| **4-C** | LLE | ✓ | ✓ | X | no | yes* |
| **5-Si** | SPE | ✓ | X | X | yes | no |
| **5-C** | LLE | ✓ | ✓ | X | no | yes* |

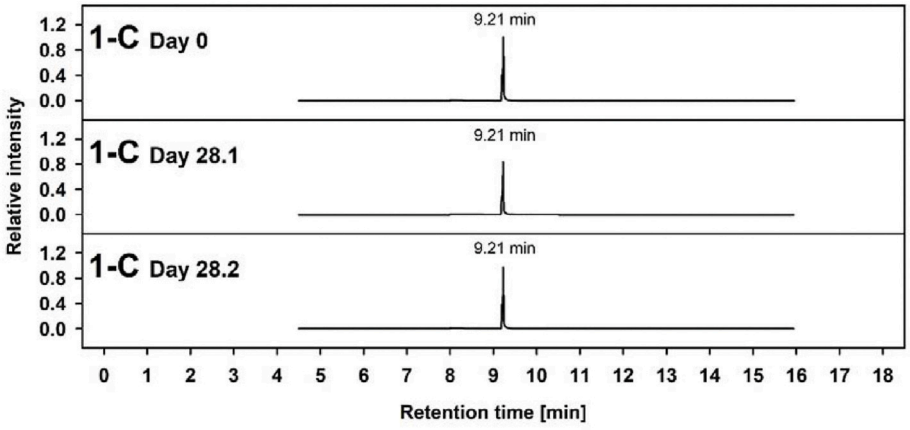



**Fig. 2.** Gas chromatograms of substance **1-C** ($t_R$ = 9.21 min) at the beginning of the CBT (day 0) and at the end of the test (day 28, duplicates) in SIM mode.

2000). However, an improved biodegradation of compound **2-C** in the CBT was expected, as both hydrolysis products, ethanol, and acetone, are readily biodegradable (Birch and Fletcher, 1991). Comparing the biodegradation curves of substances **2-Si** and **2-C** (Fig. 1), it is noticeable that they show similar degradation behavior during the 28 d test period.

### 3.1.3. *Substances **3-Si** and **3-C***

For substance **3-Si**, degradation of 34% was observed within 28 d. Therefore, this substance cannot be classified as readily biodegradable. GC-MS analysis could not add further information because substance **3-Si** was not detected in samples of day 0 from the CBT (Fig. 3). As detection of substance **3-Si** was not successful in samples of day 0, samples of day 28 were not extracted. Comparable to substance **2-Si**, the low biodegradation degree was due to the biodegradation of the hydrolysis product methanol, which is known to be readily biodegradable (Wagner, 1976). Up to three molecules could be released from substance **3-Si** because Si–O bonds hydrolyze fast (Bains and Tacke, 2003; Rücker and Kümmerer, 2015). The remaining molecule after complete hydrolysis, propyl silanetriol, was probably not biologically degraded as organosilanols are not biodegradable (Moriones et al., 2019; Rücker and Kümmerer, 2015). It is possible that these molecules condensate to oligomers (Issa and Luyt, 2019). In a previous study, substance **3-Si** showed 54% of biodegradation after 28 d using OECD 301A (ECHA, 1994). This result is comparable to the result obtained in this study (34%). Differences of around 20% are within the error range of biological degradation tests (OECD, 1992). The tests differ mainly in the amount of the tested substance, the amount of inoculum, and the measuring principle. In the CBT, the concentration of the test substance and the density of bacteria and thus the diversity of degrading bacteria is lower, making the test more accurate than OECD 301A, which means the latter one often results in higher biodegradation rates for the same compound.

Substance **3-C** was biologically degraded to 74% during the CBT and hast to be classified as readily biodegradable. This substance was not extractable from aqueous samples with the applied method and, therefore, not detectable in the extracts. This can be explained by the fact that substance **3-C** hydrolyses easily because it is an ortho ester (Deslongchamps et al., 2000). Probably, hydrolysis was too fast to extract the parent compound from aqueous samples. Butyric acid and methanol are known to be the hydrolysis products of substance **3-C** (Ahmad et al., 1979). Both are readily biodegradable (ECHA, 1996; Wagner, 1976). In this case, the carbon compound was better degradable than the silicon analogue as one hydrolysis product of substance **3-Si**, propyl silanetriol, was not biodegradable.

### 3.1.4. *Substances **4-Si** and **4-C***

Substance **4-Si** is not readily biodegradable. Degradation of 19% was observed after 28 d in the CBT. Similar to substance **3-Si**, substance **4-Si** released methanol via hydrolysis of the parent compound (Moriones et al., 2019). The other hydrolysis product, methylphenyl silanediol, was not biodegradable (Rücker and Kümmerer, 2015). Substance **4-Si** was detected in CBT samples at day 0 and day 28, but both times with very low intensities (Fig. 4). This indicates that the parent compound was not completely hydrolyzed into methylphenyl silanediol and methanol. Although, it can be assumed that only one biodegradable hydrolysis product was formed (methanol) and hydrolysis of the parent compound was not complete. In addition, the carbon content in the non-degradable methylphenyl silanediol is higher than in propyl silanetriol, the hydrolysis product of **3-Si**, and correspondingly the resulting biodegradation is lower. The chromatograms of substance **4-Si** (Fig. 4) also show signals at 9 min and after 12 min. These signals could not be assigned to specific substances based on MS spectra. Therefore, it is assumed that they are interference peaks from sample preparation and/or parts of the separation column.

Substance **4-C**, another ketal in this group of substances, was readily biodegradable with biodegradation of 87%. Elimination over 80% indicates complete mineralization. Values of around 100% are improbable because microorganisms can use the test substance as a carbon source for their anabolism. Therefore, it can be assumed that substance **4-C** was mineralized completely. After 28 d, only 2.7% of substance **4-C** was

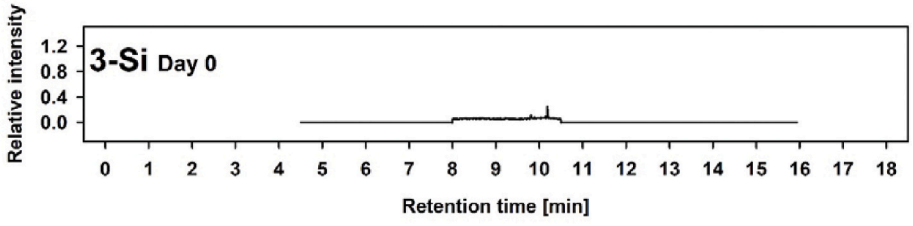



**Fig. 3.** Gas chromatogram of substance **3-Si** ($t_R$ = 8.98 min) at the beginning of the CBT (day 0) in SIM mode. Chromatograms of day 28 do not exist because samples of day 28 were not extracted as substance **3-Si** could not be detected on day 0.

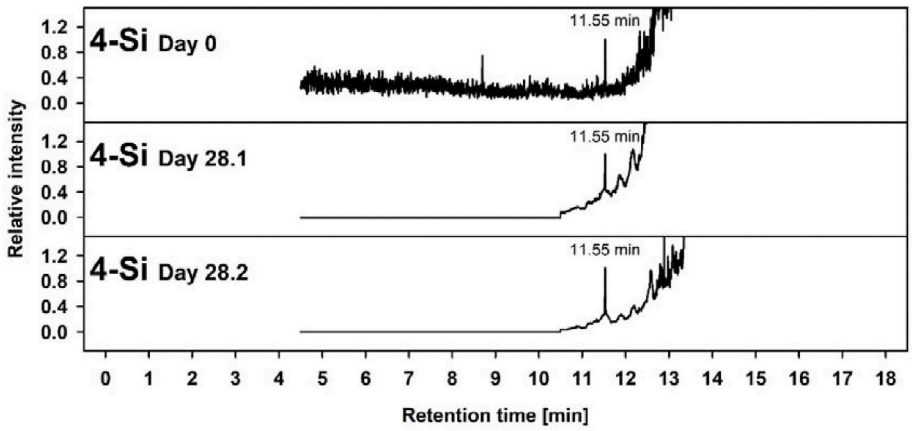



**Fig. 4.** Gas chromatograms of substance **4-Si** ($t_R$ = 11.55 min) at the beginning of the CBT (day 0) and the end of the test (day 28, duplicates) in SIM mode.

detected (Fig. 5). This confirms the results of the dissolved oxygen measurements during the CBT. Substance **4-C** formed acetophenone and methanol via hydrolysis (Cordes and Bull, 1974). These products were both readily biodegradable, explaining the high biodegradability of 87% (Chemicals Inspection and Testing Institute, 1992; Wagner, 1976). The obtained results are similar to those of substances **3-Si** and **3-C**. The carbon compound was much better degradable.

The chromatograms of substance **4-Si** (Fig. 4) and substance **4-C** (Fig. 5) also show signals at 9.00, 11.00, and after 12.00 min. These signals could not be assigned to specific substances based on MS spectra. Therefore, it is assumed that they are interference peaks from sample preparation and/or bleeding of the separation column.

### 3.1.5. *Substances **5-Si** and **5-C***

Substance **5-Si** is not readily biodegradable but showed a biodegradation degree of 31% after 28 d. As can be seen in Fig. 6, substance **5-Si** was not detected in CBT samples (day 0 and day 28). Other interference peaks were detected at 11.00 min and after 12.80 min, which could be caused by column bleeding or carry-overs from sample preparation. The partial degradation of substance **5-Si** could be achieved by the release of biodegradable methanol via hydrolysis of the parent compound. The remaining silicon-containing compound, phenyl silanetriol, is not biodegradable (Moriones et al., 2019; Rücker and Kümmerer, 2015). Substance **5-Si** is listed as non-biodegradable in the ECHA database (ECHA, 2009b). However, this result was achieved by read-across of trichlorophenyl silane, which was tested in the OECD 310 test and showed 0% of biodegradation (OECD, 2014). Trichlorophenyl silane does not hydrolyze to readily biodegradable substances such as methanol, which explains the low degradability. However, the biodegradability of the remaining silicon-containing hydrolysis product phenyl silanetriol can be derived from trichlorophenyl silane. When trichlorophenyl silane is exposed to water, hydrochloric acid is formed, and phenyl silanetriol is generated as with substance **5-Si**.

Substance **5-C** was biodegraded to 87%, indicating ready biodegradability. Substance **5-C** could be detected in samples of the biodegradation test start (day 0) and could not be detected after 28 d of testing (Fig. 7), which supports the finding of the biodegradation of 87% obtained by measuring the oxygen consumption in the CBT. This result can be explained similarly to substance **4-C** as all hydrolysis products of the parent compound (benzoic acid and methanol) were easily formed and readily biodegraded by aerobic microorganisms (Ahmad et al., 1979; Cordes and Bull, 1974; ECHA, 2009a; Wagner, 1976). Again for this pair of analogues, it could be observed that the carbon compound was much better biodegradable than its silicon analogue.

## 3.2. *Are carbon compounds better degradable than their related silicon analogues?*

The main results are presented in Table 4 summarizing the most important findings. In total, three of five carbon compounds and no organosilicon compound were readily biodegradable (60% threshold). One organosilicon substance (**1-Si**) was better degradable than its carbon analogue (**1-C**). Except for this one, all carbon compounds were better biodegradable compared to their organosilicon analogues.

Nearly all of the tested compounds hydrolyzed fast, resulting in several hydrolysis products that were subsequently biodegraded by the

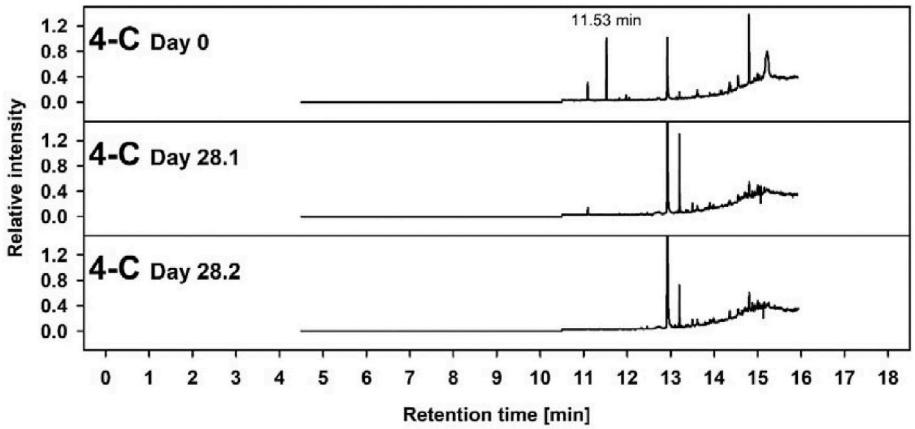



**Fig. 5.** Gas chromatograms of substance **4-C** ($t_R$ = 11.53 min) at the beginning of the CBT (day 0) and the end of the test (day 28, duplicates) in SIM mode.

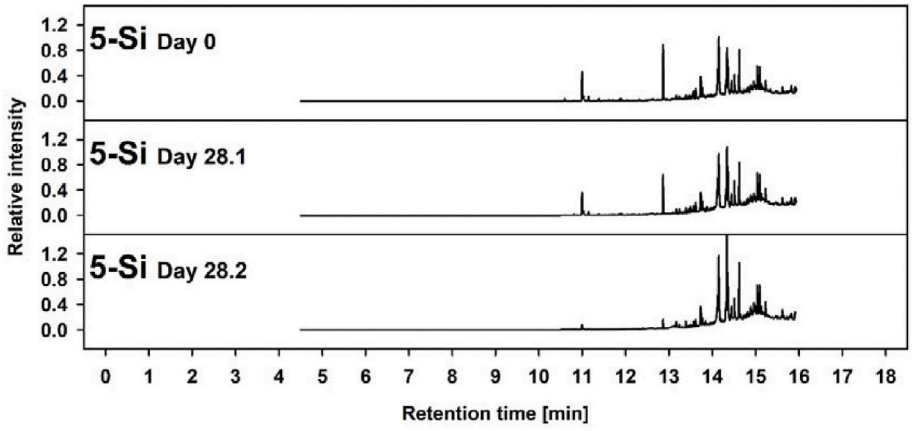



**Fig. 6.** Gas chromatograms of substance **5-Si** ($t_R$ = 11.93 min) at the beginning of the CBT (day 0) and the end of the test (day 28, duplicates) in SIM mode.

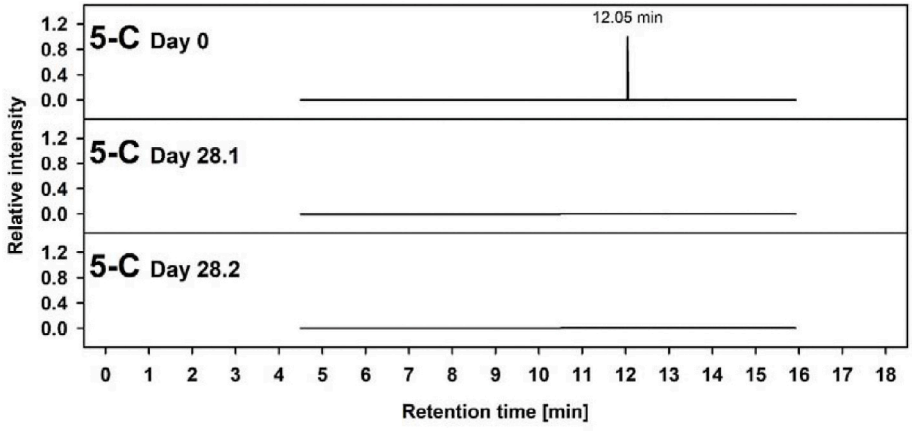



**Fig. 7.** Gas chromatograms of substance **5-C** ($t_R$ = 12.05 min) at the beginning of the CBT (day 0) and the end of the test (day 28, duplicates) in SIM mode.

microorganisms in the CBT. Hydrolysis seems to be a mandatory step before biodegradation for this class of substances. Without this proceeding abiotic process, no biodegradation occurred as it was shown with substance **1-C**. All known hydrolysis products of the carbon compounds are readily biodegradable. Thus, degradation over 60% was reached for the carbon-containing parent compounds **3-C**, **4-C**, and **5-C**, indicating mineralization. For substance **2-C**, biodegradation less than 60% was found, although its hydrolysis products are readily biodegradable. In this case, hydrolysis seemed to be the rate-determining step. Nevertheless, partial biodegradation of the parent compound could be observed in all cases, even if the degradation is below 60% (except substance **1-C**).

In the case of the silicon-containing compounds, always non-biodegradable hydrolysis products were formed: trimethyl silanol, dimethyl silanediol, propyl silanetriol, methylphenyl silanediol, and phenyl silanetriol. Obviously and in accordance with data from the literature, these silanols are not at all biodegradable. They are also able to condense to form oligomers, which are often less soluble than their monomers and, therefore, less bioavailable, which results in slower and lower rates of biodegradation (Issa and Luyt, 2019). This is in agreement with the findings of Büttner et al. (2007). They also showed that silicon analogues of odorants were not readily biodegradable. The increased lipophilicity of the silicon analogues compared to their related carbon compound resulted in a lower bioavailability (Büttner et al., 2007).

Substance **1-Si**, which hydrolyzed very fast and was better degradable than its carbon analogue, is the only compound having a Si–N bond. This bond is more polar than a Si–C bond, prone to hydrolysis, and often used to design pro-drugs being an active pharmaceutical ingredient after hydrolysis (e.g. pro-drugs of the O-, N-, or S-silyl type, Bains and Tacke, 2003). The insertion of heteroatoms, especially nitrogen, changed the degradability in aqueous media. As shown by Grabitz et al. aromatic substances possessing a Si–N bond are better photodegradable, because the $–NR_2$ group caused a better overlap with the emission spectrum of the used lamp (Grabitz et al., 2020). This is another example, where Si–N bonds caused a better degradability.

## 4. Conclusion

In this study, the biodegradability of organosilicon compounds and their carbon analogues was investigated. GC-MS analysis was applied to support the results of the biodegradation test. The results demonstrate that reliable biodegradation data on organosilicon compounds and their carbon analogues can be gained and that none of the tested organosilicon compounds was readily biodegradable. Furthermore, in general, organosilicon compounds were less biodegradable than their related carbon analogues, albeit one exemption was found. Hydrolysis is a preceding mandatory step for biodegradation by microorganisms. However, the found biodegradability was due to readily biodegradable organic carbon compounds generated by hydrolysis, which do not contain silicon atoms anymore. The generated silicon-containing products of hydrolysis were all not biodegradable. Introducing nitrogen atoms can improve the speed of hydrolysis because of the weak bond between silicon and nitrogen. Substances that need to maintain their functionality in water are unsuitable for this modification. However, if substances are applied in a water-free environment, and the substance only begins to degrade after entering the aquatic environment, this

modification is very promising. This is often the case for polysiloxanes. Therefore, inserting nitrogen into polysiloxane chains can be a promising approach to improve their environmental degradation into smaller parts and thus to more environmentally benign organosilicon compounds. However, this would be only the first step as it can be expected that the silicon-containing fragments generated by hydrolysis are still resistant to environmental biodegradation. These assumptions need to be studied extensively by testing the biodegradability of modified polysiloxanes.

## CRediT authorship contribution statement

**Elisa Grabitz:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Marco Reich:** Methodology, Writing - review & editing. **Oliver Olsson:** Conceptualization, Writing - review & editing, Supervision. **Klaus Kümmerer:** Resources, Writing - review & editing, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2020.100331.

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# Supplementary material

**Title:** Using Structure Biodegradability Relationships for Environmentally Benign Design of Organosilicons – An Experimental Comparison of Organosilicons and their Carbon Analogues

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**Keywords:** Biodegradation; Extraction; Gas Chromatography; Heteroatom; Hydrolysis

# Table of content

# 1 Materials and methods

## 1.1 Chromatograms of extracted compounds – referring to Section 2.3

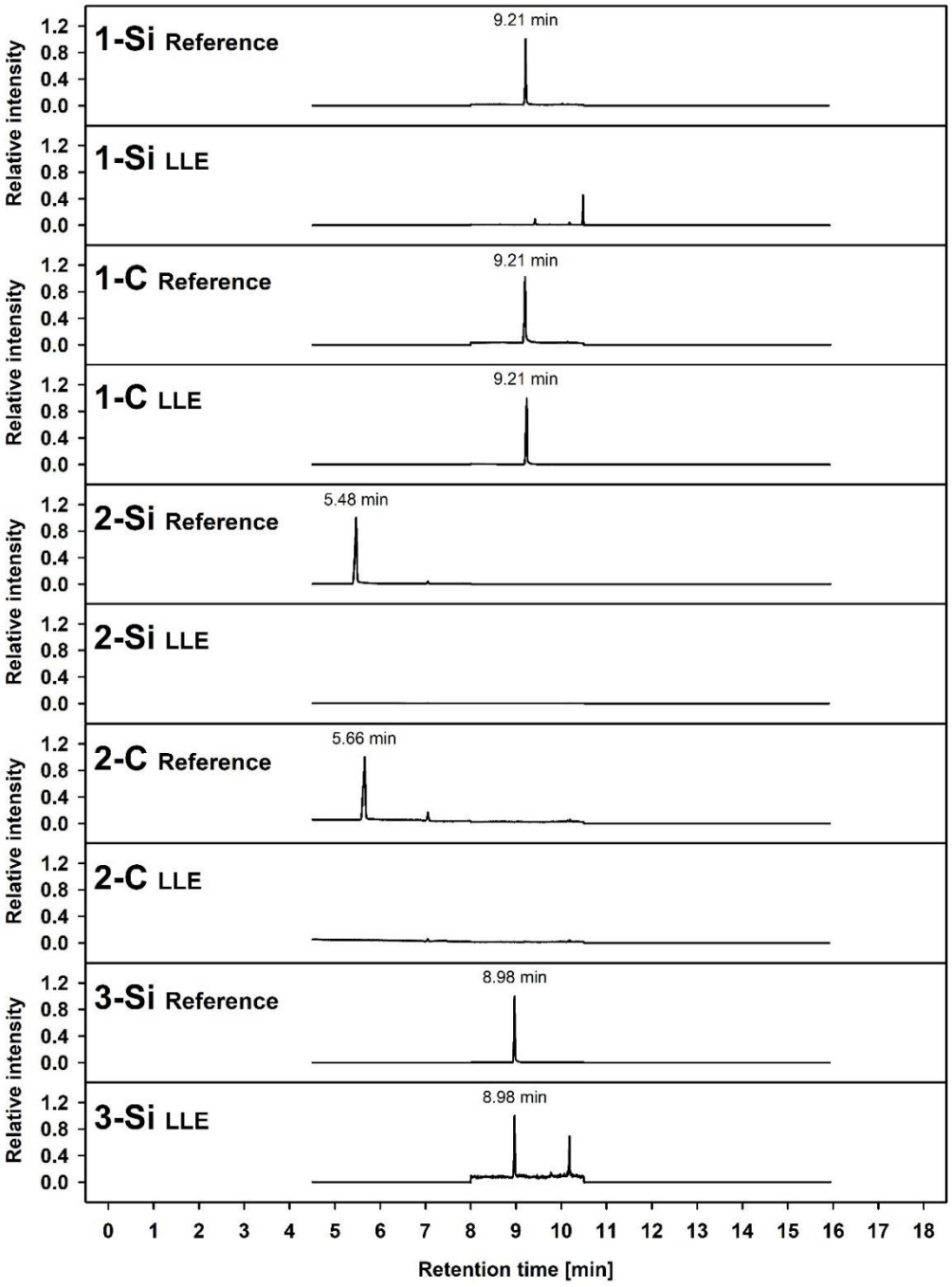


Figure S1: Chromatograms of the selected compounds (**1-Si**–**3-Si**) after liquid-liquid extraction (LLE) with chloroform and methanol (2:1) and dissolving with 100 µL *n*-hexane. SIM mode of each substance were displayed compared to a reference sample (SIM mode) dissolved in *n*-hexane (1 mg $L^{-1}$) without any extraction process. Concentration of aqueous solutions, which were extracted, was set to 2 mg $L^{-1}$ per substance with 1% DMSO as a co-solvent.

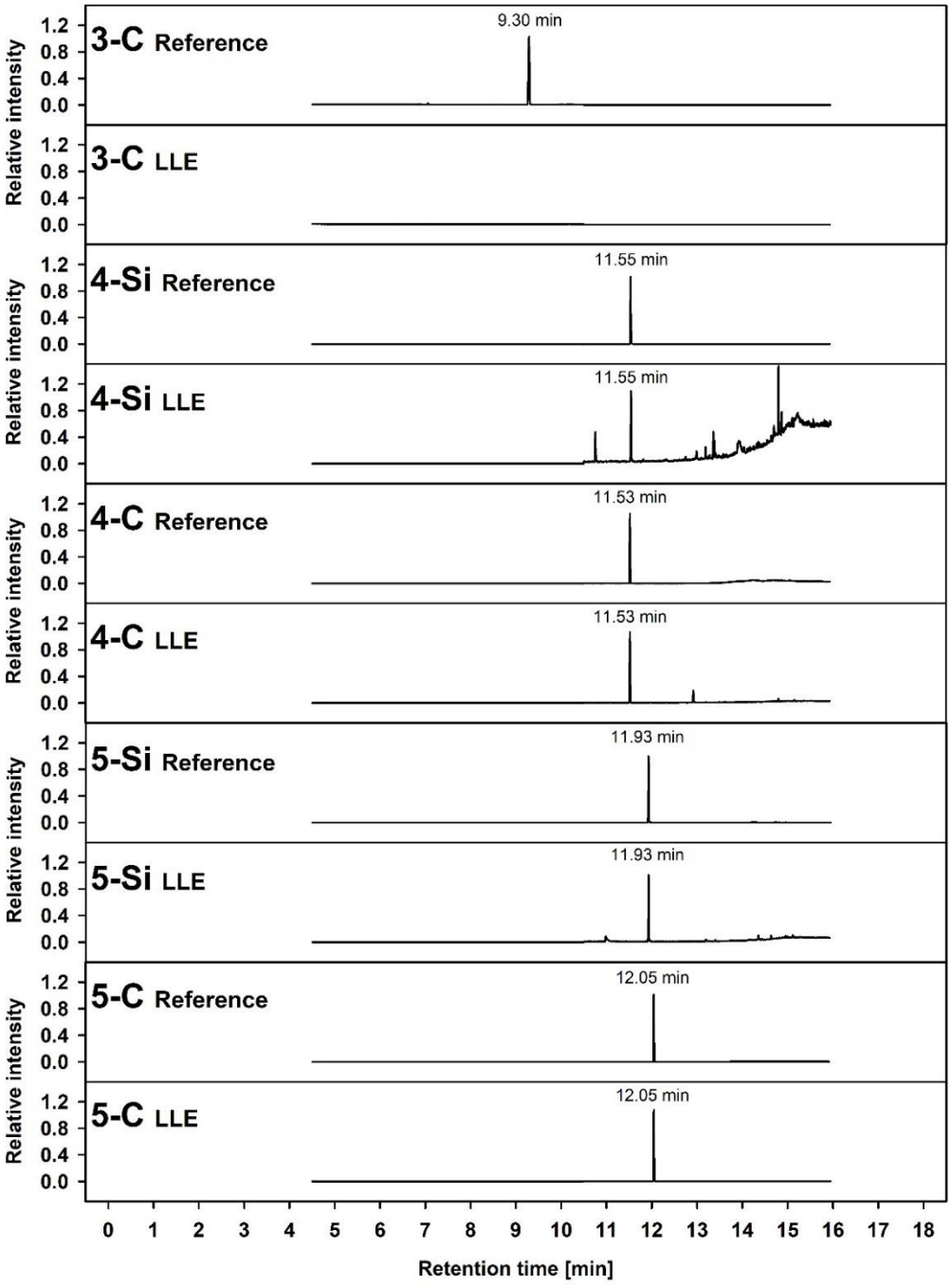


Figure S2: Chromatograms of the selected compounds (**3-C**–**5-C**) after liquid-liquid extraction (LLE) with chloroform and methanol (2:1) and dissolving with 100 µL *n*-hexane. SIM mode of each substance were displayed compared to a reference sample (SIM mode) dissolved in *n*-hexane (1 mg $L^{-1}$) without any extraction process. Concentration of aqueous solutions, which were extracted, was set to 2 mg $L^{-1}$ per substance with 1% DMSO as a co-solvent.

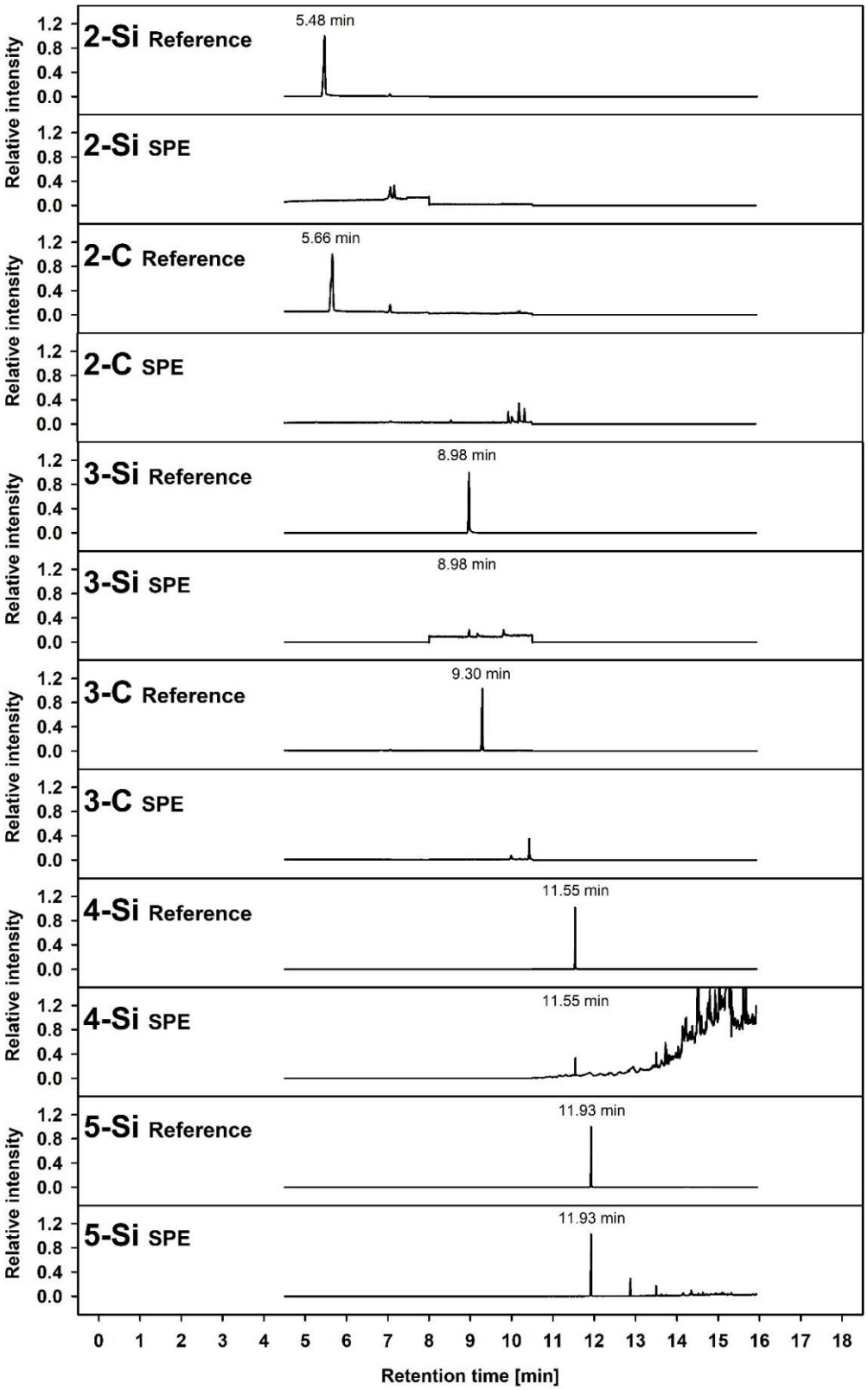


Figure S3: Chromatograms of the selected compounds (**2-Si**–**4-Si**; **5-Si**) after solid phase extraction (SPE). The dried extracts were dissolved in 100 µL *n*-hexane for analysis. SIM mode of each substance were displayed compared to a reference sample (SIM mode) dissolved in *n*-hexane (1 mg $L^{-1}$) without any extraction process. Concentration of aqueous solutions, which were extracted, was set to 2 mg $L^{-1}$ per substance with 1% DMSO as a co-solvent.

## 1.2 Chemical analysis with GC-MS – referring to section 2.4

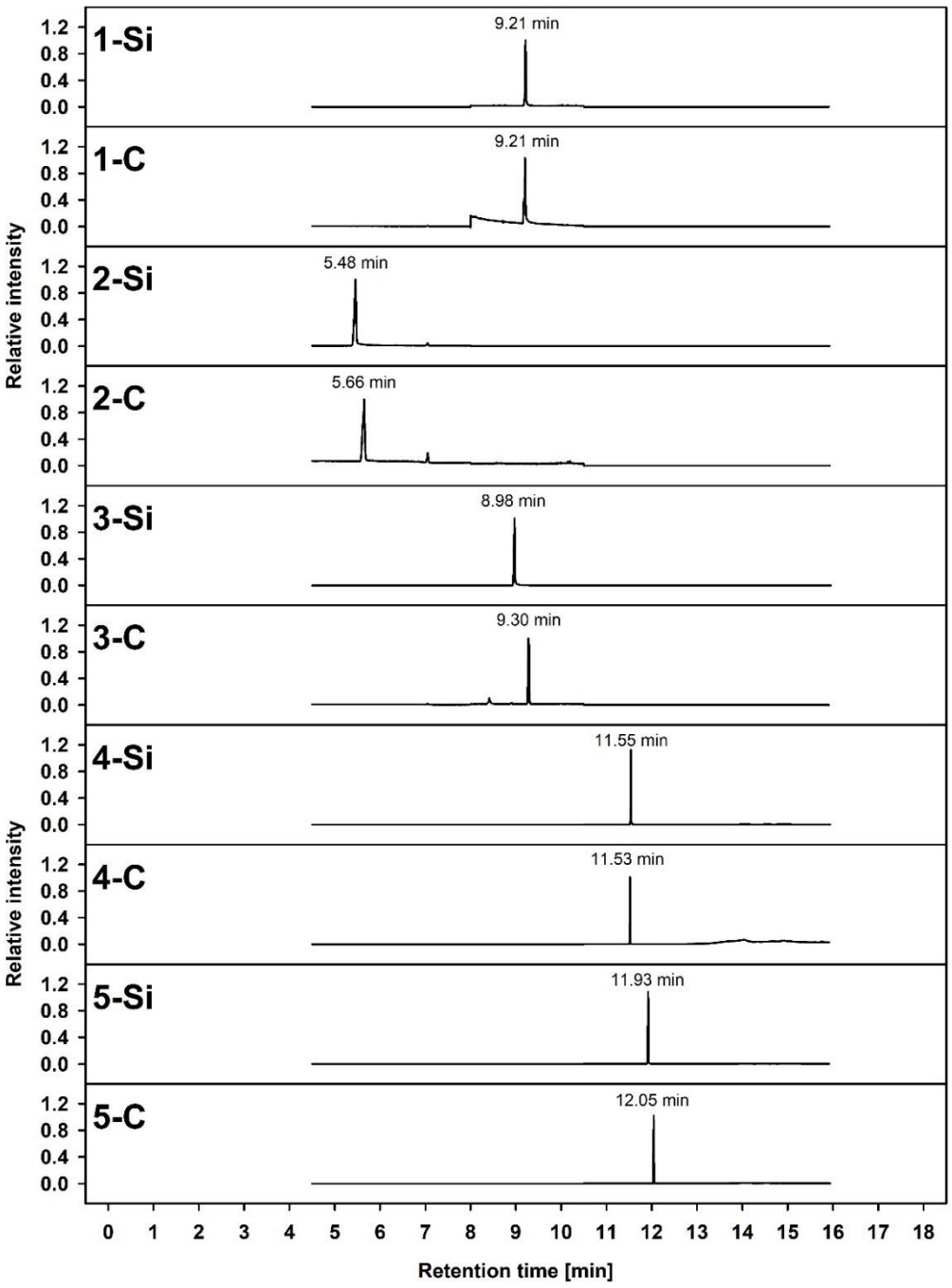


Figure S4: Gas chromatograms of the tested substances **1-Si**–**5-C** dissolved in *n*-hexane including 1% DMSO. The displayed chromatograms show the results of the SIM mode with the substance specific mass fragments.

Table S1: GC-MS settings

| **Method Setup** | | | |
|---|---|---|---|
| Method type | Acquisition - general | | |
| MS transfer line temp. | 260 °C | Ionisation mode | EI |
| Ion source temp. | 270 °C | Run completion | GC run time |
| **Scan Mode** | | | |
| **Time [min]** | **Mass List or Range [amu]** | **Dwell or Scan Times [sec]** | **Tune File Name** |
| 3.00 | 40–206 | 0.2 | (Last Saved) |
| **Groups** | | | |
| **Time [min]** | **Total Scan Time [sec]** | | |
| 3.00 | 0.204 | | |
| **SIM Mode** | | | |
| **Time [min]** | **Mass List or Range [amu]** | **Dwell or Scan Times [sec]** | **Tune File Name** |
| 4.50 | 117; 132; 133; 148 | 0.05 | (Last Saved) |
| 8.00 | 58; 75; 91; 100; 105; 115; 116; 121; 131; 148; 164 | 0.025 | (Last Saved) |
| 10.50 | 120; 151; 166; 167; 182; 198 | 0.05 | (Last Saved) |
| **Groups** | | | |
| **Time [min]** | **Total Scan Time [sec]** | | |
| 4.50 | 0.216 | | |
| 8.00 | 0.348 | | |
| 10.50 | 0.324 | | |

**TriPlus RSH Autosampler – GC Liquids**

| **General** | | **Washes** | |
|---|---|---|---|
| Injector port | | Number of solvent(s) | Single |
| Injector | Injector A {SSL_font} | Wash station | Standard wash station |
| Type | Single | Pre-injection | |
| Injector mode | Basic | Solvent | A |
| Rapid mode | | Cycles | 2 |
| Rapid mode | Disable | Solvent volume (µL) | 5.0 |
| Syringe type | | Rinse | |
| Syringe volume (µL) | 10.0 | Rinses | 2 |
| Needle length (mm) | 57 | Rinse volume (µL) | 1.5 |
| Sampling | | Post-injection | |
| Sample volume (µL) | 1.0 | Solvent | A |
| Plunger strokes | 5 | Cycles | 3 |
| Air and filling mode | Auto | Solvent volume (µL) | 5.0 |
| Injection | | **Advanced parameters** | |
| Injection depth | Standard | Wash solvent depth (mm) | 40 |
| Pre-injection dwell time (s) | 1.5 | Waste depth (mm) | 10 |
| Post-injection dwell time (s) | 2.0 | Needle speed in vial (mm/s) | 20 |
| Sampling depth in vial | | Solvent filling speed (µL/s) | 2 |
| □ Bottom sense | | Bubble elimin. pullup (µL/s) | 5 |
| Height from bottom (mm) | / | Delay between strokes | 2.0 |
| Sample vial depth (mm) | 30.0 | **Sync** | |
| Sample viscosity | | GC synchro start | |
| Sample type | Non viscous | Synchro type | Standard |
| S/SL (front) | | Carrier mode | Constant flow |
| S/SL mode | Splitless | Carrier flow | |
| Inlet | | Flow (mL/min) | 1.5 |

| | | | |
|---|---|---|---|
| Temperature (°C) ✓ | 260 | Surge | |
| Split flow (mL/min) □ | | Surge pressure (kPa) | |
| Split ratio | | Surge duration (min) | |
| Splitless time (min) | 1.00 | Carrier options | |
| Septum purge | | Vacuum compensation | ✓ |
| Purge flow (mL/min) | 5.0 | Carrier gas saver | ✓ |
| Constant septum purge | ✓ | Gas saver flow (mL/min) | 20.0 |
| Stop purge for (min) | | Gas saver time (min) | 2.00 |

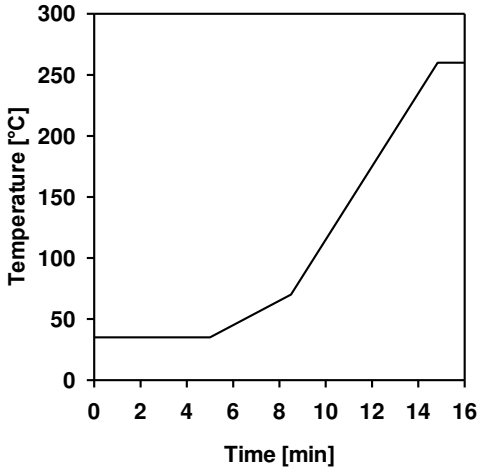


Figure S5: Temperature profile of the GC oven.

# 2 Results and discussion

## 2.1 Biodegradation graphs of blind and positive controls – referring to section 3.1

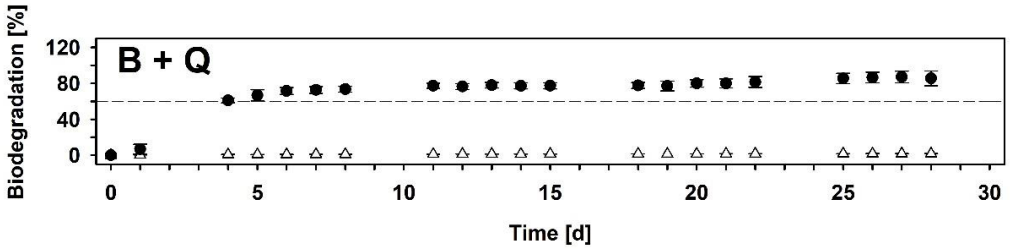


Figure S6: Biodegradation graphs of the blind (white triangles) and positive control (black points). The biodegradation in percent is presented as a function of time. Closed bottle test (CBT) was used to determine biodegradation within 28 d by measuring the depletion of oxygen. Removal of ≥ 60% ThOD within a 10-d window within the 28-d period after 10% of ThOD has been reached means ready biodegradability (dashed line). The test was performed three times with duplicates ($n$ = 6).

## 2.2 Biodegradation graphs of toxicity controls – referring to section 3.1

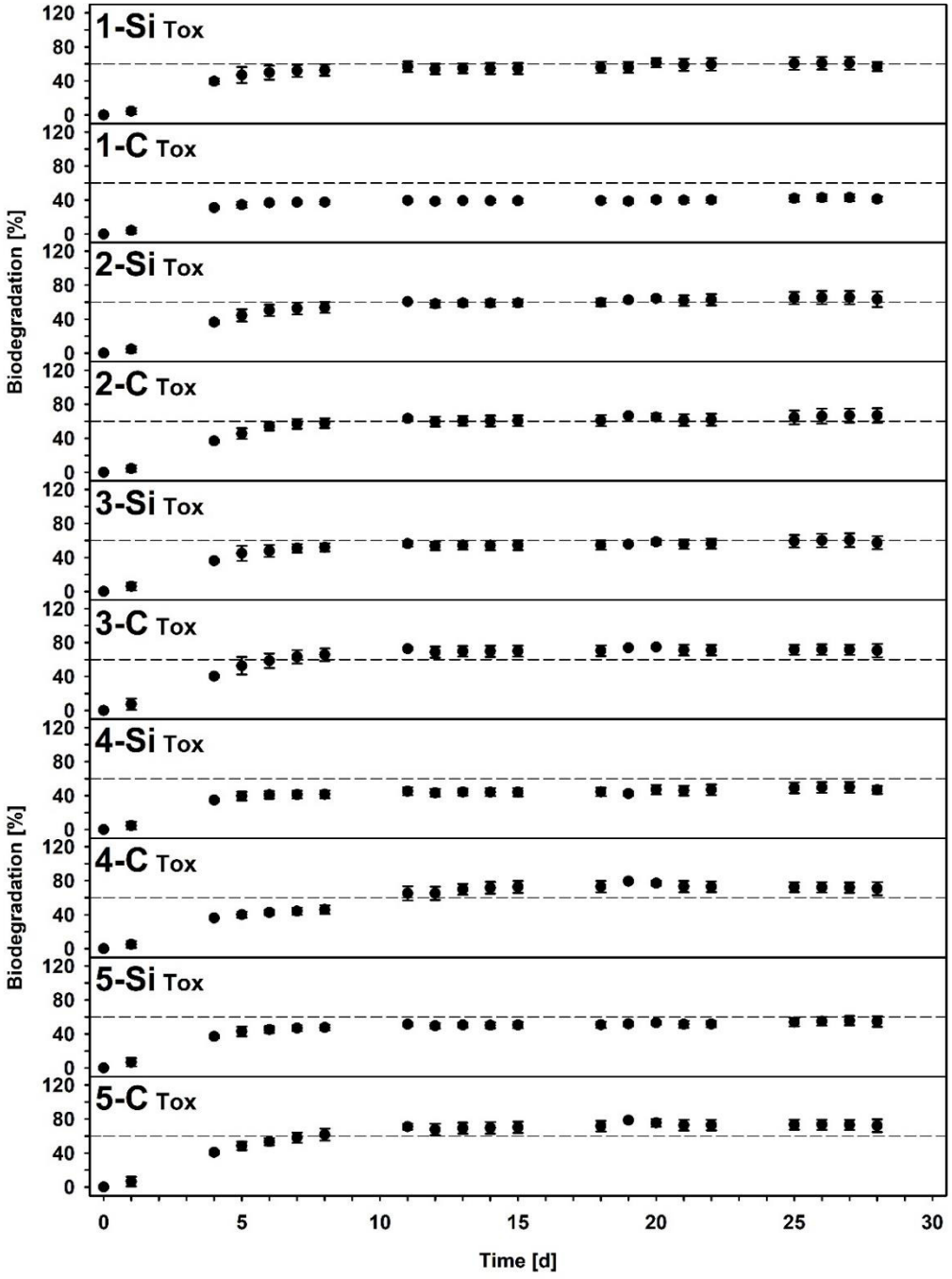


Figure S7: Biodegradation graphs of the toxicity controls of the ten tested compounds (test substance combined with the positive control, sodium acetate). The biodegradation in percent is presented as function of time. Closed bottle test (CBT) was used to determine biodegradation within 28 d by measuring the depletion of oxygen. Removal of ≥ 60% ThOD within a 10-d window within the 28-d period after 10% of ThOD has been reached means ready biodegradability (dashed line). The test was performed three times with duplicates ($n$ = 6).

# Publikation 3

Towards the design of organosilicon compounds for environmental degradation by using structure biodegradability relationships

Elisa Grabitz; Oliver Olsson; Klaus Kümmerer

2021

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# Towards the design of organosilicon compounds for environmental degradation by using structure biodegradability relationships

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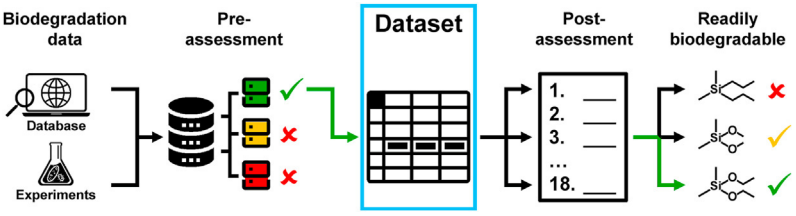
## HIGHLIGHTS

- Collection of biodegradation data of the ECHA database and own experiments.
- Grouping of the substances to derive general findings.
- 12 out of 182 organosilicon substances were readily biodegradable.
- Hydrolysis was a mandatory step prior to biodegradation.
- Groups like ethers, esters, oximes, amines, and amides can improve biodegradability.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Organosilicon compounds have numerous applications in consumer products. After entering the environment most of them are resistant against microbial degradation and they persist in the environment. Accordingly, they are ubiquitously present in the environment.

Therefore, better environmentally degradable organosilicon compounds are urgently needed. A systematic investigation of environmental degradability of organosilicon compounds allows to derive some general design principles, which in turn would enable chemists to reduce or better avoid environmental persistence of organosilicon compounds in the environment. Therefore, in this study, all organosilicon substances registered in the European Chemicals Agency (ECHA) database were evaluated for their environmental biodegradability. Results of own experiments with different organosilicon substances were added to extend the data basis. A dataset was generated. An assessment of all data was done and invalid data were excluded. The remaining 182 substances were grouped regarding their structure to derive general rules for the environmental biodegradability of organosilicon compounds. Non-biodegradable at all were for example cyclic, linear and branched siloxanes. Groups like ethers, esters, oximes, amines, and amides were prone to hydrolysis, which can result in readily biodegradable intermediates if they do not contain silicon functional groups anymore. This knowledge could be used for the design of better degradable organosilicon compounds as non-degradable substances should be avoided if they enter the environment after their usage.



## 1. Introduction

Organosilicon compounds have posed a challenge since they are used in many applications. Their production volume is very high. Typical applications are e.g. lubricants, adhesives, surfactants,

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coatings, sealants, and as defoamers or foam stabilizing agents and many others (Benkeser and Krysiak, 1953). Therefore, they are used in industrial applications and in consumer products like personal-, household-, and automotive care products (Allen et al., 1997). They were detected in every compartment of the environment, which confirms their persistence. Most organosilicon polymers, also named silicones, are not degradable in sewage treatment plants, a known fact since long (Hobbs et al., 1975). As the toxicity of organosilicon compounds is not finally understood, the European Chemicals Agency (ECHA) proposed the restricted usage of the cyclic siloxanes $D_4$, $D_5$, and $D_6$ in personal care products (ECHA, 2019). Besides the possible toxicity, the accumulation of persistent compounds in the environment is not preferable. If it were possible to achieve full mineralization (Kümmerer et al., 2018, 2019) and to prevent accumulation e.g. by using predetermined breaking points (Rücker and Kümmerer, 2013), this could be an important step towards more environmentally friendly silicones. Therefore, it is the key to understand the structure degradability relationships of organosilicon compounds.

Until now, silicone degradation is mostly reported under harsh conditions, e.g. acids and bases (De Buyl, 2001), high temperatures (Kim et al., 2007), application of Fenton's reagents (Wu et al., 2018), UV-light (Cai et al., 2016) or UV-light combined with $H_2O_2$, peroxydisulfate or peroxymonosulfate (Lin et al., 2020). Biodegradation data of silicones is very scarce. There are only a few studies investigating biodegradation in higher organisms in *vivo*, e.g. in lymph nodes of rats (Pfleiderer et al., 1999), in vocal prostheses (Slavícek et al., 2000) or in lacrimal system (Komínek et al., 1998) of humans. Biodegradation in rats was ascribed to oxidation and hydrolysis reactions of the polymer. The authors found out that the degradation rate is slower for polymers than for oligomers (Pfleiderer et al., 1999). Slavícek et al. investigated implanted prostheses after different time intervals and isolated micrococcus as a silicones assimilating species, which grows on the prosthesis (Slavícek et al., 2000). In the lacrimal system of humans, no biodegradation of siloxanes was observed (Komínek et al., 1998). Another study from Rościszewski et al. investigated the biodegradation of various polyorganosiloxanes under the influence of different bacterial strains. The biodegradability of the substances was in relation to their structure, composition, and the type of bacteria (Rościszewski et al., 1998), but their conclusions were contradictory. Rücker and Kümmerer (2013) analyzed hydrolysis rates in water and resumed that some Si—O bonds hydrolyzed fast and Si—Cl and Si—N bonds hydrolyzed very fast. Grabitz et al. (2020a, 2020b) investigated the biodegradability of different organosilicon compounds in tests simulating environmental conditions. They found that organosilicon compounds, which are benzene derivatives were not biodegradable but hydrolyzable and photodegradable (Grabitz et al., 2020a). An amino group in *para*-position at the aromatic ring improved the photodegradability, but not the biodegradability. In another study (Grabitz et al., 2020b) the environmental biodegradability of organosilicon compounds was compared with their carbon analogues to understand the influence of silicon in organic compounds. One organosilicon substance was found to be better degradable than its carbon analogue. First, it was hydrolyzed and one of the hydrolysis products was biodegraded (Grabitz et al., 2020b). However, outside of these studies, there is no summary and no interpretation of a bigger dataset of organosilicon compounds with respect to structure biodegradability relationships.

Therefore, the main aim of this study was to develop a dataset with reliable information on environmental biodegradability of organosilicon compounds. On the one hand a comprehensive review of organosilicon compound data in the ECHA database was done to get an overview of existing biodegradation data. The ECHA database (ECHA, 2020b) is a summary of data of all registered substances in the European Union, which contains substances from a production quantity of at least one ton per year. This database was chosen because literature data of organosilicon compounds is very scarce and partially contradictory. Another advantage of this database is the accessibility for each person with connection to the World Wide Web. Bioaccumulation data (Petoumenou et al., 2015), ecotoxicity data (Cesnaitis et al., 2014; Saouter et al., 2019), and acute fish toxicity data (Austin et al., 2015) from the ECHA database were successfully used in research. This is the first time that biodegradation data from the ECHA database were used for the environmentally benign design of organosilicon compounds.

On the other hand, biodegradation data were generated in our lab using standardized test settings to extend the dataset. Thereby, the impact of diverse functional groups regarding biodegradability and stability in aqueous solutions for further 54 organosilicon compounds was studied for the first time in two Organization for Economic Co-operation and Development (OECD) conform tests investigating ready biodegradability (OECD 301D and 301 F). In total, results of previous studies (Grabitz et al., 2020a, 2020b; Rücker and Kümmerer, 2013), own hitherto unpublished data from lab experiments and the data from the ECHA database were used to create the dataset. For data structuring, the substances were grouped according to their structural properties. After the assessment, the dataset was used to identify links between structural features and biodegradability to derive general findings that can be used for the future design of environmentally benign organosilicon compounds.

## 2. Materials and methods

In the following, a workflow is given in Fig. 1. It shows the procedure how the dataset was generated and assessed. The biodegradation data were obtained from two sources: a database of the ECHA and data from biodegradation experiments in our lab. Some were generated within this study and others within previous biodegradability studies of organosilicon compounds employing the same tests as published in Grabitz et al. (2020a), Grabitz et al. (2020b), Rücker and Kümmerer (2013). All accessible data were categorized according validity and reliability. After the elimination of non-conforming data, the remaining substances were assessed by grouping structure and biodegradability relationships.

### 2.1. Data gathering and assessment of the European Chemicals Agency database

The ECHA database provides data about different properties and information including environmental fate and degradation pathways. The dataset obtained from the ECHA database had in total 1134 entries for organosilicon compounds, using the search terms "sila" (469 entries), "silo" (100 entries), "silyl" (307 entries) (May 20, 2020), and "sili" (258 entries) (August 4, 2020).

The used data belong to the subsection "Biodegradation in water: screening test". The biodegradation data were manually extracted from the registration dossiers of the substances. The number of biodegradation endpoints per substance belong to the information, which were provided from the registrant. For some substances only the biodegradation rate in percent is provided and for some substances more than one test result and other validation criteria were given. Biodegradation data from the database were suitable for the dataset if the test name, test duration, test parameter, biodegradation rate and reliability (1 or 2 in Klimisch rating (Klimisch et al., 1997)) were reported.

Within the pre-assessment, overlaps of the entries because of

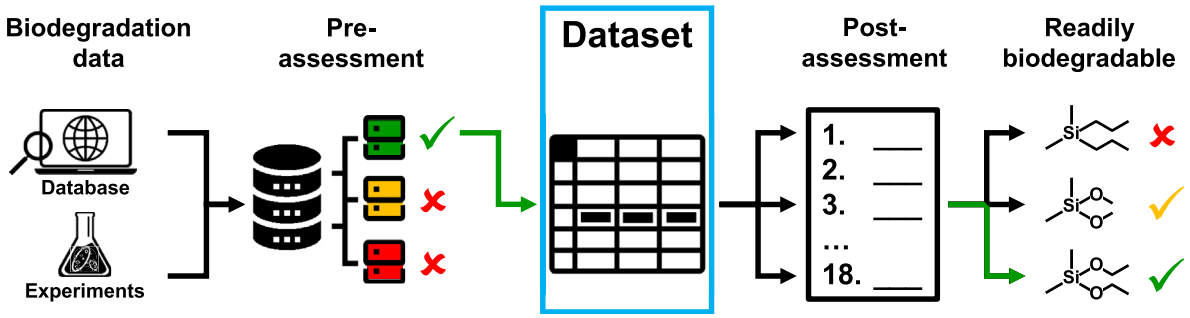



**Fig. 1.** Workflow for creating the dataset and for deriving findings. Biodegradation data came from the ECHA database and from lab experiments. The selection was made according to validation criteria and the quality of information. Only valid data were used for the dataset. The substances were grouped and analyzed to derive findings regarding their biodegradability.

IUPAC, trivial, or product names and some silicon-free substances were checked and the dataset was corrected accordingly and overlaps were eliminated. Some product names include the syllables "sila" and "silo" even if they do not contain silicon. One substance can have more than one entry because they can be registered as full registration, intermediate, and NONS (notification of new substances). Full registrations fulfill mostly the criteria for the dataset. Intermediate and NONS registrations have often data gaps. Intermediate registrations have other data requirements as full registrations as it is expected that intermediates stay in the system and were not exposed to the environment. These compounds were often unsuitable for the dataset. The substances can be also registered in different tonnage bands: 1–10 t $a^{-1}$, 10–100 t $a^{-1}$, 100–1000 t $a^{-1}$, and more than 1000 t $a^{-1}$, which results in different data requirements. Reaction mixtures, polymers and inorganic substances were excluded, only mono-constituent organic substances were chosen as the biodegradation data should represent specific structural elements. Read-across and calculated quantitative structure-activity relationship (QSAR) data were eliminated because only valid experimental data were used to derive findings.

### 2.2. Chemicals

All structures of the investigated substances with their specific numbers and CAS registry numbers, if available, are presented in Fig. S1 (supplementary material). The tested substances were obtained from ABCR GmbH (Karlsruhe, Germany), Acros Organics (Nidderau, Germany), Sigma Aldrich (Darmstadt, Germany), and Alfa Aesar (Karlsruhe, Germany) with the highest purity, which was available (≥95%). The polyether trisiloxanes Rewocare BDS15 and Break Thru S233 were obtained from Evonik Industries AG (Essen, Germany) and Silwet L-77 from Momentive Performance Materials GmbH (Leverkusen, Germany). Substances 2.1–2.9 (Schäfer and Troegel); 6.3; 6.4; 7.11, 7.12; 7.13; 10.2; 10.4; 10.6; 10.7; 10.11; 10.12, 16.5–16.8 were provided by the Nuremberg Institute of Technology Georg Simon Ohm, the Julius-Maximilians-University of Würzburg, the Fraunhofer Institute for Silicate Research ISC, and the University of Bielefeld. Dimethyl sulfoxide (DMSO, ≥ 99%) was purchased from Alfa Aesar (Karlsruhe, Germany). All compounds used for mineral medium in the biodegradation test had a purity of at least 98.5%. Ultrapure water was used to prepare aqueous solutions.

### 2.3. Aerobic biodegradation testing

The closed bottle test (OECD 301D) and the manometric respirometry test (OECD 301 F) were performed according to OECD guidelines (OECD, 1992a). They were chosen because they are very strict, easy to handle, and comparable with results from other databases as they are the most common tests to determine the ready biodegradability of substances important in a regulatory context. The biochemical oxygen demand during OECD 301D was monitored by measuring the dissolved oxygen concentration, using the established approach at our lab with a fiber optic oxygen meter (Fibox 3) of Friedrich et al. (2013). The OECD 301 F was conducted with an OxiTop® respirometer to determine the oxygen consumption due to the pressure decrease of carbon dioxide formed and adsorbed on sodium hydroxide. Effluent of a municipal wastewater treatment plant (AGL Lüneburg, Germany) was used as inoculum. The relevant parameters are listed in Table 1. A blind control without any substance, a positive control with sodium acetate, and a toxicity control with the test substance and sodium acetate and the test substance itself (duplicates) were included into the setup. For OECD 301 F, a sterile control with sodium azide was added. Because of the low solubility of the organosilicon substances and improved handling, 1% DMSO was added to the test solution. DMSO showed a low and consistent depletion of oxygen (0.6–2.2 mg $L^{-1}$). A low content of mineral medium was added for optimum bacterial growth (OECD, 1992a). The biodegradation rate in percent was calculated by using the theoretical oxygen demand of the tested substances and the measured oxygen consumption by microorganisms during 28 days. The formulas are written down in the OECD guideline (OECD, 1992a).

All validation criteria must be fulfilled to include the results to the dataset. These criteria were the following: The differences between the duplicates should not exceed 20% after 28 d, the blind control should not be higher than 1.5 mg $L^{-1}$ of the theoretical oxygen demand (ThOD), at the end of the test, the oxygen concentrations must be higher than 0.5 mg $L^{-1}$, and the positive control should have a biodegradation rate above 60% and the toxicity control of at least 25% on day 14. To claim a substance as readily biodegradable, the removal must be above 60% of ThOD within a 10-d window within the 28 d after 10% of ThOD has been reached (OECD, 1992a). Information integrated to the dataset was the test

**Table 1**
Specifications of both conducted biodegradation tests OECD 301D and OECD 301 F. ThOD – theoretical oxygen demand.

| Test | OECD 301D | OECD 301 F |
|---|---|---|
| Measuring system | Fibox 3 | OxiTop® |
| ThOD of test substance [mg $L^{-1}$] | 5 | 30 |
| Inoculum per liter test solution | 2 drops | 80 mL |
| pH | 7.4 | |
| Temperature [°C] | 20 ± 1 | |
| Duration [d] | 28 | |

method, test duration, parameter, reliability, and biodegradation rate. Since the results were recorded over a very long period, some substances were tested more often than others.

Some substances, which were present in the ECHA database were tested in our lab too. Results were compared according to the test method and the achieved biodegradation rate.

### 2.4. Dataset assessment

Besides the biodegradation data, the structure, substance class, SMILES code, CAS registry number, and information of the binding partners of the silicon atom were included to the dataset.

The substances were grouped according to their structural similarities to derive general findings regarding to their biodegradability. The grouping was performed manually because grouping with the software Schrödinger (Canvas version 4.3.013 downloaded from https://www.schrodinger.com/downloads/releases) and QSAR Toolbox (version 4.4.1 downloaded from https://qsartoolbox.org/download/) was not successful as both programs generated one large group consisting of up to 84 unique substances and around 25 groups consisting of 1–3 compounds.

Decisive for the grouping were similar leaving groups after hydrolysis (e.g. ethanol), functional groups (e.g. oximes, ketones), binding partners at the silicon atom (e.g. nitrogen, chlorine), or general properties (e.g. cyclic, branched, and linear). All groups are displayed in Table 2. There were some substances, which fit to more than one group according to their structure. These substances were included in the group, where the structural properties had the greater influence on the degradability based on experimental results. Some substances did not really fit to the generated groups. They were put into groups, which fit the most according to their properties.

Due to the OECD criteria for ready biodegradability, the substances were claimed as readily biodegradable, 10 day (10-d) window fail, or not readily biodegradable. Substances claimed as 10-d window fail are expected to have a moderate degradability in the environment as the biodegradation rate is only slower than for readily biodegradable substances. Subsequently, each group was checked regarding the potential biodegradation pathway. General statements were derived from the biodegradation behavior of the substances.

## 3. Results and discussion

### 3.1. Integration of data from ECHA

The ECHA database was checked according to the criteria mentioned in section 2.1. Inorganic substances, polymers and reaction masses were eliminated. The remaining substances were checked regarding reliability. There were 121 entries obtained via read-across, 25 entries without reliability, 8 entries, which were not assignable, and 4 biodegradation data based on QSAR evaluations. Data obtained via read-across were excluded because the quality of these data were inconsistent for similar structures and the dataset should contain only experimental data. The explanations due to the read-across data were very different for similar structures. Sometimes the test compound was compared with a structural analogue, which can hydrolyze. The silicon-free hydrolysis products (e.g. ethanol) are mostly biodegradable. Therefore, the test compound was declared as readily biodegradable. In other cases, the test compound was compared with compounds, which are similar after hydrolysis e.g. trimethyl silanol. Potentially biodegradable hydrolysis products were not involved in the decision of biodegradability of the test compound. Therefore, the test compound was declared as not readily biodegradable. Both approaches have their reasons, but it should be consistent. Data obtained via QSAR models were excluded, because it is often incomprehensible in the ECHA database, which QSAR model and which dataset was used to obtain the biodegradation results, let alone the reliability of prediction. After elimination of these entries, 142 reliable data points for biodegradation including replicates remained. In sum, 128 substances were included to the dataset from the ECHA database.

The reliable ECHA database entries for biodegradability rely on the following tests: OECD 301 A (11 substances), OECD 301 B (36 substances), OECD 301C (21 substances), OECD 301D (17 substances), OECD 301 F (40 substances) (OECD, 1992a), OECD 306 (OECD, 1992b, 2 substances), OECD 310 (OECD, 2014, 14 substances), OECD 302C (OECD, 2009, 1 substance), and a biodegradation test described by Bourquin (Bourquin, 1975, 1 substance). This means that there was only one test, which was not OECD conform. The test OECD 301 E was not performed for any substance. The tests of the OECD 301 and 310 guideline were used to determine ready biodegradability (OECD, 1992a, 2014). Test OECD 306 does not determine ready biodegradability, but it is used to get information about the degradation behavior of compounds in a marine environment (OECD, 1992b) and test OECD 302C is used to determine inherent biodegradability (OECD, 2009). An overview about the different tests and their conditions is provided in the supplementary material (Table S1).

Finally, the ECHA database provided 12 substances that were readily biodegradable, 10 substances that did not meet the 10-d window, but showed a high degree of biodegradation, 1 substance (13.22) that was degradable in a marine environment, and 105 substances that were not readily biodegradable according to the OECD criteria.

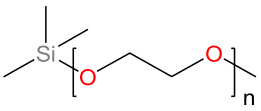
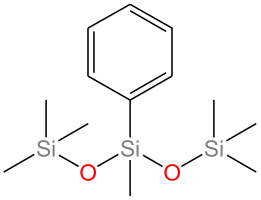
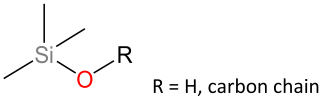
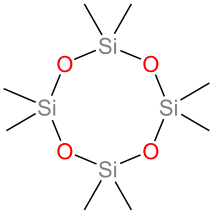
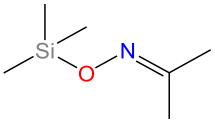
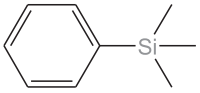
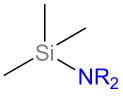
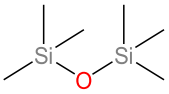
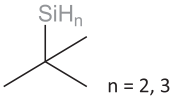
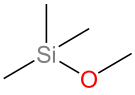
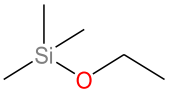
### 3.2. Dataset extension by aerobic biodegradation testing

According to the validation criteria for biodegradation tests (OECD, 1992a), 108 valid biodegradation endpoints (incl. replicates) for 60 substances could be obtained (Table 3). There were 48 substances tested in OECD 301D and 23 substances in OECD 301 F. 11 substances were tested in both tests. One substance (12.6) had a biodegradation rate above the threshold for ready biodegradability (60%) in OECD 301 F, but failed the 10-d window, and 59 substances were not readily biodegradable. Only 10 substances reached a biodegradation degree above 30%. The remaining substances showed less or no biodegradation. Negative values resulted from the calculation of the biodegradation rate. Results of blind controls were subtracted from the value received for the tested substance, respectively. This means that no biodegradation was observed. Mostly, the biodegradation rates obtained with OECD 301 F are higher than obtained with OECD 301D. The reason is the higher bacterial density and diversity in the test setup of OECD 301 F compared to OECD 301D. The more and the more diverse microorganisms are present in the test vessel, the higher the probability of degrading bacteria. However, non-biodegradable structures cannot be degraded with increased bacterial densities and diversities.

### 3.3. Comparison of data from own experiments with data reported in the ECHA database

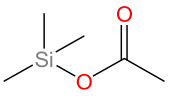
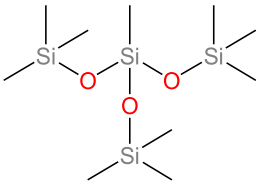
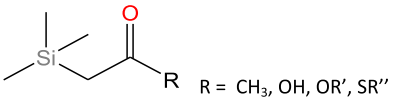
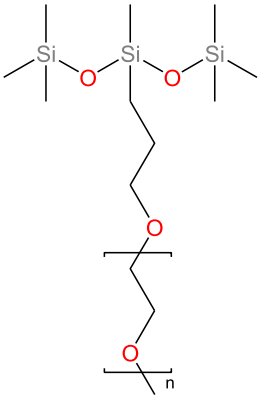
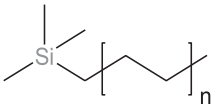
Six out of the 60 experimentally tested substances also have entries in the ECHA database. By comparing the differently generated data, conclusions can be drawn about the reliability of the ECHA data. The substances with data from both sources showed in sum low biodegradation, except substance 12.7, but no substance was readily biodegradable (Table 4). There were only 2 out of 6

**Table 2**
Overview of the generated groups including group number, group name, an example structure, and the amount of substances (AoS) per group.

| Group | Name | Example structure | AoS |
|---|---|---|---|
| **1** | Oligoethers |  | 3 |
| **2** | Aromatic trisiloxanes |  | 9 |
| **3** | O–$SiC_3$ |  | 4 |
| **4** | Cyclic siloxanes |  | 5 |
| **5** | Oximes |  | 4 |
| **6** | Organo-silanes (Si–$C_4$) |  | 7 |
| **7** | Aromatic organosilanes |  | 13 |
| **8** | Chlorides |  | 8 |
| **9** | Amines, amides (Si–N) |  | 11 |
| **10** | Linear siloxanes |  | 14 |
| **11** | Silanes (Si–H) |  | 3 |
| **12** | Methoxy siloxanes |  | 40 |
| **13** | Ethoxy siloxanes |  | 29 |

(*continued on next page*)

**Table 2** (*continued*)

| Group | Name | Example structure | AoS |
|---|---|---|---|
| **14** | Siloxane esters |  | 10 |
| **15** | Branched siloxanes |  | 6 |
| **16** | Ketones, carboxylic acids, esters |   | 8 |
| **17** | Polyether trisiloxanes |  | 3 |
| **18** | Longer carbon chain |  | 5 |

substances, which were tested in the same test (OECD 301D, ECHA and own lab). For substances 8.1; 9.2; 10.2; and 10.4 only one test was executed, respectively. Both ECHA and own results have one substance each (4.3 and 12.7), which has results of 2 different tests. For the tested substances of the ECHA database, 4 different biodegradation tests were executed (OECD 301 A, OECD 301D, OECD 310, and a test described by Bourquin (1975)) and in our lab, only 2 different tests (OECD 301D and OECD 301 F) were executed. Results of the different tests showed only slight differences in the biodegradation results. For 2 substances (9.2 and 12.7), the biodegradation rates from the ECHA database were a little bit higher than the results obtained in our lab, but leading to the same classification according to the OECD test guidelines: "not readily biodegradable". Slight differences resulted from different test settings (e.g. OECD 301 A vs. OECD 301D). In OECD 301 A, a higher amount of inoculum and of the test substance were used as in OECD 301D. Additionally, the amount of minerals was in OECD 301 A 10-times higher than in OECD 301D. The measuring principle is also different. In OECD 301D the oxygen demand is determined and in OECD 301 A, the DOC is determined and therefore the threshold for ready biodegradability classification is 70% instead of 60%.

Only a few substances were both tested in our lab and presented in the ECHA database. The biodegradation results were in the same order of magnitude, respectively. Thus, the data from the ECHA database seem to be a reliable source of biodegradation data. For better comparability, it would be good to apply one test only. The OECD 301D would be the most recommendable one, as it is very stringent due to the low bacterial density and diversity. This avoids false negatives, which is precautionary and again a fundamental principle of EU environmental policy and risk assessment.

### 3.4. Analysis of the complete dataset

In the ECHA database, biodegradation data came from unnamed study reports. No literature is cited because there is less literature about the biodegradation of organosilicon compounds. In this case, the registrant has to provide the necessary data.

Data from the ECHA database were generated between 1984 and 2019 (status of Aug 4, 2020, Fig. 2). Only 46 of the 254 data points of biodegradation were generated between 1984 and 1999, i.e. the majority of the data were generated after 2000. The chronological development of biodegradation results shows an accumulation of provided data in 1994, 2002, and 2017. Data from recent laboratory experiments are available for the period 2010–2019 (Fig. 2). These data represent, therefore, the most current data set on the biodegradability of organosilicon compounds. By far, most of the tests in our lab were performed in 2017, followed by 2018 and 2012.

The complete dataset includes 182 organosilicon substances with 212 different biodegradation test results, but 254 biodegradation endpoints incl. replicates. For 155 substances, only one kind of biodegradation test was done, for 24 substances two different tests were executed and for 3 substances three different biodegradation tests were performed (excl. replicates). The number of substances investigated in the different biodegradation tests is

**Table 3**
Overview of the biodegradation data of the 60 substances, which were tested according to OECD 301D and OECD 301 F in our lab. Besides the biodegradation rates in percent (<30% (orange), 30–60% (yellow), >60% (green)), the number of the substance is displayed. One endpoint consists of two parallel determined results (n = 2). If more than one test was conducted, means ± standard deviation are given (n = 4: 2.3; 2.5; 7.6; 7.8; 7.9; 10.7; 11.3; 13.1 [301 F]; 16.4; 17.2 [301 F]; 17.3 [301D + 301 F]; n = 6: 12.17; 12.25; 17.1 [301D]; 17.2 [301D]; n = 8: 9.1; 12.16; 17.1 [301 F]; n = 10: 12.7; 13.1 [301D]).

| No. | OECD 301D [%] | OECD 301F [%] | No. | OECD 301D [%] | OECD 301F [%] |
|---|---|---|---|---|---|
| 2.1 | −3 | | 10.8 | −3 | |
| 2.2 | 5 | | 10.11 | −1 | |
| 2.3 | 21±17 | | 10.12 | 0 | |
| 2.4 | 0 | | 11.3 | | 0±2 |
| 2.5 | 12±1 | | 12.6 | | 62 |
| 2.6 | 8 | | 12.7 | 33±8 | 47 |
| 2.7 | 3 | | 12.13 | | 22 |
| 2.8 | 4 | | 12.16 | 19±5 | |
| 2.9 | 4 | | 12.17 | 31±5 | |
| 3.3 | 8 | | 12.18 | | 13 |
| 4.3 | 0 | | 12.25 | 26±4 | |
| 6.3 | 10 | | 13.1 | 41±9 | 35±23 |
| 6.4 | 10 | | 13.3 | | 42 |
| 6.7 | −5 | | 13.16 | | 21 |
| 7.6 | 3±2 | −7 | 13.17 | | 24 |
| 7.7 | −2 | −10 | 14.7 | −2 | |
| 7.8 | 0±2 | 8 | 14.8 | | 34 |
| 7.9 | 6±8 | −4 | 14.9 | | 24 |
| 7.10 | −2 | −3 | 14.10 | | 31 |
| 7.11 | 5 | | 16.1 | 5 | |
| 7.12 | 15 | | 16.2 | −5 | |
| 7.13 | 10 | | 16.3 | | −3 |
| 8.1 | −2 | | 16.4 | | 25±5 |
| 8.8 | −2 | | 16.5 | 8 | |
| 9.1 | 34±16 | 43 | 16.6 | 16 | |
| 9.2 | −3 | | 16.7 | 38 | |
| 10.2 | −3 | | 16.8 | 34 | |
| 10.4 | 1 | | 17.1 | 8±7 | 32±6 |
| 10.6 | −2 | | 17.2 | 2±0 | −3±4 |
| 10.7 | 0±1 | | 17.3 | 8±6 | 42±4 |

**Table 4**
Biodegradation data in percent of the 6 substances, which are registered in the ECHA database and tested in experiments in our lab. Blue highlighted values came from ECHA and pink highlighted values are from own experiments. Biodegradation data were obtained using the following tests: OECD 301 A, OECD 301D, OECD 301 F, OECD 310 and a test described by Bourquin (1975). The number and CAS registry number (CAS) is presented in the first columns.

| | | ECHA | | | | Own lab | |
|---|---|---|---|---|---|---|---|
| No. | CAS | OECD 301A [%] | OECD 301D [%] | OECD 310 [%] | Other [%] | OECD 301D [%] | OECD 301F [%] |
| 4.3 | 556-67-2 | | | 4 | 0 | 0 | |
| 8.1 | 75-77-4 | | | 0 | | −2 | |
| 9.2 | 999-97-3 | | 15 | | | −3 | |
| 10.2 | 2627-95-4 | | 1 | | | −3 | |
| 10.4 | 107-51-7 | | | −4 | | 1 | |
| 12.7 | 1067-25-0 | 54 | | | | 33±8 | 47 |

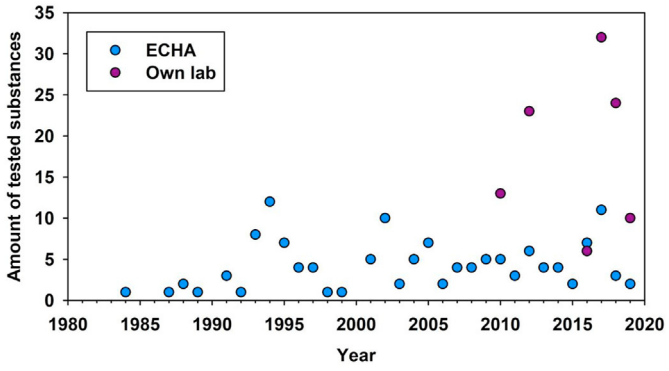



**Fig. 2.** Time line of the experiments for the generation of the biodegradation data. Data from ECHA are displayed as blue dots and data from our own experiments as pink dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

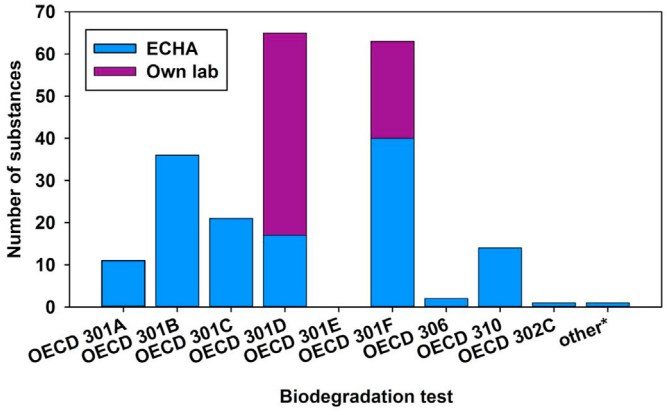



**Fig. 3.** Number of organosilicon substances, which were tested in various biodegradation tests. Data came from the ECHA database (blue bars) and from experiments of our lab (pink bars). *This test was described by Bourquin (1975). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

shown in Fig. 3. In total, nine different biodegradation tests were performed to generate the data. Eight of these tests were OECD conform, which means that they follow standardized guidelines according to the conduction, the source of inoculum, and the validation criteria. Most of the substances were tested with biodegradation tests from the OECD 301 series. Only 18 substances were tested in other tests (OECD 306, OECD 310, OECD 302C, and a test described by Bourquin (1975)). The biodegradation tests OECD 301D and OECD 301 F were the most often performed tests. This trend is towards the standardization of test procedures. We recommend that only selected standardized test procedures for ready and inherent biodegradability should be included into the ECHA database. Regarding handling, comparability, and strictness, the tests OECD 301D and OECD 301 F are good candidates for this suggestion and for filling this data gap.

From a total of 254 biodegradation rates, 154 rates were below 30% of biodegradation, 70 were between 30% and 60%, and 30 were higher than 60%. This means that only 11.8% of the biodegradation results have the potential to claim a substance readily biodegradable, which is in agreement with the finding that many organosilicon substances can be detected in the aquatic environment. Since the biodegradation rates must always be considered in relation to the test, the validation criteria, and the principle of measurements, it is not possible to conclude that all 30 values above 60% mean that these substances are readily biodegradable. In fact, only 12 substances are readily biodegradable according to the OECD criteria, but another 11 substances had biodegradation rates above 60% (ThOD) or 70% (dissolved organic carbon, DOC), but failed the 10-d window. This means that the biodegradation rate was too slow for classifying the substances as readily biodegradable. However, it can be expected that these substances are degradable in the environment within reasonable time periods. There are therefore of

interest for deriving design rules. The remaining substances were analyzed in tests, where the DOC was measured and the rate was between 60 and 70% or in tests, where the marine biodegradability (OECD 306) was determined. The threshold for claiming the substance readily biodegradable by measuring the DOC is 70% (OECD, 1992a).

If one substance was tested in more than one test (incl. replicates), differences in the tests results of about 20–40% were determined only for 10 substances. This means that the range of biodegradation rates for one substance was small. The other results have smaller deviations. Differences of about more than 40% could not be observed.

### 3.5. Structural features and environmental biological degradability

The 182 substances of the dataset were grouped as described in section 2.4. The groups and some additional information regarding the substances in the groups are presented in Table 5. In sum, 18 groups could be identified. Group 1 contains oligoethers, group 2 aromatic trisiloxanes with substituents in *para*-position, group 3 compounds with O–$SiC_3$, which fit to no other group, group 4 cyclic siloxanes, group 5 oximes, group 6 organosilanes, group 7 aromatic organosilanes, group 8 organosilanes with at least one Si–Cl bond, group 9 amines and amides, group 10 linear siloxanes, group 11 silanes, group 12 methoxy siloxanes, group 13 ethoxy siloxanes, group 14 siloxane esters, group 15 branched siloxanes, group 16 organosilanes with keto, carboxylic acid, and ester groups in the carbon chain, group 17 polyether trisiloxanes, and group 18 organosilanes with longer aliphatic carbon chains. The groups contain 3–40 substances. There are seven groups with 3–5 substances (groups 1, 3, 4, 5, 11, 17, and 18), six groups with 6–10 substances (groups 2, 6, 8, 14, 15, and 16), three groups with 11–15 substances (groups 7, 9, and 10), and the two largest groups with 29 and 40 substances (groups 12 and 13).

There are 5 groups, which contain readily biodegradable classified substances (groups 1, 9, 12, 13, and 14), and 5 slightly different groups, which contain substances being biodegradable in an OECD test, but failing the 10-d window (groups 1, 9, 12, 13, and 18). Groups with readily biodegradable substances contain often substances, which also showed low biodegradation rates (except group 1). The ready biodegradability was determined via the tests OECD 301 A (3 substances), OECD 301 B (3 substances), OECD 301C (1 substance), OECD 301D (1 substance), OECD 301 F (4 substances) and OECD 310 (2 substances).

Fig. 4 illustrates the distribution of biodegradation rates within the groups. The box plot diagram was chosen as it displays the middle 50% of the values as boxes and the range without outliers as whiskers. Based on this box plot diagram, it is obvious that some groups comprise only substances, which were not at all biodegradable (groups 2, 3, 4, 6, 7, 8, 10, and 15). Substances 2.3, 7.5, and 10.14 are exceptions within these groups, but they contain besides the specific silicon part of the molecule, which is the basis for the attribution to the group, a bigger carbon moiety, which is partially biodegradable. This indicates, however, that the silicon related structures are a challenge for biodegradation.

Group 2 contains aromatic trisiloxanes being very stable against biodegradation. It was hypothesized that different functional groups could enhance the biodegradability of recalcitrant molecules as the functional groups could act like a starting point for a microbial reaction (Alexander and Lustigman, 1966; Boethling et al., 2007). However, at least in case of the compounds studied here this was not the case. Enhanced non-biotic degradation in dependence of functional groups was only observed during photolysis experiments for analogue structures, which could be related to a shift in the absorbance spectrum of the substance (Grabitz et al., 2020a). The shift resulted in an improved absorption due to a better overlap of the emission spectrum of the irradiation source and the absorption spectrum of the tested compound.

Substances from group 3 contain the structural element O–$SiC_3$. For these substances, hydrolysis of the Si–O bond is expected (Bains and Tacke, 2003). As the hydrolysis products of substances of this group (e.g. trimethyl silanol) are not readily biodegradable (ECHA, 2020a), the non-biodegradability of the parent compounds can be explained by this.

The cyclic siloxanes of group 4 were also not biodegradable, which is supported by Graiver et al. (2003). The limited biodegradability also explains the presence of these substances in the environment, which is caused by their persistence (see section 1).

Group 6 contain organosilicon compounds with the structural element $SiC_4$. The structural element $SiC_4$ can be regarded as structural analogue to the quaternary carbon atom, which is known to hinder biodegradation (Boethling et al., 2007).

Substances of group 7 bear at least one aromatic ring at the silicon atom. These compounds are very stable against microbial

**Table 5**
Overview of the generated groups including group number, group name, the amount of substances (AoS) per group, the number of substances, which are readily biodegradable (RB) according to all OECD conform biodegradation tests, the number of substances, which showed the 10-d window fail (10-DWF), the mean biodegradation within the group, and the standard deviation (SD).

| Group | Name | AoS | RB | 10-DWF | Mean | SD |
|---|---|---|---|---|---|---|
| **1** | Oligoethers | 3 | 2 | 1 | 83 | 13 |
| **2** | Aromatic trisiloxanes | 9 | | | 8 | 11 |
| **3** | O–$SiC_3$ | 4 | | | 3 | 3 |
| **4** | Cyclic siloxanes | 5 | | | 1 | 2 |
| **5** | Oximes | 4 | | | 17 | 18 |
| **6** | Organo-silanes (Si–$C_4$) | 7 | | | 5 | 6 |
| **7** | Aromatic organo-silanes | 13 | | | 4 | 9 |
| **8** | Chlorides | 8 | | | −1 | 3 |
| **9** | Amines, amides (Si–N) | 11 | 1 | 2 | 33 | 29 |
| **10** | Linear siloxanes | 14 | | | 3 | 12 |
| **11** | Silanes (Si–H) | 3 | | | 21 | 27 |
| **12** | Methoxy siloxanes | 40 | 2 | 4 | 35 | 18 |
| **13** | Ethoxy siloxanes | 29 | 5 | 2 | 44 | 25 |
| **14** | Siloxane esters | 10 | 3 | | 40 | 32 |
| **15** | Branched siloxanes | 6 | | | 0 | 2 |
| **16** | Ketones, carboxylic acids, esters | 8 | | | 16 | 16 |
| **17** | Polyether trisiloxanes | 3 | | | 16 | 16 |
| **18** | Longer carbon chain | 5 | | 1 | 46 | 15 |

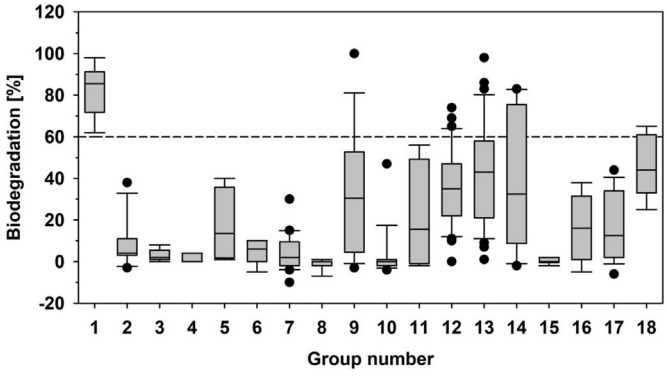



**Fig. 4.** Grouping of all substances with valid biodegradation data. The boxes with the median (black line within the box) symbolize the middle 50% of all values in each group. The whiskers determine the range of data without outliers (black dots). Negative values resulted from the calculation of the biodegradation via subtraction of the blind control meaning no biodegradation was observed. The dashed line symbolizes the threshold for ready biodegradability obtained via the measurement of the oxygen demand.

degradation (Grabitz et al., 2020a).

Group 8 contains substances, which have at least one Si—Cl bond. This group is comparable with group 3 as after hydrolysis similar products (e.g. trimethyl silanol) are formed by hydrolysis (ECHA, 2020a), which are not biodegradable. In contrast to group 3, no organic molecules are released, only hydrochloric acid. As these substances were mostly used as intermediates during siloxane synthesis, environmental concerns are limited to accidental release during manufacturing processes (Allen et al., 1997).

Substances from group 10 have similar structural elements like group 4. In group 10, only linear siloxanes were included. Under specific conditions, they are able to hydrolyze and condensate to form oligomers (Issa and Luyt, 2019), but the oligomers are not biodegradable.

The last group, which is not biodegradable at all, is group 15 consisting of branched siloxanes. This group showed similar biodegradation behavior like the cyclic and linear siloxanes of groups 4 and 10. Substances of these eight groups (groups 2, 3, 4, 6, 7, 8, 10, and 15) were definitely not biodegradable. It should be avoided that these substances enter the environment as they or their products of hydrolysis do not biodegrade there. If such compounds are applied in closed systems without any chance to enter the environment, e.g. pure business-to-business products, which do not enter the consumer market, they are ideal candidates as then these substances could be used for a long time avoiding new synthesis.

Substances of the ten other groups showed moderate biodegradability (groups 1, 5, 9, 11, 12, 13, 14, 16, 17, and 18). This is often due to the presence of hydrolyzable bonds resulting in hydrolysis products that partially biodegrade. For these products, the rules known for the design of organic carbon compounds for environmental degradability can be applied for reducing the persistence of organosilicon compounds in the environment. Biodegradable hydrolysis products are e.g. short chained linear alcohols, carboxylic acids, ketones, and aldehydes, respectively (Boethling et al., 2007; ECHA, 2020a). Substances of the groups 1, 9, 12, 13, 14, 16, and 17 hydrolyze to such products. Group 1 contains oligoethers, which could hydrolyze. In this case, the Si-free hydrolysis products (alcohols) can undergo biodegradation. Substances of group 5 belong to the group of oximes. The biodegradability of these substances depends on the oxime set free by hydrolysis of the organosilicon compound. The more branched the oxime is, the lower the biodegradability of the compound. This is well known from other organic molecules – the higher the degree of branching at carbon or nitrogen atoms, the lower the biodegradability (Boethling et al., 2007).

Group 9 includes substances having a Si—N bond. This bond hydrolyzes fast (Rücker and Kümmerer, 2013) under OECD 301D conditions to form an amine or amide and a silanol. If the amine or amide is biodegradable (e.g. cyclohexyl amine (ECHA, 2020b)), a certain biodegradability of the parent compound results.

Substances of group 12 and 13 bear methoxy or ethoxy groups at the silicon atom, respectively. Via hydrolysis, methanol or ethanol are released, which were both readily biodegradable (Birch and Fletcher, 1991; Wagner, 1976). In this case, the biodegradation rate of the parent compound is mainly the contribution of the biodegraded methanol or ethanol.

For group 14, similar to the release of alcohols by hydrolysis, carboxylic acids are formed with contact to water as the substances of this group have ester functions at the silicon atom. Many carboxylic acids are known to be biodegradable (e.g. acetic acid or benzoic acid (ECHA, 2020b)).

Group 16 comprises substances with carbonyl functions in the molecule, but not directly bonded to the silicon atom. If the carbonyl function is terminal, the biodegradation rate is very low. However, if the carbonyl function is in the middle of the molecule, e.g. ester or thioester, they could hydrolyze and the formed product could be biodegraded (Boethling et al., 2007).

Substances of group 17 are polyether trisiloxanes, which could hydrolyze or oxidize to a certain degree to form diols like substances of group 1, but the trisiloxane moiety, which is also a product of hydrolysis, behaves like substances of group 10 and is not biodegradable. Substance 17.1 was tested previously and showed more than 70% of biodegradation in OECD 301 F (Kuppert, 2013), but it was not possible to reproduce this result with our test setting of the OECD 301 F and the used inoculum. We assume that the reason for the poor reproducibility could be due to microorganisms adapted to siloxanes, which were not present in our inoculum and which is not the normal situation in the environment neither allowed for valid test results according to OECD test guidelines.

There was one group of organosilicon compounds (group 18), which did not have any hydrolyzable bond, but showed moderate biodegradability. These substances have longer carbon chains. It is assumed that these chains were degraded via $\beta$-oxidation. Normally, fatty acids were degraded by this mechanism (Schulz, 1991) starting from the methyl end. It is plausible that this also works for longer alkyl chains. Boethling et al. confirmed this assumption as they reported that longer alkyl chains can undergo this mechanism (Boethling et al., 2007). It is also known that e.g. *E. coli* is able to degrade fatty acids by $\beta$-oxidation (Schulz, 1991) and *E. coli* is often part of the effluent (Anastasi et al., 2012) or the bacterial mass in the aerobic treatment in sewage treatment plants. Both the active sludge as well as effluent from sewage treatment plants are used as a source for the inoculum for biodegradation tests, including the ones we employed in this study.

Summarizing, substances, which are readily or moderately (incompletely) biodegradable, very often contain functional groups that are able to hydrolyze. Depending on the position of the hydrolyzable bond and the generated products, some compounds are better degradable than others. If the hydrolyzable bond is directly connected to the silicon atom, the released products have mostly a higher carbon content. If these hydrolysis products are readily biodegradable, they are the reason for an improved biodegradability of the parent compound. Up to Si—OH and Si—$CH_3$, common reactions for carbon compounds can occur. However, complete mineralization by microorganisms will not be possible due to these organosilicon structures. *Ortho*-silicic acid is a preferable final product as in this case a natural inorganic product of hydrolysis results in addition to organic molecules (e.g. alcohols), but very often Si—C bonds remain in the molecule. The hydrolysis susceptible bonds are Si—O and Si—N. Functional groups, which could be at the silicon atom are ethers, esters, oximes, amines, and amides. The more Si—N and/or Si—O bonds the molecule has, the more degradable hydrolysis products are released, the better the biodegradability. This is due to the larger proportion of such substituents in the molecular weight of an organosilicon compound and thus the larger proportion of the molecule that is degradable after hydrolysis.

If the organosilicon compound bears a terminal functional group, the possibility that this compound is readily biodegradable is lower as if the functional group is directly connected to the silicon atom. This could be explained by the smaller carbon moiety of the degradable hydrolysis products or that no products of hydrolysis were formed, which can be biodegraded.

### 3.6. Strengths and limitations of the use of data from the ECHA database

The data situation for organosilicon substances is in need of

improvement because there were a lot of substances without reliable experimental data. For registrations of intermediate substances in the ECHA database, the registrant do not have to provide so much data and for full registrations, read-across data can be submitted. However, the quality of read-across data is often not consistent. Therefore, read-across data should be checked extensively by the ECHA during the registration process. It would be helpful for the registrant if some general rules existed for the generation of read-across data.

When experimental data was available, the used tests were mostly OECD conform. This is a good trend in the quality of experimental biodegradation data. In the best case, only the OECD 301D test would be performed in the future as this test is the most stringent one regarding the amount of inoculum and the validation criteria. This would also improve the comparability of the results.

Some advantages of the ECHA database are that it is free of charge and everybody connected to the World Wide Web have access to these data. Registrants are also responsible for keeping the data up to date. To ensure this, the ECHA will review 20% of the registration dossiers in future instead of 5% as before (ECHA, 2020a).

The used approach is limited by the ECHA registrations. Compounds, of which less than one ton per year is produced, are not registered in the ECHA database. Compounds, which are not imported to the European Union, but used e.g. in the United States of America or China, are not included in the ECHA database. A globally used database can solve a part of the problem. Also, not all data and references was public. The deposited study reports were only accessible for people and organizations (e.g. German Federal Institute for Risk Assessment), who are authorized to proof the database entries.

Another disadvantage is that only data is available that is provided by the registrant. The quality and reliability respectively of the provided data is primarily assessed by the registrant.

## 4. Conclusion

This is the first time that such a huge dataset for the biodegradability of organosilicon compounds was generated, which is quite surprising given the huge amounts and variety of organosilicons produced, used in everyday life, and their ubiquitous presence in the environment. It is also the first time that these substances were grouped according to their structural similarities to derive findings about the biodegradability of organosilicon substances. The dataset and the grouping extends the existing knowledge about the environmental biodegradability of organosilicon substances. This enabled the assessment of the groups according to ready biodegradability, which allowed the identification of structures that enhance biodegradation. For ready biodegradability, preceding hydrolysis of the parent compound is necessary. The silicon-free hydrolysis products were often readily biodegradable according to the knowledge on the biodegradability of organic carbon compounds, whereas the silicon-containing products persist. In contrast, groups could be identified, which are not biodegradable at all (e.g. linear, branched, and cyclic siloxanes). These substance classes should be avoided if they enter the environment within their life cycle.

The generated knowledge from this study could be used to design better environmentally degradable organosilicon compounds. The results generated in our lab represent a good contribution to the state of the art and generate a decisive added value with regard to the degradability of these compounds. Nevertheless, experimental data on organosilicon compounds should be extended, especially through standardized tests to obtain better comparability of the biodegradation results, to enlarge the database, and its applicability domain. Furthermore, it could be shown that complete mineralization can only occur if no methylsil(ox)ane backbone is present. Long-term, alternative basic structures are needed that enable complete degradation in the environment.

## Credit author statement

Elisa Grabitz: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization; Oliver Olsson: Conceptualization, Writing – review & editing, Supervision; Klaus Kümmerer: Conceptualization, Resources, Writing – review & editing, Supervision

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130442.

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# Supplementary material

**Title:** Towards the Design of Organosilicon Compounds for Environmental Degradation by Using Structure Biodegradability Relationships

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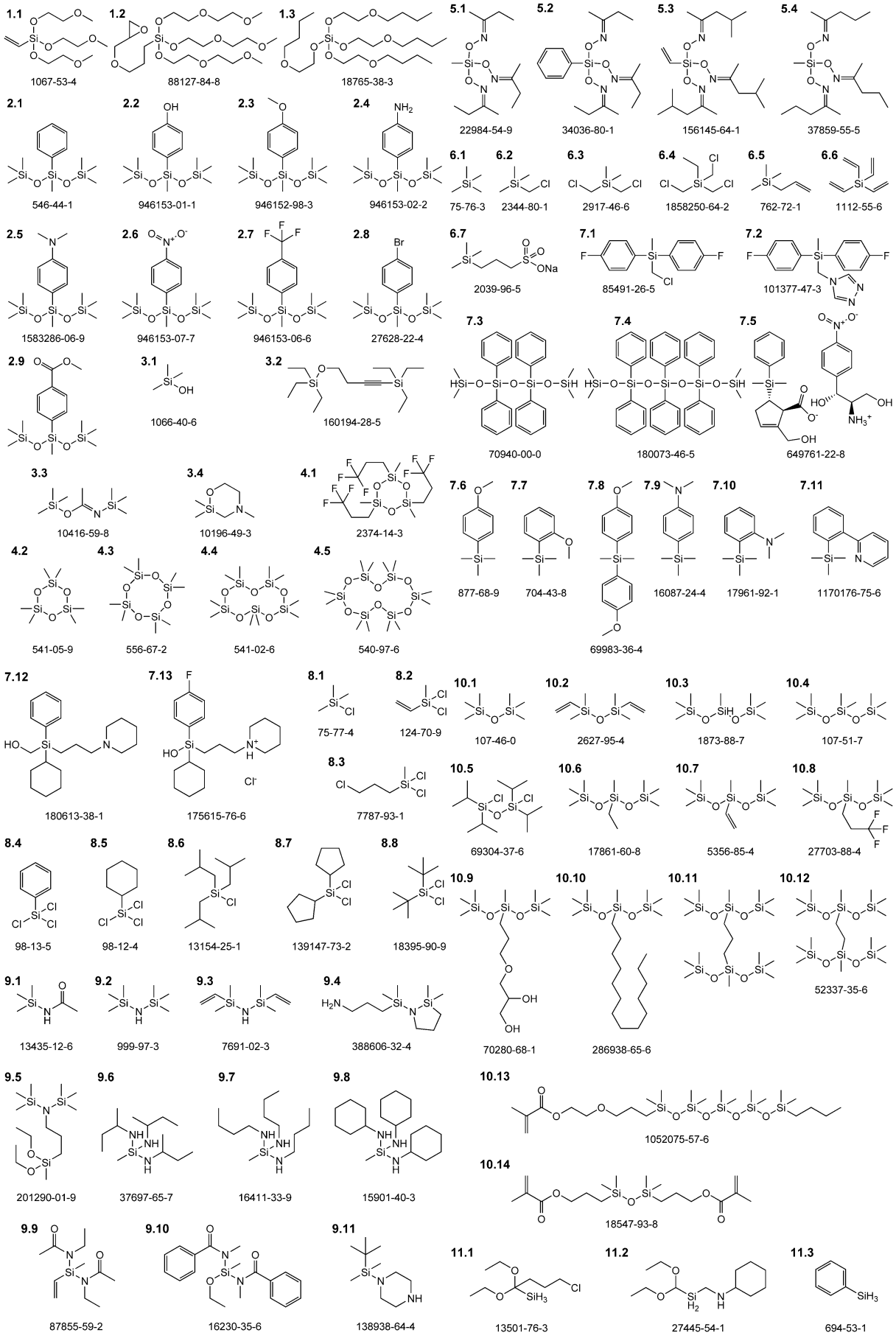
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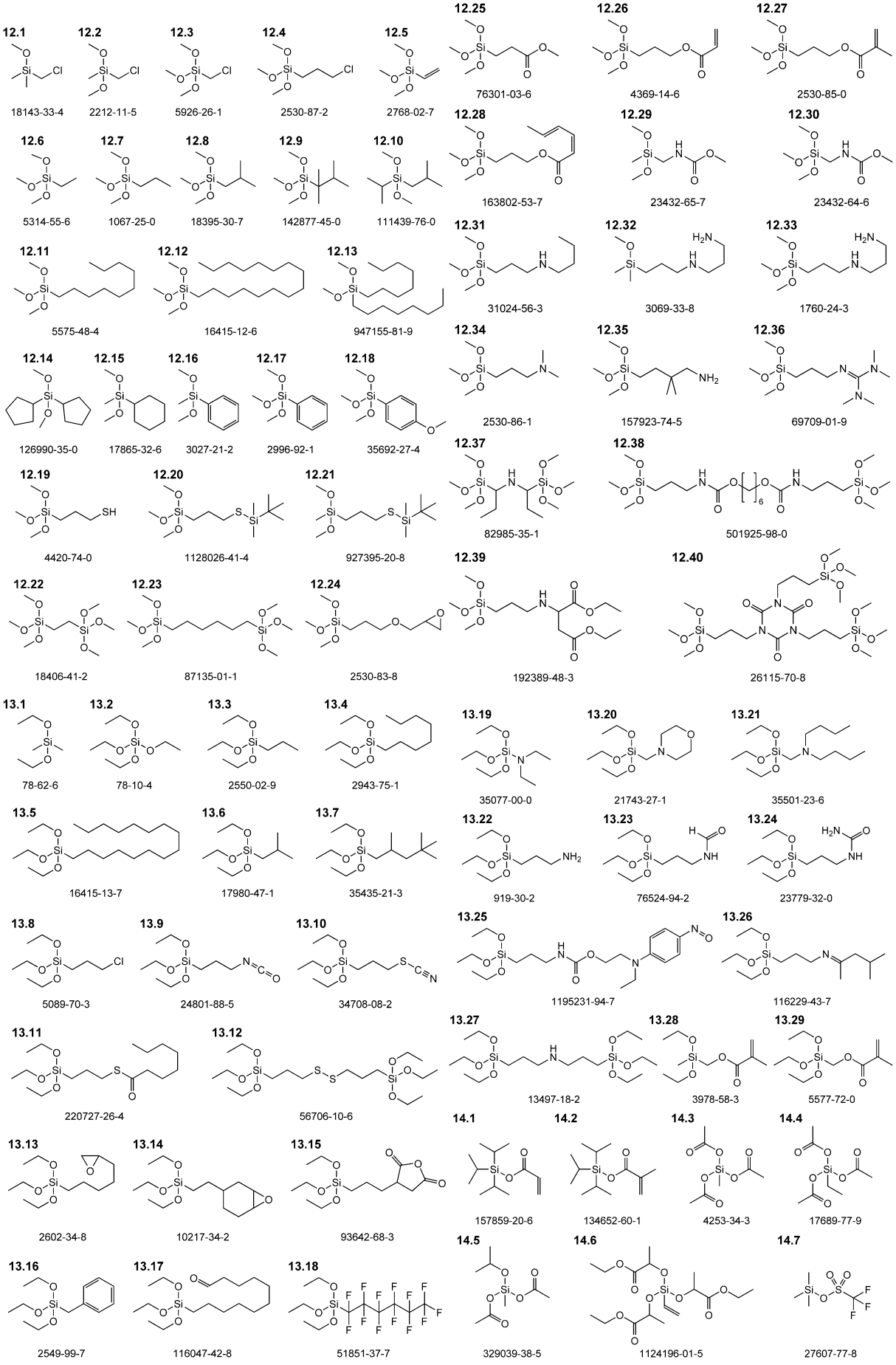
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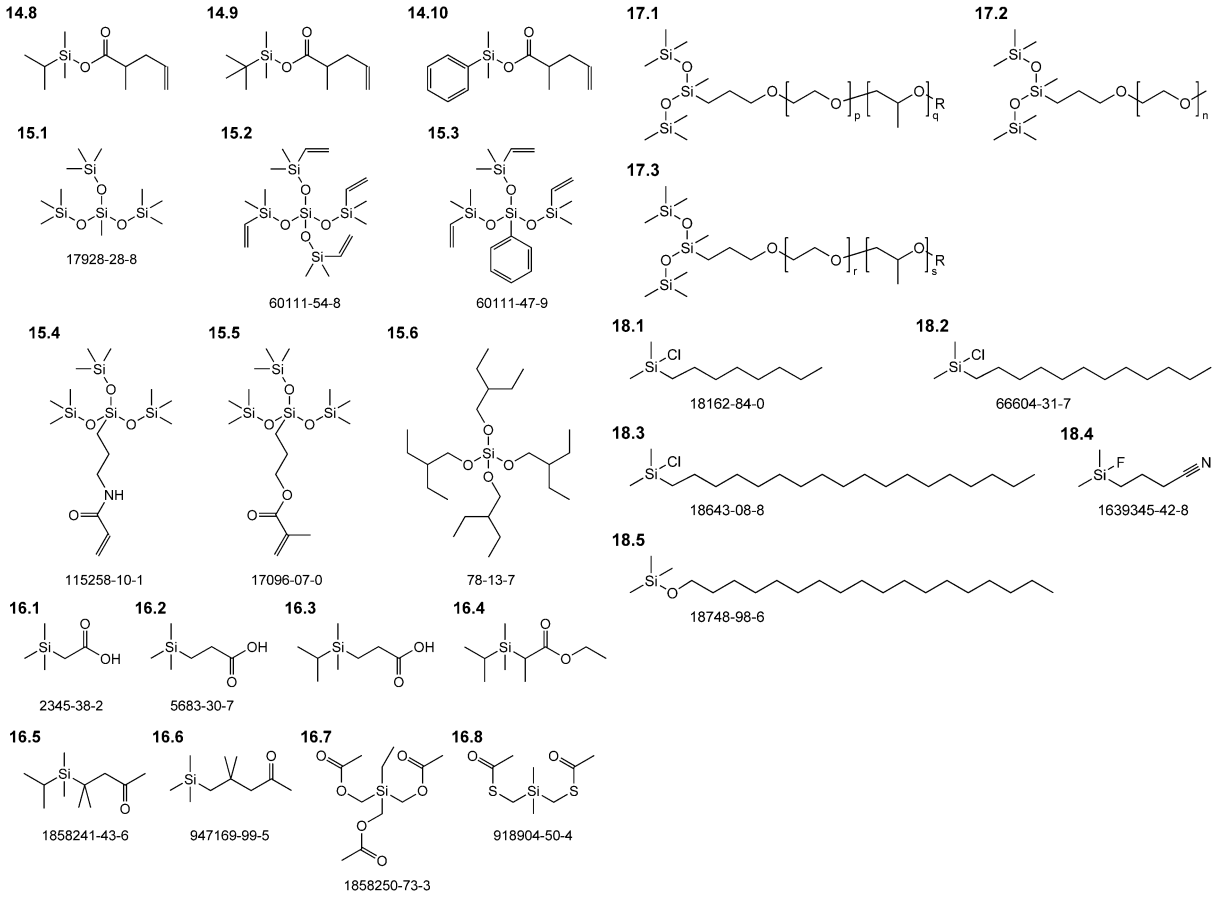


Figure S1: Structural formulas of all investigated compounds including their number and their CAS registry number, if available.

Table S1: Overview of the conditions of the biodegradation tests according to Bourquin, 1975; OECD, 1992a, OECD, 1992b, OECD, 2009, and OECD, 2014. AoS – Amount of Substances, DOC – Dissolved Organic Carbon, ThOD – Theoretical Oxygen Demand, SS – Suspended Solids, * – Not available

| **Test** | **OECD 301A** | **OECD 301B** | **OECD 301C** | **OECD 301D** | **OECD 301F** | **OECD 306** | **OECD 310** | **OECD 302C** | **Bourquin** |
|---|---|---|---|---|---|---|---|---|---|
| AoS | 11 | 36 | 21 | 17 | 40 | 2 | 14 | 1 | 1 |
| Concentrations of the test substance: | | | | | | | | | |
| mg/L | | | 100 | 2–10 | 100 | 2 | | 30 | * |
| mg DOC/L | 10–40 | 10–20 | | | | 5–40 | 20 | | * |
| mg ThOD/L | | | | 2–10 | 50–100 | | | | * |
| Concentrations of inoculum: | | | | | | | | | |
| mg/L SS | ≤ 30 | ≤ 30 | 30 | | ≤ 30 | Seawater instead of distilled water | 4–30 | 100 | * |
| mL effluent/L | ≤ 100 | ≤ 100 | | ≤ 5 | ≤ 100 | | 1–10 | | * |
| Concentration of elements in mineral medium (in mg/L): | | | | | | | | | |
| P | 116 | 116 | 29 | 11.6 | 116 | 116 | 116 | 116 | * |
| N | 1.3 | 1.3 | 1.3 | 0.13 | 1.3 | 1.3 | 1.3 | 1.3 | |
| Na | 86 | 86 | 17.2 | 8.6 | 86 | 86 | 86 | 86 | |
| K | 122 | 122 | 36.5 | 12.2 | 122 | 122 | 122 | 122 | |
| Mg | 2.2 | 2.2 | 6.6 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | |
| Ca | 9.9 | 9.9 | 29.7 | 9.9 | 9.9 | 9.9 | 9.9 | 6.6 | |
| Fe | 0.05–0.1 | 0.05–0.1 | 0.15 | 0.05–0.1 | 0.05–0.1 | 0.05–0.1 | 0.05–0.1 | 0.05–0.1 | |
| Duration d | 28 | 28 | 28 | 28 | 28 | 28 | 28 | 14–28 | * |
| Parameter | DOC | $CO_2$ | $O_2$ | $O_2$ | $O_2$ | DOC or $O_2$ | DOC or $CO_2$ | $O_2$ | * |
| pH | 7.4 ± 0.2 | 7.4 ± 0.2 | 7 | 7.4 ± 0.2 | 7.4 ± 0.2 | * | 7.4 ± 0.2 | 7.0 ± 1 | * |
| Temperature °C | 22 ± 2 | 22 ± 2 | 25 ± 1 | 22 ± 2 | 22 ± 2 | 15–20 | 20 ± 1 | 25 ± 2 | * |

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