Science of the Total Environment 579 (2017) 506–513

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

An approach to the environmental prioritisation of volatile methylsiloxanes in several matrices

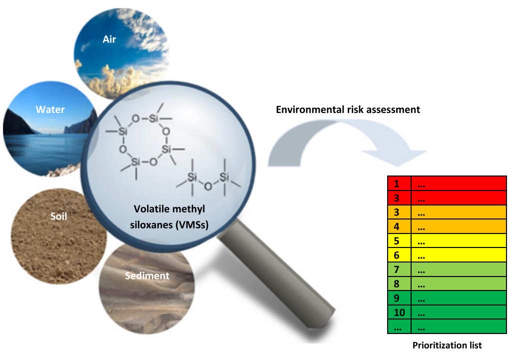
Vera Homem [a],*, Daniela Capela [a], José Avelino Silva [a], Alessandra Cincinelli [b], Lúcia Santos [a], Arminda Alves [a], Nuno Ratola [a]

[a] LEPABE—Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Department of Chemistry, University of Florence, Sesto Fiorentino, Florence, Italy

HIGHLIGHTS

- A hazard assessment method based on worst-case scenarios was applied to VMSs.
- Cyclic VMSs present higher risks than linear VMSs.
- VMSs showed a high impact on water and sediments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form 19 October 2016
Accepted 11 November 2016
Available online 18 November 2016

Editor: D. Barcelo

Keywords:
Volatile methylsiloxanes
Environment
Risk assessment
Prioritisation

ABSTRACT

Siloxane-based compounds are widely used in personal care, pharmaceutical and household products as well as in industrial applications. Among the wide variety of these chemicals, special attention has been given to volatile methylsiloxanes (VMSs). These compounds have been extensively detected in several environmental compartments, as they are not effectively removed from wastewater and may migrate through different matrices and being lipophilic, bioaccumulate and biomagnify in living organisms. In this work, a prioritisation methodology for several VMSs in different environmental matrices was applied, estimating a hazard quotient by combining exposure evaluation through measured or predicted environmental concentrations (MEC or PEC) and effects using ecotoxicity data to establish no effect concentrations (PNEC). VMSs show quite different hazard potentials in the environment: for linear VMSs it is not considerable, while for cyclic VMSs the hazard is disperse. D4 and D5 may have adverse effects in water, as well as D5 and D6 in sediments. This first multi-matrix approach for the prioritisation of VMSs sets the ground for more accurate studies in the future, provided that more field-based data are reported.

1. Introduction

Siloxane-based compounds have been raising concerns in recent years due to their widespread use and potential hazardous characteristics (Howard and Muir, 2010). In fact, the Centre Européen des Silicones

---

* Corresponding author.
E-mail address: vhomem@fe.up.pt (V. Homem).

http://dx.doi.org/10.1016/j.scitotenv.2016.11.068
0048-9697/

(CES) verified a global market for silicones of approximately 2,000,000 t in 2002 and 2,600,000 t in 2009 (Lassen et al., 2005; Arespacochaga et al., 2015). Until 2022, a growth of 6% per year is expected, due to increasing end-use markets (Arespacochaga et al., 2015). For instance, the International Nomenclature of Cosmetic Ingredients (INCI), elaborated by the European Commission, lists about 200 organosiloxanes and organosiloxane derivatives used in their formulations (Lassen et al., 2005). Apart from personal care products, organosiloxanes are also employed in several industrial applications, household cleaning products, construction, textiles, medical/pharmaceutical preparations, paints or coatings (MST, 2014). Among the wide variety of these chemicals, special attention has been given to volatile methylsiloxanes (VMSs, linear and especially cyclic), reflecting their extensive environmental presence in biota, aquatic media, wastewater, sludge, air, sediments and soil (Wang et al., 2013).

VMSs have a widespread use in daily life and therefore are likely to be released via down-the-drain emissions, reaching wastewater treatment plants (WWTPs). Due to their physicochemical properties, they are usually not degraded during wastewater treatment, but instead they are removed from the water line through volatilization and sorption to sludge (Sanchís et al., 2013; van Egmond et al., 2013). Nevertheless, effluent discharges are still the major route for surface water and aquatic biota contamination (Sanchís et al., 2016) and the use of sludge/biosolids for agricultural purposes is a direct input into soils (Liu et al., 2014). This practice is increasingly common as >50% of the generated sludge in the EU-27 WWTPs is reused for agricultural purposes (either applied directly or after composting) (Kelessidis and Stasinakis, 2012).

Being semi-volatile and suspected to be persistent in air (half-life ≥2 days), VMSs are prone to travel long distances in the atmosphere and, due to their lipophilic behaviour combined with low biodegradation rates, to bioaccumulate and biomagnify in living organisms. However, these are controversial issues. Some authors suggest the presence of VMSs in remote regions (Arctic and Antarctic region) as a result of long-range atmospheric transport (Sanchís et al., 2015), but others explain their presence as a consequence of choosing sampling locations in proximity of human communities rather than transport over a long range (Warner et al., 2010). Regarding the bioaccumulation and biomagnification potential of VMSs, the same type of controversy has emerged. Wang et al. (2013) reviewed literature for the environmental fate of some cyclic VMSs (D4, D5 and D6) and found evidences that D4 and D5 do not biomagnify in aquatic food webs, although some aquatic organisms showed a high degree of bioconcentration and bioaccumulation. However, Borgå et al. (2013) and Jia et al. (2015) reported that cyclic methylsiloxanes undergo trophic biomagnification.

There are some silicon compound classes that present strong biological effects (Tacke and Linoh, 1989; Rücker and Kümmerer, 2015). In the study performed by Kent et al. (1994), D4 showed weak toxicity to aquatic organisms, but on the other hand estrogenic and anti-estrogenic activity in rats (McKim et al., 1998) and, in a dose-dependent manner, suppressed ovulation in rats (Quinn et al., 2007). Some negative effects were also found on the reproductive system of this species, at high inhalation doses of D4 (Meeks et al., 2007; Siddiqui et al., 2007a), which also leads to the formation of uterine tumours (Brooke et al., 2009c). Also for D5 there are some studies that can compromise its use. In contrast to D4, D5 did not exhibit reproductive effects in rats (Siddiqui et al., 2007b). However, on high chronic exposure levels (aerial exposure), D5 was considered carcinogenic for rats (Brooke et al., 2009a). Different tests were also performed to verify the ecotoxicity of this compound. For example, in soil, D5 showed adverse effects on barley (*Hordeum vulgare*) growth and on sprigtail (*Falsomia candida*) survival and even reproduction, although at high concentrations (Velicogna et al., 2012). Other studies point out that at environmentally relevant concentrations, D5 does not affect adversely the tested species (fathead minnows, benthic invertebrates) (Norwood et al., 2013; Parrott et al., 2013). For D6, the authors did not found specific studies, but due to its similar structure to D4 and D5, it is suspected to cause some adversities (Brooke et al., 2009b). Lieberman et al. (1999) also acknowledged that when a mixture of cyclic siloxanes, or even pure D4 is administrated to female mice, it can cause serious effects on liver and lung tissue, or even death (D4: $LD_{50} = 6–7\ g\ kg^{-1}$). The toxicological information regarding the linear compounds is scarce, showing that this area is still in progress. However, the one study found reports that L2 can be considered a weak antiestrogen compound (McKim et al., 2001a, 2001b).

Taking into account this information and the growing number of studies describing the worldwide presence of VMSs in environmental matrices, it is important to assess the risks associated with the presence of these emerging contaminants. Some documents reviewing the environmental risk of individual cyclic VMSs have been issued (Fairbrother et al., 2015; Gobas et al., 2015; Mackay et al., 2015), namely to comply with regulations in certain countries, such as the UK and Canada (Brooke et al., 2009a, 2009b, 2009c; Environment Canada and Health Canada, 2008a, 2008b, 2008c). Denmark is also in the forefront of siloxanes screening and evaluation of health hazards, having recently proposed a quality criterion for ambient air with respect to siloxanes content (MST, 2014). However, to our knowledge, there is a lack of dedicated studies prioritising linear and cyclic VMSs according to the potential risks in different environmental compartments.

Thus, in order to evaluate the overall impact of the linear and cyclic VMSs on the environment, an environmental risk approach was employed (Fig. 1). First, information on environmental concentrations as well as toxicity data of 18 linear (L2 to L14) and cyclic (D3 to D7) siloxanes was compiled. Then, this information was complemented with data resulting from the monitoring of 8 VMSs (L2–L5 and D3–D6) in air and soils under the Portuguese-funded project SILOQUEST (Ratola et al., 2016). Finally, the compounds were prioritised according to their hazard quotients (HQ). This framework intends to help decision-makers to be aware of the needs to assess the potential risk of VMSs, contributing at the same time to optimise the very much needed future monitoring plans and supporting analytical methodologies.

2. Materials and methods

2.1. Data collection

An extended literature review (1995–2016) was performed using several electronic databases: Scopus®, Elsevier®, Taylor & Francis®, ACS Publications®, Springer® and Google® Scholar. Maximum VMSs concentrations in treated wastewater and sludge were collected in order to estimate the predicted environmental concentrations (PEC) for the worst-case scenario. When available, maximum measured environmental concentration (MEC) in water, soil and air were also recorded. To complement this information, data from the monitoring plan carried out under project SILOQUEST (Ratola et al., 2016) was also used (Supporting information, Tables S2–S7).

Toxicity data for the target compounds (short-term as L(E)C50 and/or long-term as NOEC) was collected from the literature for different species—aquatic; sediments; soil (Supporting information, Table S8). When more than one toxicity value was available, the lowest limit was chosen in order to estimate the ecological threat under a worst-case scenario.

2.2. Environmental hazard characterisation

The environmental hazard characterisation was carried out using the hazard quotient (HQ) approach. The HQs were calculated according to the European Guidelines (European Commission, 2003):

$$HQ = \frac{MEC\ or\ PEC}{PNEC} \quad (1)$$