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SQC (EQS_{sed}) – Proposal by the Ecotox Centre for: *Tebuconazole*

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Please note that the suggested EQS and contents of this dossier do not necessarily reflect the opinion of the external reviewer.

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Summary

SQC (EQS_{sed}): 2.8 µg/kg d.w.

In the framework of the Module Sediment, which is intended to help cantons in sediment quality assessment, the Ecotox Centre develops proposals for Environmental Quality Criteria for sediment (SQC). SQC are derived applying the methodology described in the EU-Technical Guidance (TGD) for Deriving Environmental Quality Standards (EQS). In order to ensure that the dossiers are internationally comparable, the English terminology of the TGD will be used in the remainder of the dossier. These criteria provide a first screening tool to evaluate sediment chemical quality and the potential risk for the aquatic ecosystem. Based on the scientific literature available at present a generic SQC for tebuconazole of 2.8 µg/kg d.w. is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 2.8 µg/kg TS

Im Rahmen des Sedimentmoduls, das den Kantonen bei der Bewertung der Sedimentqualität helfen soll, entwickelt das Oekotoxzentrum Vorschläge für Umweltqualitätskriterien für Sedimente (SQK). Diese Kriterien dienen als Methode für ein erstes Screening zur Bewertung der chemischen Sedimentqualität und des potenziellen Risikos für aquatische Ökosysteme. Auf der Basis von Literaturdaten für die Wirkung von Cypermethrin und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschriebenen wird, schlägt das Oekotoxzentrum einen allgemeines SQK für tebuconazole von 2.8 µg/kg TS für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 2,8 µg/kg p.s.

Dans le cadre du module Sédiments qui devrait aider les cantons à évaluer la qualité des sédiments, le Centre Ecotox élabore des propositions de critères de qualité environnementale pour les sédiments (CQS). Les CQS sont dérivés en appliquant la méthodologie décrite dans le Guide Technique de l'UE (TGD) pour la Dérivation des Normes de Qualité Environnementale (EQS). Afin que les dossiers soient comparables au niveau international, la terminologie anglaise du TGD est utilisée ci-dessous. Ces critères fournissent un premier outil de dépistage pour évaluer la qualité chimique des sédiments et le risque potentiel pour l'écosystème aquatique. Sur la base des données sur les effets existants dans la littérature un CQS générique pour le tebuconazole de 2,8 µg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.

Sommario

CQS (EQS_{sed}): 2,8 µg/kg p.s.

Nell'ambito del modulo Sedimenti, che è finalizzato ad aiutare i Cantoni nella valutazione della qualità dei sedimenti, il Centro Ecotox sviluppa proposte per i criteri di qualità ambientale per i sedimenti (CQS). I CQS sono derivati applicando la metodologia descritta nella Guida Tecnica dell'UE (TGD) per la Derivazione degli Standard di Qualità Ambientale (EQS). Per garantire che i dossier siano comparabili a livello internazionale, viene utilizzata la terminologia inglese del TGD. Questi criteri forniscono un primo strumento di screening per valutare la qualità chimica dei sedimenti e il potenziale rischio per l'ecosistema acquatico. Sulla base della letteratura scientifica disponibile allo stato attuale un CQS generico per il tebuconazol di 2,8 µg/kg p.s. è proposto per sedimenti standard con 1 % CO.

Table of content

1 General information

Selected information on the fungicide tebuconazole relevant for sediment is presented in this chapter. Existing registration information and dossiers for tebuconazole are:

- Oekotoxzentrum (2016). EQS-Vorschlag des Oekotoxzentrums für: Tebuconazol. 25 pp.
- EFSA (European Food Safety Authority) (2008). Conclusion on the peer review of tebuconazole. EFSA Scientific Report 176, 1-109.
- EFSA (European Food Safety Authority) (2014). Conclusion on the peer review of the pesticide risk assessment of the active substance tebuconazole. EFSA Journal 2014;12(1):3485, 98 pp. doi:10.2903/j.efsa.2014.3485
- EU DAR (2007). Draft Assessment Report Report (DAR) of the European Commission. Volume 1. Initial risk assessment provided by the rapporteur Member State Denmark for the existing active substance Tebuconazol of the third stage (part B) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC.
- ECHA (European Chemical Agengy) (2020) Information on Registered Substances 4-(1,1,3,3-tetramethylbutyl)phenol, CAS 140-66-9 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.100.535. Last modified: 24-Mar-2020.
- ECHA (2013). Annex 1: Background document to the Opinion proposing harmonised classification and labelling at Community level of tebuconazole. Committee for Risk Assessment (RAC).

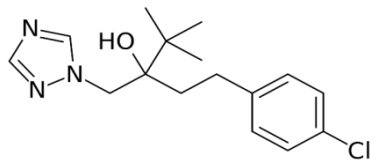
1.1 Identity and physico chemical parameters

Tebuconazole is an antifungal azole from the triazole family. Tebuconazole as technical grade material is in the form of a racemic mixture 1:1 (ECHA 2013).

The log K_{oc} reported for tebuconazole are in the range of 2.67-3.10, with a geometric mean of 3.01 (Appendix 1). The log K_{ow} is 3.70 (Table 1). Both the log K_{oc} and log K_{ow} trigger an effects assessment for sediments according to the EC TGD EQS (EC 2018).

Table 1 summarizes the identity and physico-chemical parameters for tebuconazole. Where available, experimentally collected data is identified as (exp.) and estimated data as (est.). When not identified, it means that no indication is available in the cited literature.

Table 1 Information required for EQS derivation according to the TGD (EC 2018).

Characteristics	Values	References
IUPAC name	(*RS*)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazole-1-ylmethyl)-pentan-3-ol	ECHA (2020)
Chemical group	Triazole	ECHA (2020)
Structural formula		Oekotoxzentrum (2016)
CAS-Number	107534-96-3	ECHA (2020)
EC Number	403-640-2	ECHA (2020)
Molecular formula	$C_{16}H_{22}ClN_3O$	ECHA (2020)
SMILES-Code	CC(C)(C)C(O)(CCC1=CC=C(Cl)C=C1)CN1C=NC=N1	ECHA (2020)

Molecular weight [g/mol]	307.8	ECHA (2013)
Melting point [°C]	[1] 104 [2] 105 (99.9 % purity) (exp.) [3] 102.86 (est.)	[1] ECHA (2020) [2] Krohn (1993a) cited in ECHA (2013) [3] EPI (2011) cited in Oekotoxzentrum (2016)
Boiling point [°C]	[1] Not measurable, decomposition before boiling reaches (>165 °C) (exp.) [2] 394.85 (exp.) (adapted Stein and Brown method)	[1] Mix & Berg (1988) cited in ECHA (2013) [2] EPISuite (2011) cited in Oekotoxzentrum (2016)
Vapour pressure [Pa]	Gas saturation method (exp.): 1.7×10^{-6} (20 °C) (extrapolated) 3.9×10^{-6} (25 °C) (extrapolated) **Low volatility**	Krohn (1993b) cited in ECHA (2013)
Henry's law constant ($Pa \cdot m^3/mol$) at 20°C	1×10^{-5} (exp.) **Non-volatile**	Krohn (1988a) cited in FAO (2015)
Water solubility [mg/l]	[1] 29 (20 °C, independent of pH) [2] 38 (20 °C, purity 99.5 %, pH 5.3) [3] 36 (20 °C, purity 99.5 %, pH 7.2) [4] 36 (20 °C, purity 99.5 %, pH 9.4) **Low**	[1] EC (2007) [2-4] Krohn (1995) cited in ECHA (2013)
Dissociation constant (pK_a)	Tebuconazole is a very weak base, which can only be completely protonised in non-aqueous systems in the presence of very strong acids. It is not possible to specify a pK value for water.	Placke (1987) cited in ECHA (2013)
Octanol-Water partition coefficient (log K_{ow})	[1] 3.70 (20 °C, purity 99.1 %) (shake-flask method, OECD 107) (exp.) [2] 3.10 (25 °C) (HPLC Method) (exp.) [3] 3.89 (calculated from EPIsuite 1.4) (est.)	[1] Krohn (1984) cited in ECHA (2013) [2] Eyrich & Bogdoll (2007a) cited in FAO (2015) [3] Creusot et al. (2020)
Organic carbon adsorption coefficient (log K_{OC})	[1] 2.86-3.27, average 3.00 (soil exp. EPA-Guideline 163-1, N = 6) [2] 3.186 (est.) (MCI Method) [3] 2.86 (sediment exp. batch equilibrium, 95 % fines, 1.7 % OC) [4] 2.86 (soil exp. batch equilibrium, 95 % fines, 1.5 % OC) [5] 2.67 (soil exp. batch equilibrium, 97 % fines, 1.2 % OC)	[1] Fritz (1998) and (1993) cited in EU DAR (2007); Appendix I [2] EPI (2011) cited in Oekotoxzentrum (2016) [3-5] Vallée et al. (2014)
Sediment adsorption coefficient (K_d [l/kg])	[1] 9.88-23.84 (soil exp. EPA-Guideline 163-1, N = 6) [2] 12.37 (sediment exp. batch equilibrium, 95 % fines, 1.7 % OC)) [3] 10.94 (soil exp. batch equilibrium, 95 % fines, 1.5 % OC) [4] 5.77 (soil exp. batch equilibrium, 97 % fines, 1.2 % OC)	[1] Fritz (1998) and (1993) cited in EU DAR (2007) [2-4] Vallée et al. (2014)
Aqueous hydrolysis (DT_{50} [d])	**[1] Stable** at pH 5, 7 and 9 in sterile, aqueous phosphate buffers, at 25 °C in darkness. No degradation observed over a 28 days period **[2] Stable** at pH 4, 7 and 9 at 25 °C in darkness, half-life > 1 year	[1] Coffman & Sietsema (1984) cited in ECHA (2013) [2] Wiche and Bogdoll (2007) cited in FAO (2015)

Aqueous photolysis (DT_{50} [d])	**[1] Stable** at pH 7 and pH 9 at 22 °C after 30 days of irradiation (photolysis products not observed) [2] 73 h estimated after irradiation of 8 h to light resembling sunlight	[1] Coody (1987) cited in ECHA (2013) [2] DEFRA (1993) cited in INERIS (2011)
Biodegradation in aqueous environment (DT_{50} [d])	[1] 198 (first order kinetics, freshwater); no data on seawater	[1] EU DAR (2007) Annex I.
Biodegradation in water-sediment system (DT_{50} [d])	54 (average dissipation DT50 for the total (water/sediment) in outdoor micro/mesocosm) > 365 (sediment), 43 (water phase) in outdoor micro/mesocosm (exp.)	Heimbach (2003) and Chapple et al. (2003) cited in ECHA (2013)
Biodegradation in soil (DT_{50} [d])	[1] > 365 (lab, 20 °C, aerobic) (exp.) [2] 77 (worst case, dissipation field studies) (exp.)	[1] Lee and Hann-Bey (1987) cited in ECHA 2013 [2] ECHA 2013

1.2 Regulation and environmental limits

Table 2 summarizes existing regulation and environmental limits in Switzerland, Europe and elsewhere for tebuconazole.

Table 2 Existing regulation and environmental limits for tebuconazole in Switzerland and elsewhere.

Europe	
Status under Reg. (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC	Annex I of 1107/2009 lists the zones for PPPs Tebuconazole is regulated under 1107/2009 by https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32014R0921 ➔ Approval as candidate for substitution Current expiry date is 31.8.2020 https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1557499937583&uri=CELEX:32019R0707
Reg. (EU) No 921/2014 (*Amending Implementing Regulation (EU) No 540/2011 as regards the conditions of approval of the active substance tebuconazole – Text with EEA relevance*)	Part A of the Annex to Implementing Regulation (EU) No. 540/2011: - Only uses as fungicide and plant growth regulator may be authorised. Member States must: - Pay particular attention to the potential groundwater contamination in particular the occurrence of the metabolite 1,2,4,-triazole - Submit to the Commission further information addressing the potential endocrine disrupting properties of tebuconazole within two years after the adoption of OECD test guidelines on endocrine disruption Candidate for Substitution (CfS), very persistent.
Directive 98/8/CE (Biocide products Directive) by Decision 2008/86/EC Regulation 528/2012 (Regulation for biocide products)	Approved for: - Product Type 7: film preservative (approval end date 30/06/2025) - Product Type 8: wood preservative

	(approval end date 30/09/2022) - Productive Type 10: construction materials preservative (approval end date 30/06/2025)
Harmonized classification – Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) Classification Reg. 1272/2008	Acute Toxicity 4 – H302: Harmful if swallowed Repr. 2 – H361d: Suspected of harming the fetus Aquatic Acute 1 – H400 Aquatic Chronic 1 – H410 Aquatic Chronic 2 – H411: Toxic to aquatic organisms in the long term, causes long-term adverse effects
Authorized in	AT, BE, BG, CY, CZ, DE, DK, EE, EL, ES, FI, FR, HR, HU, IE, IT, LT, LU, LV, MT, NL, PL, PT, RO, SI, SK, UK
Directive 98/83/CE	0.1 µg/l (pesticide) for water intended for human consumption
Switzerland	
Ordinance on phytosanitary products (OPPh) (31.01.18)	Annex 1: Approved active substances whose incorporation is allowed in plant protection products Part A: Chemical substances (as fungicide) Part E: Substance considered for substitution (in accordance with Article 5, since one of the conditions set out in Annex II (Ch. 4) of Regulation (EC) No. 1107/2009 is fulfilled; either the active substance presents a potential risk (RS 916.161) or is persistent in soil (DT50> 6 months)
Water protection ordinance (WPO) (31.01.18)	Annex 2: Requirements on Water Quality for plant protection products 0.1 µg/l per individual substances. Annex 22: Additional requirements for groundwater which is used for drinking water or is intended as such 0.1 µg/l per individual substances.
EQS proposal (Oekotoxzentrum 2016)	MAC-EQS = 1.4 µg/l AA-EQS = 0.24 µg/l
France	
NQE (Norme de qualité environnementale) INERIS (2011) Freshwater organisms: Secondary poisoning of predators: For freshwater sediments (*calculated with Equilibrium Partitioning Method*):	 AA-QS = 1 µg/l MAC-EQS = 1 µg/l $QS_{biota(dry\ weight)}$ = 2 mg/kg_{biota} QS_{water} = 0.03 mg/l 51 µg/kg d.w. (5 % OC)

1.3 Use and emissions

Tebuconazole is used as fungicide, seed disinfectant or phytoregulator either alone or associated with other active substances in diverse crops, like on cereals (in the field or on the seeds), vegetables, fruits, tea or coffee (Tomlin 2006). Commercial products classified as fungicides either contain tebuconazole alone or associated with one or two of the following substances: bixafen, bupirimate, difenoconazole, fenpropidine, fluopyram, prochloraz, prothioconazole, spiroxamine or trifloxystrobine (Tomlin 2006). As fungicide, tebuconazole is used together with other triazoles (difenoconazole or prothioconazole)

in equimolar mixtures. In addition to its use as fungicide, tebuconazole is used as phytoregulator as the prevalent substance of the mixture (Tomlin 2006). Ninety homologated products containing tebuconazole are registered in Switzerland, 68 of them for use as fungicide, 14 as phytoregulator and fungicide and 8 as seed disinfectant (FOAG 2018). According to the register of active substances of the Swiss Federal Office for Agriculture (FOAG, as of 05.12.2019), tebuconazole sales ranged from 3103 tons in 2008 to 7939 tones in 2014, with a progressive decrease in the following years to 3768 tons in 2018.

According to its biocidal properties, tebuconazole is also used as preservative for wood, film and construction materials.

1.4 Mode of action and sensitivity of taxonomic groups

Tebuconazole is a demethylation inhibitor. At the molecular level, tebuconazole inhibits the demethylation at the C14 position in fungal sterol biosynthesis by inhibiting the enzyme sterol 14α-demethylase which is involved in the biosynthesis of ergostertol, a component of cell membranes in fungi and yeasts (EC 2007). Since sterol 14α-demethylase is also present in many other living organisms, tebuconazole is also expected to affect non-target organisms. The most sensitive aquatic taxa in chronic exposure are amphibians, followed by fishes, macrophytes, crustacean, algae and insecta (Oekotoxzentrum 2016).

In plants, sterol 14α-demethylase is involved in the synthesis of phytosterol whereas in animals it is involved in the biosynthesis of cholesterol. Because cholesterol is a substrate for the production of other sterols, including sexual steroids, and tebuconazole is also known to be a mild inhibitor of aromatase (Sanderson et al. 2002; Trösken et al. 2006), effects on sterol 14α-demethylase and aromatase can cause effects in sexual differentiation and reproduction (Zarn et al. 2003; Sanderson 2002).

The Danish Center for Endocrine Disruptors (ED) concluded that tebuconazole is an endocrine disruptor "category 1, i.e. the data is evaluated to fulfil the WHO definition of an ED" (Hass et al. 2012, 2018). It was also evaluated in the Tier 1 Endocrine Disruptor Screening Program (EDSP) list of the US EPA with screening determination (or weight-of-evidence (WoE) assessments) and associated data evaluation records, recommending additionally a medaka extended one-generation test (Tier 2 testing) (US EPA 2015[1]). In a 21 d metamorphosis assay with the amphibian *Xenopus laevis,* tebuconazole caused a decrease of wet weight, size of snout-vent length, hind limb length and median development stage at concentrations ranging from 17 to 341 µg active ingredient/l. US EPA (2015) concluded that the thyroid and developmental findings in the assay were inconsistent with a direct, thyroid-related delay and may be more reflective of treatment-related growth inhibition. In addition, tebuconazole has potential to interact with the estrogen and androgen signaling pathways. In 21 d fish short-term reproduction assay with *Pimephales promelas,* significant effects were observed on plasma vitellogenin for females at 11.3 µg/l. At the highest concentration (19.5 µg/l), significant disturbances appeared in gonado-somatic index (males and females), gonadal histopathology and plasma vitellogenin (females) (US EPA 2015).

INERIS recently performed a complete assessment of evidence related to the ED activity for tebuconazole in relation to EQS derivation based on ECHA and EFSA guidance for the identification of

[1] https://www.epa.gov/endocrine-disruption/endocrine-disruptor-screening-program-tier-1-screening-determinations-and

ED chemicals (James-Casas et al. 2019). This assessment reviewed 213 entries, with 31 entries for *in vitro* (mechanistic, only humans and mammals), 72 entries for *in vivo* data on wildlife, and 110 entries for *in vivo* data for mammals (rat) that were considered relevant and reliable according to CRED, Klimisch et al. (1997) and ToxRtool. INERIS concluded that ED criteria are met as regards mammals. The INERIS study concluded that there is a link between adversity and endocrine activity through steroidogenesis inhibition and anti-AR (androgen receptor), and there is sufficient evidence to establish a mode of action with high biological plausibility. As regards wildlife, ED criteria are not met for tebuconazole but, strictly applying the ECHA/EFSA guidance, there is a need for additional data from standardized tests on thyroid mode of action. It was also concluded that further assessment/expertise of the mode of action was needed for invertebrate data.

2 Environmental fate

2.1 Stability and degradation products

Abiotic degradation

According to ECHA (2013) tebuconazole is hydrolytically stable. A study using radio-labelled tebuconazole run at pH 5, 7 and 9 at 25 °C for 28 days in sterile aquatic system reported no degradation of tebuconazole (mass balance 97-107 % in agreement with nonvolatility of the substance (Coffman and Sietsema 1984, cited in ECHA 2013)). However, INERIS (2013) cited a half-life of 73 h for tebuconazole (original study not available) According to a separate study, the radio-labelled metabolite 1,2,4-triazole (M26) in sterile aqueous solution showed a half-life greater than 30 days at pH 5, 7 and 9 at 25°C under exclusion of light, therefore the metabolite is also hydrolytically stable (Spare 1983 cited in ECHA 2013).

Tebuconazole and the metabolite 1,2,4-triazole (M26) have been shown not to degrade in water by direct photo-transformation processes. A study with radiolabeled tebuconazole in sterile water at pH 5, 7 and 9 and 22 °C irradiated by natural sunlight for 30 days resulted in 94 % to 100 % recovery attributed to the parent compound and an extrapolated half-life of 590 days (Coody 1987 cited in ECHA 2013). Two photochemical degradation studies are available for M26. The first one concluded that photolytic degradation is not expected according to the measured molar absorptivity values while the second showed no significant degradation by sunlight in distilled water, humic acid solution or distilled water with acetone (ECHA 2013). INERIS (2011) cited a half-life of 73 h estimated after irradiation of 8 h to light resembling sunlight reported in DEFRA (2003)[2].

Biodegradation and dissipation

According to ECHA (2013), no data on ready biodegradability (e.g. OECD 301) is available for tebuconazole. EFSA (2008) and (2014) also reports no data submitted, thus tebuconazole was considered not ready biodegradable.

Several simulation tests (Fritz 1987a, 1988) reported in EFSA (2008) and ECHA (2013) concluded that the degradation of tebuconazole was relatively slow in water / sediment systems and soil, although degradation rates were slightly higher in a drainage ditch of a fruit orchard).

[2] DEFRA (2003) could not be obtained to check this alternative photodegradation study reporting a half-life of 73 h.

Aerobic water-sediment simulation studies reported percentages of applied radioactivity transformed into CO_2 (end product of mineralization) after 52 weeks (end of study) at 22°C of 10 and 21 % for a drainage ditch of a fruit orchard and from a recultivated gravel pit of agriculturally used areas, respectively (Fritz 1987a, Fritz 1987b and Fritz 1988 cited in ECHA 2013 and EFSA 2008). After one year, 56 % (gravel pit) or 67 % (fruit orchard) of the applied radioactivity was still attributed to tebuconazole. The amount of unchanged parent compound in surface water decreased over time and was at the end of the study (52 weeks) about 23 % in the re-cultivated gravel pit and 8 % in the fruit orchard. None of the measured metabolites accounted for more than 3 %. Approximately 34 % of the applied radioactivity was adsorbed to the sediment of the re-cultivated gravel pit system and 61 % in the fruit orchard system. There was no calculation of actual degradation rates in water but results were interpreted as indicating a relatively slow degradation for tebuconazole under environmental conditions. The dissipation of tebuconazole from the aqueous phase by degradation and adsorption to the sediment in these water-sediment systems was considered as relatively slow in the case of the system re-cultivated gravel pit and relatively rapid in case of the fruit orchard due to its higher content of organic material.

In another study conducted on outdoor microcosms (Heimbach 2003 cited in ECHA 2013) the average half-lives were 30.9 d for disappearance from the water body and 38.7 d for disappearance from the total system (water and sediment) (pH 8, dissolved oxygen 10-12 mg/l, water temperature 11-25°C, nominal concentrations of 3.2 and 32 µg/l). The average dissipation DT_{50} for the total water-sediment system was 54 d, the dissipation DT_{50} for the water phase 43 d and one year (default) for the sediment were derived by Chapple et al. (2003) based on the study of Heimbach et al. (2003).

Aerobic degradation in soil in a laboratory study with ^{14}C-tebuconazole at an application rate of 10 mg/kg soil, corresponding to 13 kg/ha, suggests a slow degradation in soil with a DT_{50} longer than 1 year with 67 % remaining after 1 year (Lee and Hann-Bey 1987 cited in ECHA 2013).

Field dissipation trials conducted in Northern and Southern Europe as reported in ECHA (2013), however, indicated that tebuconazole is moderately degradable. The geometric mean of the DT_{50} values for 18 trials performed in Northern Europe between 1987 and 1993 was 94 days, the mean value for four additional trials conducted in Northern Europe between 2000 and 2001 was 57 (36 to 77 d) while the mean DT_{50} for two studies conducted in Southern Europe was 26 d (20 to 34 d). 1,2,4-triazole (M26) was the major metabolite formed with a maximum of 9.0 % of applied radioactivity.

Existing studies indicate that no major metabolites were found in water/sediment systems (ECHA 2013). On the contrary, several studies have shown several biotransformation or degradation products in mammals, cultivated plants and soils (FAO 2015). Three major metabolites are found under biotic conditions: HMG 1608-lactone (M17, maximum 21 % of the applied radioactivity in the water/sediment system), HWG 1608-pentanoic acid (M25, 40.2 % of the radioactivity in the water/sediment system) and the 1,2,4-triazole M26 (maximum 14 % of the radioactivity applied in the water/system).

2.2 Sorption/desorption processes

Tebuconazole is considered a substance with a low mobility potential in soil. Experimental K_{OC} values for tebuconazole range from 469 to 1877 (Table 1, Appendix 1). According to the EU DAR (2007), the adsorption/desorption behaviour of tebuconazole in six different soils of low organic content was investigated by Fritz (1988 and 1993) according to EPA-Guideline 163-1. The calculated adsorption constants K_d calculated from the adsorption isotherms ranged from 7.67 to 16.39 l/kg. These values correspond to K_{OC} values between 803 and 1249 l/kg. The calculated values from desorption were

slightly higher probably due to irreversible adsorption and K_{OC} values as reported in the EU DAR (2007) range between 732 and 1877 l/kg.

Vallée et al. (2014) investigated sorption of tebuconazole in sediment and soils in a pond and a ditch in Lorraine (France) according to the batch equilibrium technique, resulting in K_{OC} of 727.65 for sediment and 729.33 and 469.11 for soils.

2.3 Bioavailability

Bioavailability is a complex process which depends on many factors including the sorption capacity of the sediment considered (e.g. OC content), the hydrophobicity of the compound, and the physiology, feeding behaviour and burrowing activity of the benthic organism considered (Warren et al. 2003).

The scientific opinion of the EFSA on the effect assessment for pesticides on sediment organisms recognizes that "*the most appropriate metric for bioavailability in soils and sediments appears to be the 'freely dissolved pore water concentration' rather than the total sediment concentration, particularly for compounds with a log K_{OW} < 5*" (EFSA 2015).

Specific information on the bioavailability of tebuconazole is scarce. However, based on the sorption behavior of tebuconazole in the dissipation and sorption studies showing increased partitioning in sediment at increasing OC content (§ 2.1 and 2.2). In the study by Fritz (1988, 1993) K_d values increased at increasing OC content (0.75 and 1.80 %). Similarly, Vallee et al. (2014) also reported K_{fads} values of 5.79 and 12.37 kg/l increasing with increasing OC content. Based on these results, it is expected that bioavailability in soil and sediment is also influenced by organic carbon content.

2.4 Bioaccumulation and biomagnification

Tebuconazole has a measured log K_{ow} of 3.7 at pH 7 and 20 °C, which leads to an estimated Bioconcentration Factor (BCF) of 140 (Tomlin 2006).

In a study with bluegill sunfish (*Lepomis macrochirus*) exposed to 60 µg/l with radio-labelled tebuconazole over a 28-day exposure period (EPA-Guideline 165-41), steady-state was achieved within 10 d (Surprenant 1988 cited in EU DAR 2007). Tebuconazole showed limited bioconcentration and was excreted rapidly by bluegill sunfish yielding a BCF of 78 (whole fish) based on the total amount of radioactivity. In a second study with bluegill sunfish exposed to radio-labelled tebuconazole over a 3 day exposure period (OECD TG 305E) at water concentrations of 211 µg/l and 18 µg/l, a BCF of 55 and 93 were obtained for whole fish based on the total amount of radioactivity and a BCF of 35 and 59 based on the parent compound (Grau et al. 1988 cited in ECHA 2013). These data indicate that tebuconazole is not potentially bioaccumulative (BCF > 2000; ECHA 2017). It is also below the threshold of 100 for deriving EQS for biota (EC 2018).

No study was found in the literature on the bioaccumulation of tebuconazole in aquatic organisms under field conditions.

3 Analysis

3.1 Methods for analysis and quantification limit

Detection limits of 0.15 µg/kg d.w. and quantification limits of 0.51 µg/kg d.w. are achieved with accelerated solvent extraction (Dionex) and detection and quantification by high resolution liquid chromatography tandem mass spectrometry (LC-HRMS/MS; Creusot et al. 2020). A multi-residue method for the analysis of current-use and legacy pesticides in sediments from the US Geological

Survey using gas chromatography coupled to mass spectrometry operating in electron ionization mode (GC/EI-MS) reports limits of detection between 1.6 and 2.9 µg/kg d.w. (Smalling & Kuivila 2008, Smalling et al. 2012). Analytical capacities in routine analysis laboratories may reach LOQ of 5 µg/kg d.w. using gas chromatography-tandem mass spectrometry.

Table 3 Methods for tebuconazole analysis in sediments and corresponding limits of detection (LOD) and limits of quantification (LOQ) (µg/kg d.w.). n. a. means not reported.

LOD	LOQ	Analytical method	Reference
0.15	0.51	HRMS/MS	Creusot et al. (2020)
5	n.a.	GC-MS-MS	Oniris, LABERCA (personal comm.)
1.6-2.9	n.a.	GC/EI-MS	Smalling & Kuivila (2008); Smalling et al. (2012)

3.2 Environmental concentrations

Measured environmental concentrations (MEC) in sediments for Switzerland range from <0.15 to 4.63 µg/kg d.w. The highest concentrations are quantified in small streams affected by agricultural pressure, with higher concentrations measured in June than in September. The concentrations measured in Lake Geneva in 2015 and 2016 ranged between <0.15 and 0.54 µg/kg d.w. (N=8). Overall, tebuconazole has been detected in 28 of the 39 sediment samples studied in Switzerland, which is approx. 72 % detection frequency (Creusot et al. 2020). In another study on the occurrence of tebuconazole in sediments, the quantification frequency was only 6 % with maximum concentration of 3.44 µg/kg d.w (Ecotox Centre, unpubl. data).

The concentrations in Switzerland are relatively low compared with those in the US and Spain. For example, maximum concentrations in the Llobregat, Guadalquivir and Ebro River Basins in Spain are 11.4, 12.7 and 15.4 µg/kg d.w., respectively, with a detection frequency of 5, 3 and 33 % (Masiá et al. 2013, 2015; Ccanccapa et al. 2016). In California (US), maximum concentrations of 1380 µg/kg d.w. have been reported in high elevation sites, with a detection frequency 41 % (LOD = 1.6 µg/kg d.w.; Smalling et al. 2012). Smalling et al. (2012) measured the maximum tebuconazole concentration in Sequoia National Park suggesting the use of tebuconazole in forests may be relevant.

Table 4 Measured concentrations of tebuconazole in sediments from Switzerland and other countries.

Country	MEC (min-max) [µg/kg d.w.]	Nr sites (detection frequency)	Comments	Reference
Switzerland	Jun.: 0.48; Sept.: 0.25 Jun.: 4.63; Sept.: 1.92 Jun.: 0.17; Sept.: 0.70 Jun.: 0.17; Sept.: 0.10	4	Small streams affected by agricultural pressure	Creusot, N. (personal communication)
	0.54 (max)	6	Lake Geneva	
	0.49 (max)	5	Different types of water bodies	
	0.50-4.10	3	Venoge river, upstream-downstream gradient	

Country	MEC (min-max) [µg/kg d.w.]	Nr sites (detection frequency)	Comments	Reference
	--	18 (6 %)	Small streams affected by diverse pollution sources	Ecotox Centre (unpublished data)
USA	< 1.6-1380	12	Different types of waterbodies, mainly in California but also around US	Smalling et al. (2012)
Spain	2.29-11.42 (mean 7.09)	(5 %)	Llobregat River Basin	Masiá et al. (2015)
	2.6-12.7 (mean 1.1)	24 (13 %)	Guadalquivir River Basin	Masiá et al. (2013)
	1.66-15.38 (mean 2.36)	24 (33 %)	Ebro River Basin	CCanccapa et al. (2016)

4 Effect data (spiked sediment toxicity tests)

A non-filtered bibliographic search was performed for tebuconazole (by CAS numbers) in the US Ecotox Data Base (U.S. EPA 2016) which did not yield data on sediment organisms. Likewise, a search in the German Environmental Office database ETOX did not yield any relevant results. A key word search was performed on Scopus (tebuconazole + sediment + toxicity, no restriction regarding publication date) resulting in 7 publications, only one based on spiked sediment tests.

Potentially unpublished data was searched for in registration information, risk assessment dossiers and EQS dossiers. Only the EFSA pesticide risk assessment report lists one study performed with a benthic organism (*Chironomus riparius*) exposed via spiked sediment (EFSA 2014). The original report is not available and very limited information is available in addition to the test species and effect concentration. The EU DAR (2007) contains information on two sediment toxicity tests that were, however, performed with spiked water (no information is provided on tebuconazole concentrations in the sediments).

Relevance ("C" score in the table below) and reliability ("R" score in the table below) of studies are evaluated according to the CRED-criteria (Moermond et al. 2016 and Casado-Martinez et al. 2017).

According to the EU TGD (EC 2018) "*What is considered chronic or acute is very much dependent on 1) the species considered and 2) the studied endpoint and reported criterion*". According to EFSA, true chronic tests should cover a range of 28-65 d when half-life of a pesticide in sediment is >10 d (EFSA, 2015). Due to the relatively long generation time of the copepod *Attheyella crassa* (approx. 6-8 weeks), Turesson et al. (2007) developed a set of two tests that were run in parallel: a 21 d development test and a 14 d reproduction test. Because the endpoint studied is reproduction and development the test was assessed as chronic. The survival endpoint is considered acute and not used for EQS derivation. The standard test with the ostracod ostracod *Heterocypris incongruens* is run for 6 d and is considered sub-chronic, the longer exposure duration of 14 d is however considered chronic (Lefranc 2018).

Proposed SQC (EQS_{sed}) for Tebuconazole

Table 5 Sediment effect data for tebuconazole in mg/kg d.w. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Moermond et al. 2016; Casado-Martinez et al. 2017). Data used for QS derivation is underlined. Abbreviations: na = not available.

Group	Species[a]	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Value (mg/kg d.w.)	Sediment type	Normalized value (mg/kg d.w., 1% OC)	Normalized value (mg/kg d.w., 5% OC)	Chem. analysis	Note	Validity	References
Acute toxicity data in freshwater															
Crustacea (Copepoda)	*Attheyella crassa*	Tebuconazole	Static	2 d	Survival	21 d	NOEC	**0.5**	Natural surface sediment sieved at 40 µm, mixed with Merck silica gel 60, Ø=0.063-0.200 mm; 2 % TOC	0.25	1.25	Measured		R1/C1	Turesson et al. 2007
Acute toxicity data in marine water															
No data available															
Chronic toxicity data in freshwater															
Insecta	*Chironomus riparius*	Tebuconazole	Static	n.a.	n.a.	28 d	NOEC[a]	**21.45**	n.a.	n.a.	n.a.	n.a.	From pesticide risk assessment of active substance	R2/C1	EFSA 2014
Insecta	*Chironomus riparius*	Tebuconazole	Static	4 d	Emergence	28 d	NOEC	**16.5**	Artificial OECD 2018 sediment, 2 % TOC	8.25	41.25	Measured	Two concentrations tested (44.7 mg/kg d.w. with 100 % mortality, no emergence	R3/C1	Lefranc, 2018
Crustacea (Copepoda)	*Attheyella crassa*	Tebuconazole	Static	2 d	Growth (nauplii)	21 d	NOEC	**<0.5**	"	<0.25	<1.25	Measured	All concentrations exert significant effect on length	R2/C1	Turesson et al. 2007
Crustacea (Copepoda)	*Attheyella crassa*	Tebuconazole	Static	2 d	Reproduction	14 d	NOEC	**0.73**	"	0.365	1.825	Measured		R1/C1	Turesson et al. 2007
Crustacea (Amphipoda)	*Hyalella azteca*	Tebuconazole	Static	4 d	Survival	28 d	NOEC	**17.2**	Artificial OECD 2018 sediment, 2 % TOC	8.6	42	Measured	Two concentrations tested (41.7 mg/kg d.w. with 90 % mortality	R3/C1	Lefranc, 2018
Crustacea (Ostracoda)	*Heterocypris incongruens*	Tebuconazole	14 d	7 d	Growth	14 d	EC_{10}	**9.29**	Artificial OECD 218 sediment, 2 % TOC	4.64	23.23	Measured	NOEC = 5.4 mg/kg d.w.	R1/C1	Lefranc 2018
Crustacea (Ostracoda)	*Heterocypris incongruens*	Tebuconazole	14 d	7 d	Survival	14 d	EC_{10}	**10.5**	Artificial OECD 218 sediment, 2 % TOC	5.25	26.25	Measured	NOEC = 10.5 mg/kg d.w.	R1/C1	Lefranc 2018

[a] NOEC is calculated as $EC_{15}/2$

4.1 Graphic representation of effect data

All available data have been plotted independently of their relevance and reliability (Figure 2).

As only one datum for insects reports different TOC content, normalization is not performed and effect data is plotted as derived originally for 2 % OC.

The NOECs for survival and reproduction of copepods (*A. crassa*, 0.5 and 0.73 mg/kg d.w., 2 % OC) are the lowest effect concentration, followed by the EC_{10} for survival and growth of ostracods (*H. incongruens,* 10.5 and 9.29 mg/kg d.w., 2 % OC), and the NOECs for emergence for insect larvae (*C. riparius*, 16.5 mg/kg d.w., 2 % OC) and survival and growth for amphipods (*H. azteca*, 17.2 mg/kg d.w.).

In the absence of acute effect data, no ratio of relevant acute to chronic data can be derived.

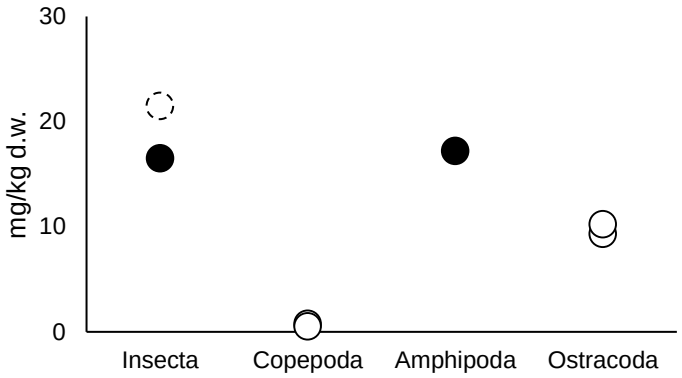


Figure 1 Graphical representation of chronic effect data from spiked sediment toxicity tests with tebuconazole. All data based on measured concentrations. Empty symbols: R1/C1 data; dotted lines: R2/C1 data; filled symbols: R3/C1 data.

4.2 Comparison between marine and freshwater species

No marine data was available.

4.3 Overview of reliable and relevant long-term studies

Four effect data are classified as being relevant without restrictions (C1) and reliable without restrictions (R1): the NOECs for *A. crassa* survival and reproduction, and the EC_{10} values for *H. incongruens* growth and survival. Additionally, three effect data are classified as relevant without restrictions (C1) but not reliable (R3) because only two concentrations were tested with two replicates: the NOEC value for *C. riparius* emergence, the NOEC value for *H. azteca* survival. These values are used as supporting information. The NOEC value derived from EC_{15} for *C. riparius* is classified as reliable with restrictions because no information on OC is available for normalization, although there is good agreement between the two NOECs available, being one derived from a sediment with 2 % OC, which is the standard OECD test sediment. The unbounded NOEC value for nauplii growth *A. crassa* growth is considered reliable with restrictions (R2).

Turesson et al. (2007): presents effect data for the freshwater copepod *Attheyella crassa* exposed to sediment spiked with tebuconazole.

- Species: *Attheyella crassa.*
- Origin: Laboratory culture originating from a single ovigerous female sampled from Lake Hallbosjörn after appropriate taxonomical identification.
- Experimental sediment: natural oxidized surface sediment from Lake Stensjön with 18.4 % OC (national park, considered relatively pristine area). Sieved at 1 mm and ultimately 40 µm with

deionized water. Then frozen (-20°C) and defrozen 1 day before spiking. For testing, mixed with Merck silica gel 60, ø0.063-0.200 mm to achieve 2 % TOC.

- Spiking and equilibration time: following OECD 218. Stock solution of tebuconazole in acetone is added to a dried aliquot of silica sand (gel). Acetone is left to evaporate and then mixed with the corresponding natural dried sediment and freshwater, then left to settle for 2 d equilibration period.
- Overlying water: filtered natural freshwater from Lake Stensjön.
- Determination of pH and dissolved oxygen throughout the test and within acceptable ranged (pH = 6.5-6.8; DO = 74—92 %), but time or frequency of measurements not provided.
- Bioassays: the data were generated using a newly developed set of two tests, a development test and a reproduction test run in parallel, and these tests were performed in 6-well microplates. Each replicate filled with a mixture of 177.9 mg silica gel (sand) + 21.3 mg natural (pre-treated) sediment + 7.5 ml filtered freshwater. Solvent control and four concentrations tested: 4, 12, 41, 124 mg/kg d.w. nominal; effect concentrations expressed as measured (time-weighted of measured concentrations at start and end of test). Test organisms fed three times per week with a microalgae suspension.
    - Development test: Static test performed during 21 days (development test) by adding 10 newly hatched (< 24h) nauplii per replicate and eight replicates per concentration. At end of test, the content of each replicate sieved after 21 day exposure and nauplii and copepodite counted under the microscope. Measured concentrations (time-weighted): 0.5, 1.6, 4.8 and 13 mg/kg d.w. Effects on survival of the adults were recorded but are neither evaluated statistically not displayed as figure or table.
    - Reproduction test: Static test performed during 14 days by adding one ovigenous female in precopula (with attached male) per replicate and 12 replicates. After 14 days, content of each well were sieved and adults and produced offspring (nauplii) were counted under the microscope. Measured concentrations (time-weighted): 0.73, 1.8, 5.0 and 16 mg/kg d.w.
- Test endpoints: mean body length of nauplii per replicate after 21 d exposure (developmental effect); adult female and male mortality and mean offspring production (reproduction test).
- Statistics: comparison through one-way ANOVA followed by Dunnett's post hoc tests.

5 Derivation of QS_{sed} using sediment effect data

According to the EC TGD for EQS, sediment toxicity tests, aquatic toxicity tests in conjunction with equilibrium partitioning (EqP) and field/mesocosm studies are used as several lines of evidence to derive QS_{sed} (EC 2018). Thus, in the following, the appropriateness of the deterministic approach (AF-Method), the probabilistic approach (SSD method) and the EqP approach was examined.

5.1 Derivation of $QS_{sed,AF}$ using the Assessment Factor (AF) method

The derivation of $QS_{sed,\ AF}$ is determined using assessment factors (AFs) applied to the lowest credible datum from long-term toxicity tests.

The lowest long-term effect datum available for tebuconazole is the unbounded NOEC of <500 µg/kg d.w. (2 % OC) or 25000 µg/kg-OC for survival of *Atheyella crassa*.

Table 6 Most sensitive relevant and reliable chronic data summarized from Table 5.

Species	Exposure duration [d]	Endpoint	NOEC [mg/kg d.w.]	OC [%]	NOEC/EC_{10} [mg/kg d.w., 1 % OC]	Reference
Chironomus riparius	28 d	Emergence	21.45	--	--	EFSA (2014)
Atheyella crassa	21 d	Reproduction	<0.5	2	0.25	Turesson et al. (2007)
Heterocypris incongruens	14 d	Growth	9.29	2	4.64	Lefranc (2018)

In case of long term tests (NOEC or EC_{10}) being available for one, two or three species representing different living and feeding conditions, the TGD recommends the application of an assessment factor of 100, 50 and 10 respectively on the lowest credible datum (Table 11 in EC (2018)).

C. riparius is an insect living on the sediment surface or burrowing into it, often forming tubes from which larvae protrude or emerge for feeding mainly on detritus, being a surface deposit-feeder.

A. crassa and *H. incongruens* are epibenthic species, also burrowing on the most superficial layers of sediment. Although they may feed selectively on different food items (bacteria, algae, organic detritus, dead and living plant material, body of invertebrates), they have similar living and feeding behaviors. Therefore, an AF of 50 is initially proposed.

$$QS_{sed,AF} = \frac{lowest\ EC10\ or\ NOEC}{AF}$$

$$QS_{sed,AF} = \frac{0.25\left(\frac{mg}{kg}, 1\ \%\ OC\right)}{50} = 0.005\ \left(\frac{mg}{kg}, 1\ \%\ OC\right)$$

The application of an AF of 50 to the lowest credible chronic datum results in a $QS_{sed,AF}$ = 0.005 mg/kg or 5 µg/kg d.w. for a sediment with 1 % OC representing a worst case scenario in Switzerland, which corresponds to 25 µg/kg d.w. for a standard sediment with 5 % OC.

5.2 Derivation of $QS_{sed,SSD}$ using the species sensitivity distribution (SSD) method

The minimum data requirements recommended for the application of the SSD approach for EQS water derivation is preferably more than 15, but at least 10 NOECs/EC_{10}s, from different species covering at least eight taxonomic groups (EC (2018), p. 43). In this case, not enough data from spiked sediment toxicity tests are available for applying the SSD approach.

6 Derivation of $QS_{sed,EqP}$ using the Equilibrium Partitioning approach

If no reliable sediment toxicity data are available, the Equilibrium Partitioning (EqP) can be used to estimate the $EQS_{sed,EqP}$. This approach, developed for non-ionic substances, is used here for comparison purposes given the small data base of sediment toxicity studies.

6.1 Selection of QS for water

An Annual Average Quality Standard (AA-EQS) has been proposed by the Ecotox Centre at value of 0.24 µg/l for the protection of pelagic species (Oekotoxzentrum 2016). This AA-EQS is derived from a NOEC

of 12 µg/l for the freshwater fish *Oncorhynchus mykiss* and an AF of 50 to account for lack of data for fungi and amphibians. This AA-EQS was assumed sufficient to protect against ED effects because the data set contained effect data for early life stage tests, which have shown to be very sensitive to demethylase inhibitors, and a fish test with an entire life cycle.

6.2 Selection of partition coefficient

One of the main factors influencing the application of the EqP model is the choice of the partition coefficient. It is stipulated in the ECHA 2017 guideline (p. 143, ECHA 2017) that "To increase the reliability of PNEC sediment screen derived using the EqP, it is imperative that a conservative but realistic partitioning coefficient (e.g. K_d, K_{OC}, K_{OW}) is chosen. A clear justification must be given for the chosen coefficient and any uncertainty should be described in a transparent way."

Here, a log K_{OC} of 3.01 is used in the calculation representing the geomean of available K_{OC} values for soil and sediments and one value derived from the K_{OW} (Appendix 1).

6.3 Selection of OC content for a reference sediment

To account for the influence of OC content on $QS_{sed,EqP}$ development, calculations have been performed for an standard sediment according to the EU TGD with 5 % OC (EC 2018). To account for the variability at the national level, a worst case scenario is set at 1 % OC.

6.4 Derivation of $QS_{sed,EqP}$

The derived $QS_{sed,EqP}$ ranges between 2.86 µg/kg d.w. for the worst case scenario (sediment with 1 % OC) to 12.74 µg/kg d.w. for the standard sediment in the TGD (with 5 % OC).

An additional AF of 10 should be applied to the resulting $QS_{sed,EqP}$ for substances with log K_{ow} >5. Reported log K_{ow} ris 3.70 (Table 1). The application of the additional AF is not warranted (Table 7).

Table 7 Derived $QS_{sed,EqP}$ for a geometric mean K_{OC} based on Appendix I and the AA-EQS for water derived by Oekotoxzentrum 2015 (0.26 µg/l). The partition coefficient solid-water sediment (Kp_{sed}) is estimated for a sediment with 5 % OC (standard EC TGD sediment) and 1 % TOC (worst case scenario in Switzerland).

	$QS_{freshwater}$ [µg/l]	K_{OC} [l/kg]	Kp_{sed} [l/kg]	$K_{sed\text{-}water}$ [m^3/m^3]	$QS_{sed,EqP}$ [µg/kg w.w.]	$QS_{sed,EqP}$ [µg/kg d.w.]	Additional AF
1 % OC	0.24	1030	10.3	5.95	1.10	**2.86**	-
5 % OC	0.24	1030	51.5	26.55	4.90	**12.74**	-

The only available proposal for EQS_{sed} is available from INERIS derived using the EqP, which is set at 51 µg/kg d.w. for a sediment with 5 % OC (INERIS 2011) or 11.5 µg/kg d.w. recalculated for 1 % OC. The difference between this value and the $QS_{sed,EqP}$ derived here arises from the AA-EQS derived by INERIS which is higher than that derived by the Ecotox Centre due to a lower assessment factor applied in the derivation (10 instead of 50) and slight difference in the chosen K_{OC} (992 instead of 1030). It should be noted that INERIS proposed to increase the AF by 10 to account for ED effects not accounted for in the current AA-EQS (James-Casas et al. 2019). This would result in a decrease of the AA-EQS to 0.1 µg/l and the derived $QS_{sed,EqP}$ accordingly.

7 Determination of QS_{sed} according to mesocosm/field data

A mesocosm study was performed with the commercial product Lynx (active ingredient –a.i.- concentration unknown) in the USA (Maciorowski 1996) to evaluate ecological effects on fish, aquatic community structure and ecosystem functions, as well as physical and chemical water quality. The study was classified as reliable for the purpose. However, effects to non-target organisms associated with sediment were not adequately investigated. Direct or indirect effects in oligochaete communities at sediment concentrations ranging from 10 to 370 µg a.i./kg d.w. were inferred (concentration at start and end of study). No information on sediment properties is provided in the study report to normalize these concentrations for OC content. A detailed summary of the study is provided in Appendix II.

This study cannot be used for EQS sediment derivation but is used as supportive information

8 Toxicity of degradation products

As detailed in section 2.1, field dissipation studies have reported 1,2,4-triazole (M26) as the major metabolite in soil with a maximum of 9.0 % of applied radioactivity, being relevant for risk assessment but with negligible risk for soil-dwelling or -inhabiting organisms, partially because of the low release rate of the metabolite from tebuconazole and partially because the metabolite showed similar or lower toxicity to various organisms (ECHA 2007; EFSA 2014).

Similar conclusions were reached for water, with the three major metabolites formed by degradation in natural water under the influence of light, HWG 1608-lactone (M17), HWG 1608-pentanoic acid (M25) and 1,2,4-triazole (M26) proving to be of no concern for water organisms. Effect concentrations (EC_{15}) for sediment relevant species include 28 d chronic toxicity in water-only exposure for *Chironomus riparius* of 86.9 mg/l for M25 and 51.2 mg/l for M17, estimated as NOEC (EC_{15}/2), one order of magnitude higher than the EC_{10} reported for the parent compound of 2.45 mg/l (EFSA 2014). Partitioning of these degradation products to sediment (K_{OC} 29.6 l/kg for M25, 1840 l/kg for M17 and 89 l/kg for M26; EFSA 2014) would trigger sediment risk assessment for M17. A $QS_{sed,EqP}$ can be roughly estimated as 24.0 mg/kg d.w. for 5 % OC and 5.12 mg/kg d.w. for 1 % OC through the EqP after applying an AF of 100 to the EC_{15} available for *C.riparius.* With the information available, it is very unlikely that environmental concentrations of M17 in sediments are of concern for sediment-relevant organisms.

9 EQS_{sed} proposed to protect benthic species

The different QS values for each derivation method included in the EC EQS TGD 2018 are summarized in Table 8. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2018). In all cases, data from spiked sediment toxicity tests are preferred over the EqP approach.

Table 8 QS_{sed} derived according to the three methodologies stipulated in the EU-TGD and their corresponding AF. All concentrations expressed as µg/kg d.w.

	Sediment 1 % TOC	**Sediment 5 % TOC**	**AF**
$QS_{sed,SSD}$	-	-	-
$QS_{sed,EqP}$	2.8	12.7	-
$QS_{sed,AF}$	5	25	50
Proposed EQS_{sed}	**2.8**	12.7	-

9.1 Uncertainty analysis

According to the TGD, an AF of 50 is foreseen for $EQS_{sed,AF}$ in case of long term tests (NOEC or EC_{10}) being available for two species representing different living and feeding conditions. The AF can be reduced if the species tested can be considered to represent one of the more sensitive groups. According to the mode of action of tebuconazole, it is expected that the most sensitive taxonomic group is fungi but no effect data are available. Additionally, the Ecotox Centre dossier for the derivation of EQS for Swiss surface waters (Oekotoxzentrum 2016) reports a valid study for the amphibian *Hyla intermedia* reporting an unbounded NOEC at <5 µg/l. Although a definitive NOEC is not available, this unbounded NOEC was lower than the critical datum used to derive the EQS for surface waters (NOEC of 12 µg /l for the fish *Oncorhynchus mykiss*), indicating that amphibians are more sensitive than fish. No sediment effect data are available for fungi, amphibians or fish, the three being sediment relevant taxonomic groups even if the EU TGD does not mention these groups for sediment EQS derivation. These taxonomic groups are considered in the AA-EQS for surface waters and therefore are covered by the derived $QS_{sed,EqP}$. In addition, Turesson et al. (2007) already recorded effects on growth of *A. crassa* at the lowest tested tebuconazole concentration.

There are also uncertainties in the potential ED properties of tebuconazole. While ED criteria are met as regards mammals, ED criteria are not met as regards wildlife .There is a need for additional data from standardized tests on thyroid mode of action and for further assessment/expertise of the mode of action based on invertebrate data. This could also be taken into account in the selection of the AF. However, the AA-EQS for surface waters dataset for tebuconazole includes effect concentrations from early-life stage tests, which are considered very sensitive to demethylase inhibitors (Teigeler et al. 2007), and one fish test with an entire life cycle. These tests may be considered sufficient to possible endocrine-mediated effect of tebuconazole on aquatic organisms.

The derived $QS_{sed,AF}$ is of the same order of magnitude of the $QS_{sed,EqP}$. Based on the uncertainties above, an EQS_{sed} of 2.8 µg/kg d.w. is proposed for 1 % OC or 12.7 µg/kg d.w. for 5 % OC, as being more protective of species susceptible to potential endocrine effects exerted by tebuconazole.

The proposed EQS_{sed} requires the use of sensitive analytical techniques to achieve the appropriate detection limits.

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Appendix I. Sediment-water partition coefficient (K_{oc}) coefficient

TOC, type	Log K_{oc}	K_{oc}	Reference/Source
Soil, TOC 1.40	3.10	1254	Fritz 1988 cited in EU DAR (2007)
Soil, TOC 1.80	3.11	1281	Fritz 1988 cited in EU DAR (2007)
Soil, TOC 0.75	3.18	1512	Fritz 1988 cited in EU DAR (2007)
Soil, TOC 1.27	3.27	1877	Fritz 1988 cited in EU DAR (2007)
Soil, TOC 1.20	3.06	1146	Fritz 1993 cited in EU DAR (2007)
Soil, TOC 1.35	2.86	732	Fritz 1993 cited in EU DAR (2007)
Sediment, freshwater	2.86	728	Vallée et al. 2014
Soil	2.86	729	Vallée et al. 2014
Soil	2.67	469	Vallée et al. 2014
Estimated from K_{OW}, see Table 1	3.15	1409	Log K_{OC}=0.47*log K_{OW}+1.41
	3.01	1030	Geometric mean

Appendix II. Summary of unpublished studies used as supportive information

Lefranc (2018) presents effect data for the freshwater ostracod *Heterocypris incongruens*.

- Species: *Heterocypris incongruens.*
- Origin: newly hatch cysts from commercial provider.
- Experimental sediment: artificial OECD sediment.
- Spiking and equilibration time: stock solution of tebuconazole is added to a dried aliquot of sediment. Acetone is left to evaporate and then mixed with the rest of sediment and test water for 8 h; then left to settle for 7 d equilibration period at 20 °C.
- Overlying water: artificial freshwater.
- Bioassays: Static tests in triplicate performed during 14 days by adding 10 newly hatched ostracods in 4 ml 4:1 water/sediment system. Five concentrations, control and solvent control tested: 0, and 20, 35, 50, 65 and 80 mg/kg d.w. nominal concentrations; 5.4, 10.5, 14.4, 18.3, 21.1 mg/kg d.w time-averaged measured concentrations. Test organisms fed before start of the test with Spirulina, a microalgae solution at test start and with Tetramin® solution after 7 d exposure. At test end (14 d), organisms were sieved and counted and measured with a binocular.
- Test endpoints: mortality and growth.
- Statistics: comparison of means among treatments with non-parametric Kruskal-Wallis and post-hoc Mann-Whitney U test. ECx calculated using Weibull 2 model, best-fit model according to Akaike criteria.

Lefranc (2018) presents effect data for the midge *Chironomus riparius.*

- Origin: Home culture under standardized conditions.
- Experimental sediment: artificial OECD 218.
- Spiking and equilibration time: Stock solution of tebuconazole is added to a dried aliquot of sediment. Acetone is left to evaporate and then mixed with the rest of sediment and test water for 8 h, then left to settle for 6 d equilibration period at 20°C.
- Overlying water: de-chlorinated tap water.
- Determination of pH, dissolved oxygen and temperature in overlying water for all concentrations every week, nitrite/nitrate, phosphate, ammonia at start and end of test.
- Bioassays: Semi-static tests in duplicate performed during 28 days by adding 20 *Chironomus riparius* in 400 ml water/ 100 ml sediment system. Two concentrations tested: 0, 50 and 100 mg/kg d.w. nominal concentrations; 0, 16.5 and 44.7 mg/kg d.w. measured (geometric mean measured concentration at start and end of test). Test organisms fed twice per week.
- Test endpoints: Emergence, mean age at emergence, mean percentage of emerged males.
- Statistics: comparison of means through non-parametric Kruskal-Wallis test followed by Mann-Whitney U test (Wilcoxon-Mann-Whitney).

Lefranc (2018) presents effect data for the freshwater amphipod *Hyalella azteca.*

- Species: *Hyalella azteca.*
- Origin: Home culture under standardized conditions.
- Experimental sediment: artificial OECD sediment.
- Spiking and equilibration time: Stock solution of tebuconazole is added to a dried aliquot of sediment. Acetone is left to evaporate and then mixed with the rest of sediment and test water for 8 h, then left to settle for 6 d equilibration period at 20°C.
- Overlying water: artificial freshwater.

- Determination of pH, dissolved oxygen and temperature in overlying water for all concentrations every week, nitrite/nitrate, phosphate, ammonia at start and end of the test.
- Bioassays: Semi-static tests in duplicate performed during 28 days by adding 20 *Hyalella azteca* in 400 ml water/ 100 ml sediment system. Two concentrations tested: 0, 50 and 100 mg/kg d.w. nominal concentrations; 0, 17.2, 41.7 mg/kg d.w. measured (geometric mean of measured concentrations at start and end of test). Test organisms fed twice per week.
- Test endpoints: survival, growth.
- Statistics: non-parametric Kruskal-Wallis test followed by Mann-Whitney U test (Wilcoxon-Mann-Whitney).

Maciorowski (1996) presents mesocosm study results that evaluate ecological effects on fish, aquatic community structure and ecosystem functions:

Study design: sixteen ponds (30 meters in length by 16 meters wide, each ca. 652 l), one control group and three test levels, received 4 applications (subsurface injections) of Lynx at two week intervals ranging from 2.5 to 40 µg a.i./l (nominal). The measured concentrations were averaged over the 15 week study period, resulting in the following maximum 15-d average exposure concentrations:

1) 11.7 µg a.i./l water, 170 µg a.i./kg d.w. sediment;

2) 35.3 µg a.i./l water, 370 µg a.i./kg d.w.;

3) 149 µg a.i./l water, 1020 µg a.i./kg d.w.

For the two highest concentrations, a range of 15 d average exposure concentrations is also provided in the study report, increasing over time:

- Sediment = 10 to 370 µg a.i./kg d.w., water = 10.2 to 35.3 µg a.i./l;
- Sediment = 10 to 1020 µg a.i./kg d.w., water = 24.4 to 149 µg a.i./l.

According to the K_d for tebuconazole, roughly 10 times as much substance should bind to sediment compared to the amount solubilized in water, while measured concentrations showed 18X, 12X, and 6X as much substance in sediment as water for doses 1, 2, and 3 respectively.

Endpoints:

- Phytoplankton (community study, chlorophyll a, pheophytin a) and zooplankton (protozoans, rotifers, crustaceans) were assessed monthly; peryphyton (ass-free total biomass, chlorophyll a, pheophytin a) was studied at three specific times in glass microslides placed in floating peryphytometers below water surface after 2 week colonization period
- Ecosystem metabolism (total community respiration (mg/l), gross community photosynthesis, production to respiration ratio) were derived from biweekly DO measurements at dusk, dawn and the following dusk using.
- Macroinvertebrates (oligochaetes, ephemeroptera, trichoptera, chironomidae, coleaoptera) were assessed after two weeks of application every two weekly in grab samples, artificial substrate samplers and emergence trap samples.
- Fish (growth, survival, reproduction) was assessed from 24 adult bluegill sunfish (*Lepomis macrochirus*) initially introduced in each pond.

Statistical analysis: ANOVA was used to test for differences in biological parameters between control and doses. Biological count data was normalized by log transformation or ranking and Dunnett's Test

was used to identify differences among means. Community structure analysis was assessed through the Percent Similarity (PS) index. Cluster analysis was performed on the calculated PS values and statistically significant clusters were identified with the non-parametric bootstrap technique.

Effects in pelagic communities: tebuconazole altered juvenile fish growth and survival at the highest mesocosm test concentrations of 24.4 to 149 µg a.i./l in water, which exceeded laboratory test chronic NOECs for fish and invertebrates (12 to 120 µg a.i./l). Indirect significant biological effects were also observed on periphyton and phytoplankton and attributed to tebuconazole at the highest treatment level, but were transient and moderate.

Effects on invertebrates: although direct effects of tebuconazole on macroinvertebrates could not be inferred due to absence of effect concentrations for non-target sediment organisms, diversity of macroinvertebrates was affected at the two highest treatments (sediment = 10 to 370 µg/kg d.w., water = 10.2 to 35.3 µg a.i./l; sediment = 10 to 1020 µg a.i./kg d.w., water = 24.4 to 149 µg a.i./l). Oligochaete numbers were generally higher in treatment ponds during week 3 and were lower during week 7 when compared to control ponds. The number of taxa was significantly reduced at the highest treatment.