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SQC (EQS_{sed}) – Proposal from the Ecotox **Centre for: *Diuron***

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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}): 0.39 $\mu\text{g}/\text{kg d.w.}$

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 preliminary SQC for diuron of 0.39 $\mu\text{g}/\text{kg d.w.}$ is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 0.39 $\mu\text{g}/\text{kg TS}$

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 beschrieben wird, schlägt das Oekotoxzentrum einen vorläufigen SQK für diuron von 0.39 $\mu\text{g}/\text{kg TS}$ für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 0,39 $\mu\text{g}/\text{kg p.s.}$

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 provisoire pour le diuron de 0,39 $\mu\text{g}/\text{kg p.s.}$ est proposé pour les sédiments standards avec 1 % CO.



Sommario

CQS (EQS_{sed}): **0,39 $\mu\text{g}/\text{kg p.s.}$**

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 provvisorio per il diuron di 0,39 $\mu\text{g}/\text{kg p.s.}$ è proposto per sedimenti standard con 1 % CO.



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1 General Information

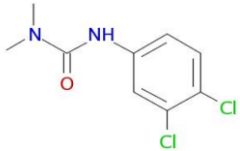
Selected information on the herbicide diuron can be found in the Ecotox Centre Dossier for diuron in water¹ (Ecotox Centre 2016). Only complementary information relevant for sediment has been added to this chapter. The following assessment reports were evaluated for the preparation of the EQS_{sed} dossier:

- EC DAR (Draft Assessment Report) 2005. Initial risk assessment provided by the rapporteur Member State Denmark for the existing active substance Diuron. Submitted to EFSA September 2003.
- EC 2005. Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 13 Diuron CAS-No. 330-54-1. Final Version. Brussels.

1.1 Identity and physico-chemical properties

Table 1 summarizes the identity and physicochemical parameters for diuron. 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 2011).

Characteristics	Values	References
IUPAC name	3-(3,4-dichlorophenyl)-1,1-dimethylurea	ESIS (EC 2010)
Chemical group	Phenylurea derivatives	Backhaus et al. (2004)
Structural formula		ESIS (EC 2010)
CAS	330-54-1	EC 2005
EINECS	206-354-4	ESIS (EC 2010)
Molecular formula	C ₉ H ₁₀ Cl ₂ N ₂ O	ESIS (EC 2010)
Code SMILES	CN(C)C(=O)Nc1ccc(Cl)c(Cl)c1	UM-BBD (University of Minnesota 2010)
Molecular weight (g/mol)	233.1	Epi-Suite 4.0 (US EPA 2008)
Melting point (°C)	158 (exp.)	Epi-Suite 4.0 (US EPA 2008)
Boiling point (°C)	[1] 353.86 (est.- adapted from Stein and Brown method) [2] Degradation starts at 330°C	[1] Epi-Suite 4.0 (US EPA 2008) [2] EC DAR (2005)
Vapour pressure (Pa)	[1] 9.20 x 10 ⁻⁶ (exp.) [2] 1.15 x 10 ⁻⁶ (25°C)	[1] Epi-Suite 4.0 (US EPA 2008) [2] EC DAR (2005)
Henry's law constant (Pa·m ³ /mol)	[1] 5.11 x 10 ⁻⁵ (exp.) [2] non-volatile	[1] Epi-Suite 4.0 (US EPA 2008) [2] Moncada (2004)
Water solubility (mg/L)	35.6 (35°C, 99.8 %)	EC DAR (2005)

¹ The dossier can be requested to info@oekotoxzentrum.ch



Characteristics	Values	References
pKa	No-pKa value between 0 and 12 (est.)	Karickhoff et al. (2009)
Octanol-water partition coefficient (log K _{ow}) ²	<p>[1] 2.87 (exp., shake flask method, OECD 107, HPLC-UV)</p> <p>[2] 2.85 (exp., shake flask method, OECD 107)</p> <p>[3] 2.67 (est. KOWIN Version 1.67)</p> <p>[4] 2.65 (exp. shake flask method)</p> <p>[4] 2.85 (exp. shake flask method)</p> <p>[4] 2.68 (exp. shake flask method)</p> <p>[4] 2.89 (est.)</p> <p>[4] 2.68 (est.)</p> <p>[4] 2.60</p> <p>[4] 2.85</p> <p><u>Average exp. data (n=5): 2.78</u></p>	<p>[1] EC DAR (2005)</p> <p>[2] Jean-Baptiste 2015 cited in EC RAR (2018)</p> <p>[3] Epi-Suite 4.0 (US EPA 2008)</p> <p>[4] Cited in Finizio et al. (1997)</p>
Sediment-water partition coefficient (K _{oc}) ²	<p>[1] 251 (est.)</p> <p>[2] 24-1738 (exp. n=153)</p> <p>[3] 145-5623 (exp. n=41)</p> <p>[4] 366-5240 (exp. n=16)</p> <p>[5] 151-871 (exp. n=52)</p> <p>[6] 212-339 (exp. n=5)</p> <p><u>Estimated from K_{ow} (phenyl urea): 258</u></p> <p>From equation (EC 2011): log K_{oc}=0.49*log K_{ow}+1.05</p> <p><u>Geometric mean exp. data (n=208) + est. from K_{ow}: 339</u></p> <p>Data in Appendix I</p>	<p>[1] Epi-Suite 4.0 (US EPA 2008)</p> <p>[2] Bockting et al. (1993)</p> <p>[3] Crommentuijn et al. (1997)</p> <p>[4] APVMA (2011)</p> <p>[5] Mackay et al. (2006)</p> <p>[6] Wang and Keller (2009)</p>
Hydrolysis (DT50)	<p>pH 4: 798 d (25°C) [1]</p> <p>pH 5: 313 d (25°C) [1]</p> <p>pH 7: stable (25°C) [1]</p> <p>pH 9: stable (25°C) [1]</p> <p>pH 4: 26 d (50°C) [1]</p> <p>pH 5: 56 d (50°C) [1]</p> <p>pH 7: stable (50°C) [1]</p> <p>pH 9: 109 d (50°C) [1]</p> <p>Limited degradation of 1-2 % (25°C, pH 5-9; DT50 > 500 d) [2]</p> <p>No data on hydrolysis of active substance and relevant metabolites [1]</p>	<p>[1] EC DAR (2005)</p> <p>[2] APVMA (2011)</p> <p>[3] Sneikus 2000 cited in EC DAR (2005)</p>
Photolysis		
-DT50 air	2.9-4.5 h [1]	
-DT50 water	43 d [1]	
	2.2-43 d (calculated to correspond to photolysis under sunlight, 30-40°N) [2]	
-DT50 soil:	173 d (silt loam soil) [2]	

² Reliability checked by the review's authors, endorsed without further reliability assessment. See section 2.2 for further details.



Characteristics	Values	References
Degradation - DT50 soil	143 d (lab; 10°C; n=1) [1] 20-112 d (lab; 20°C; n=6) [1] 35 d (lab; 20°C; n=1), DCPMU [1] 1920 d (lab, 25°C; sterile; n=1) [1] 372 d (lab; 25°C; non-sterile; n=1) [1] 1000 d (lab; 25°C; aerobic; n=1) [1] 14-90 d (field; 231 d; n=10) [1]	
- DT50 water-sediment	River Erft: 8.8 d (water)[3] Hönniger Weiher: 4.2 d (water) [3] River Erft: 48 d (whole system) [3] Hönniger Weiher: 232 d (whole system) [3] Aerobic: 20-372 d [2] Anaerobic: no degradation during anaerobic phase (30 d aerobic, then anaerobic) [2] Aerobic: 5.5-67 d (water); 35-277 d (whole system) [2] Anaerobic: 1.2 d (water) [2]	

1.2 Regulation and environmental limits

Table 2 summarizes existing regulation and environmental limits in Switzerland, Europe and the Netherlands for diuron.

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

Europe	
Directive 2013/39/EU	Identified as a priority substances in the field of water policy
EQS – European Commission (15.01.05)	AA-EQS : 0.2 µg/L MAC-EQS : 1.8 µg/L
Switzerland	
EQS- Ecotox Centre (24.08.16)	AA-EQS : 0.07 µg/L MAC-EQS : 0.25 µg/L
Ordinance on Phytosanitary Products (OPPh) (01.11.16)	Annex 1 Active substances approved as a phytosanitary products
Water protection ordinance (WPO) (02.02.16) Annex 2 Requirements on Water Quality for plant protection products Annex 22 Additional requirements for groundwater which is used for drinking water or is intended as such	Maximum concentration authorized: Surface water : 0.1 µg/L per individual substance Groundwater : 0.1 µg/L per individual substance



Ordinance on foreign substances in food products (OSEC) (01.10.15)	Annex 1 : Maximum permissible concentrations according to annex of EU regulation 777/2013
Ordinance on the Register relating to Pollutant Release and the Transfer of Waste and of Pollutants in Waste Water (PRTR) (15.12.06)	Annex 2 : Threshold value for reporting obligation of release to water and to land
The Netherlands	
MTR (Maximum Permissible Risk for sediment; Crommentuijn et al. 1997; 2000) ^a	9 µg/kg d.w.
TV (Target Value for sediment; Crommentuijn et al. 1997; 2000) ^b	0.09 µg/kg d.w.

^a The concentration above which the risk of adverse effects was considered unacceptable to ecosystems (Crommentuijn et al. 1997).

^b The concentration below which the occurrence of adverse effects is considered to be negligible (Crommentuijn et al. 1997).

1.3 Use and emissions

Diuron is a substituted urea compound registered for use as an herbicide to control a wide variety of annual and perennial broadleaf and grassy weeds on both crop and non-crop sites including forage crops, field crops, fruits, vegetables, nuts, and ornamental crops. In non-crop applications, diuron is used on industrial sites, around farm buildings, and on irrigation and drainage ditches. In Switzerland, diuron is used as an herbicide in agriculture principally in fruits production (45 %) and grapevine (46 %) (UCHEM databank; Wittmer, pers. commun.). In terms of use, it is the 20th in the rank of herbicide use in agriculture in Switzerland (2.5-10 t; Wittmer et al. 2014).

The main diffuse source of diuron in waterbodies of Switzerland is leaching from agricultural soils and building façade wash-out (Wittmer et al. 2014). The main point source of diuron is the chemical industry, by releasing the substance to waterbodies through wastewater (316 kg in 2014, OFEV 2016).

1.4 Mode of action

Diuron primarily functions by inhibiting the photosynthesis, limiting the production of high-energy compounds such as adenosine triphosphate (ATP) used for various metabolic processes. Diuron binds to the photosystem II complex in chloroplast thylakoid membranes, blocking electron transport. This process prevents CO₂ fixation and ultimately prevents plant growth (Vencill 2002 cited in Moncada 2004). According to the mode of action it is expected that the most sensitive species to diuron are primary producers.

2 Environmental fate

2.1 Stability and degradation products

This section is largely based on information provided in the environmental risk assessment of diuron from the Australian Pesticides and Veterinary Medicines Authority (APVMA 2011) and EC DAR (2005).

Under environmental conditions, diuron has the potential to persist for long periods in both soil and water. Its main metabolites, particularly N-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) and (N'-(3-chlorophenyl)-N,N-dimethyl urea (m-CPDMU) are also potentially persistent in sediment and soil. According to biodegradation studies, diuron follows two metabolic pathways for degradation. Aerobic degradation involves demethylation of the urea to give the metabolites DCPMU and 1-(3,4-



dichlorophenyl) urea (DCPU). Anaerobic degradation, which is potentially a faster route of primary degradation, involves dechlorination of the phenyl ring to give m-CPDMU and PDMU.

Aerobic aquatic metabolism of diuron was studied over a maximum period of 120 d in two sediment-water systems at 20°C and darkness using sediments from two locations in Germany: silty loam from the River Erft, a tributary of the Rhine river where microorganisms have been shown to metabolise diuron, and a sandy loamy silt sediments from the Hönniger Weiher, an artificial pond. Overall, diuron half-life in the water column was 8.8 d for the Erft and 4.2 d for the Hönniger Weiher systems respectively. The half-life of diuron for the whole system was shorter in the Erft system than in the Hönniger system, with half-lives of 48 and 232 d respectively (Sneikus 2001 cited in EC DAR 2005). Detected metabolites were DCPMU in sediments from both systems, and the dechlorinated m-CPDMU in the Hönniger system both in water and sediment. Another study performed with radiolabeled diuron applied to the water surface and incubated at 25°C using clay loam sediment under US EPA Guidelines reported a half-life for diuron of 33 d, with m-CPDMU and DCPMU as the two main metabolites.

The degradation of diuron showed to be very fast under anaerobic conditions due to reductive dechlorination, with half-life of 1.2 d reported in a study with clay loam at 25°C in the dark under nitrogen and following US EPA Guidelines. The main metabolite was m-CPDMU.

Regarding its metabolites, degradation of radiolabeled m-CPDMU in two aerobic aquatic systems at 20°C in the dark returned half-lives ranging from 44 to 69 d in water and from 183 to 415 d in the whole system³. At 20°C in the dark but under anaerobic conditions, m-CPDMU reported a half-life of 436 d in whole system.

2.2 Sorption/desorption processes

After application in the field, diuron tends to sorb to the solid phase of the soil. The geometric mean of experimental data for soils and sediments shows a low to medium K_{oc} ($\log K_{oc}=2.54$; Appendix 1). According to this relatively high K_{oc} , transport with (washing off) eroded soil particles has been considered the major process for transport to water systems compared to runoff water (Dores et al. 2009).

A field dissipation study conducted in coastal Queensland (Burnett catchment), Australia followed diuron and its metabolites in farm soil and in stream sediments in a farm operating under conventional regime of sugarcane production up to 265 days after application (APVMA 2011). Diuron was detected in all sediment samples over an approximate 5 km length of stream at concentrations between 3 and 19 $\mu\text{g}/\text{kg}$ d.w. while DCPMU was found (again in all samples) at concentrations of 4 to 31 $\mu\text{g}/\text{kg}$ d.w.. It should be noted that sugarcane produces the highest diuron concentrations compared to other land uses. In another field dissipation study performed in an irrigation ditch in the US, sediment analysis showed only positive results for 0, 2, 4 and 256 days after treatment (average concentrations of 0.76, 0.059, 0.12 and 0.065 mg/kg respectively) and only near the treatment area. This study concluded that dry weather limited diuron movement. The sample on 256 days could be due to runoff from the surrounding treated soil as it was the first time sampling occurred on a day when it rained. There were no other detections of diuron or its metabolites in any other water sample (APVMA 2011). In another field dissipation study in the US sediment analysis showed positive results in the treatment area at time zero and a concentration of diuron in the sediment near the treatment area around 0.5 mg/kg except after 179 d after treatment, when the highest concentration of 1.61 mg/kg was measured. The

³ Aerobic conditions not ensured during the study.



only metabolite detected was DCPMU, with a maximum concentration of 0.13 mg/kg by 179 days after treatment (APVMA 2011).

In a study conducted on two different water systems (River Erft and River Hönniger Weiher, Germany) under laboratory conditions, 9 to 11 % of the applied parent compound was found in sediments after 2 hours of application. The maximum proportion of diuron in the Erft sediment, which showed a high potential for degrading diuron, was found after 28 d (74 % of the applied amount of diuron, then the residues of diuron decrease to 10 % at day 120 (Sneikus 2001 cited in EC DAR 2005). In the Hönniger Weiher sediment, 58 % of the applied parent compound was found in sediments after 7 d of application and remained unchanged at this level until the end of the study.

The adsorption of diuron to sediment is positively correlated with sediment organic carbon (OC) content (0.91-19 % OC) and negatively correlated with temperature (lower the temperature is, higher is the adsorption). Diuron adsorption is not correlated to sediment cation exchange capacity (Peck et al. 1980).

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 behavior 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 $K_{ow} < 5$* ” (p. 50, EFSA 2015). This statement is particularly relevant for diuron, which has an average log K_{ow} of 2.78 (n=5 experimental data; Table 1).

The only available study that has addressed diuron toxicity in spiked sediment toxicity tests (Zhang et al. 2012) used two sediments with different physicochemical properties: one fine sediment and one sandy sediment. The highest toxicity was reported for the microalga *Raphidocelis subcapitata* (formerly known as *Pseudokirchneriella subcapitata*) growth in the sandy sediment with the lowest OC content (OC was not measured; see section 3.3 and Table 5). Another study has also shown that black carbon, a particular type of OC present in surface waters, sediments and soils at different proportions, reduces significantly diuron toxicity to *R. subcapitata* exposed to diuron through spiked waters (Knauer et al. 2007). These two studies support the hypothesis that diuron bioavailability in the aquatic environment depends not only on the quantity of OC but also on its quality (composition). Experimental studies addressing bioavailability through other exposure routes such as sediment ingestion in sediment ingesting invertebrates (not algae) are lacking.

The TGD stipulates that “For substances for which the bioavailability is dependent on the organic carbon content of the sediment, the variability introduced by the presence of toxicity values generated at different organic carbon concentrations can be accounted for by normalizing each (valid) toxicity test result (LC50m EC50, EC10, NOEC) to organic carbon and then express all results in sediment with a standard organic carbon content. The resulting sediment standard can be recalculated to any organic carbon content measured in the field.” There is few data to assess whether OC normalization reduces the variability in the observed effect concentration data. Available data shows that normalization based on measured sediment OC reduced the variability between effect data for *R. subcapitata* from a factor of 3.6 to 2.7 (Zhang et al. 2012), although this conclusion is partly based on estimated OC concentrations in test sediments therefore entail a large level of uncertainty.



2.4 Bioaccumulation and biomagnification

According to its low K_{ow} ($\log K_{ow} < 3$), diuron is not expected to bioaccumulate nor biomagnify. This is apparently confirmed by bioconcentration factors reported by the Netherlands (cited in APVMA 2011), which were 15-85 for laboratory exposures and 190-300 from a field study.

3 Analysis

3.1 Methods for analysis and quantification limit

Table 3 includes limits of detection and quantification for diuron according to published results from studies on field sediments performed in Switzerland (Chiaia-Hernandez 2014; Müller et al. 2016) and France (Mazzella 2014).

Table 3 Methods for diuron analysis in sediments and corresponding limits of detection and quantification ($\mu\text{g}/\text{kg d.w.}$).

Limit of detection	Limit of quantification	Analytical method	Reference
0.2	0.5	GC-MS/MS and LC-MS/MS	Mazzella (2014)
Not reported	0.117-0.169	LC-HRMS	Müller et al. (2016)
0.31	1	LC-ESI-HRMS	Chiaia-Hernandez (2014)

3.2 Environmental concentrations

The availability of measured environmental concentrations of diuron in sediments from Swiss waterbodies is limited. However, measurements have been performed in sediments from two lakes, the Greifensee (Müller et al. 2016) and Lake Constance (Hauzenberger et al. 2015) (Table 4). Sediment concentrations at Lake Constance range from 0.87 to 1.3 $\mu\text{g}/\text{kg d.w.}$, with median concentration of 0.955 $\mu\text{g}/\text{kg d.w.}$ ($n=4$). At Lake Greifensee, maximum concentrations of diuron is 1.5 $\mu\text{g}/\text{kg d.w.}$ and 2.4 $\mu\text{g}/\text{kg d.w.}$ of DCPMU.

Because the database of measured environmental concentrations of diuron in surface waters from Switzerland is more extensive than that for sediments, the equilibrium partitioning model (Di Toro et al. 1991) was used to estimate concentrations in sediment from the measured concentrations in surface waters (Table 4). Overall, the predicted sediment concentrations ($PEC_{sed,EqP}$) are in accordance with the range of measured concentrations in sediment.

Table 4 Measured Environmental Concentrations (MEC_{sed}) in sediments from Switzerland and Predicted Environmental Concentrations (PEC_{EqP}) derived from measured concentrations in surface waters using the equilibrium partitioning model (Di Toro et al. 1991) and default values from the TGD (EC 2011). All concentrations expressed as $\mu\text{g}/\text{kg d.w.}$

Substance	MEC_{sed}	Nr sites	Comments	Reference
Diuron	median: 0.955 min: 0.87; max: 1.3	2	Lake Constance, $n=4$	Hauzenberger et al. (2015)
Diuron DCPMU	min: 0.15; max: 1.5 ^a min: 0.3; max: 2.4 ^a	-	Lake Greifensee, ≥ 3 sites above LOQ	Müller et al. (2016)
Substance	PEC_{EqP}^b [$\mu\text{g}/\text{kg d.w.}$]	Nr sites	Comments	Reference
Diuron	median: 0.08 min: 0.06; max: 0.11	1	Lake Geneva ($n=7$; geometric mean in water: 0.004 $\mu\text{g}/\text{L}$)	CIPEL (2016)
Diuron	90 th percentile: 1.67 max: 334	Detected at 286	All over Switzerland, lakes and rivers	Munz et al. (2013)



		of 530	(water: 90 th percentile 0.09, max: 18 µg/L)	
Diuron	max: 55.7	5	Small streams (water: 3 µg/L)	Doppler et al. (2017)

^a Only extreme values available.

^b Predicted Effect Concentration based on the EqP model (Di Toro et al. 1991) for a standard sediment (5 % OC, K_{oc}= 399) using diuron concentration measured in the water phase.

4 Effect data (spiked sediment toxicity tests)

A bibliographic search was performed in existing data bases (Ecotox Centre 2016; EC 2005; US EPA 2016) for relevant sediment toxicity test data. Relevance and reliability of studies were evaluated according to CRED criteria (Moermond et al. 2016) adapted for spiked-sediment toxicity tests (Casado-Martinez et al. 2017). Test species were considered relevant without restrictions according to the document on Effect Assessment of Pesticide on Sediment (EFSA 2015)⁴.

Only one study that reports effect concentration values for sediments was found (Table 5). This study (Zhang et al. 2012) reports effect data for diuron for the 72 h growth test on the algae *R. subcapitata* exposed as immobilized algal beads prepared with 4 % alginate. According to EFSA, this approach is in principle appropriate for the effect assessment of pesticides in the sediment compartment⁵. As the life cycle of this test species is short, NOECs or EC10s from this test are considered chronic values⁶. Values are reported for two types of sediments representing different OC content and grain size: one is natural sediment only with 1.4 % OC and 29 % clay, 66 % silt and 5 % sand; the other is natural sediment mixed with 90% of acid washed sand (estimated OC content 0.14 %). OC content was measured in the natural sediment, whereas OC content after amendment with acid washed sand was estimated assuming no OC in the acid washed sand.

In accordance with the assumption that increasing OC in sediments decreases diuron bioavailability, effect concentrations for the *R. subcapitata* study were lower for the spiked sediment with higher clay content and OC than in sediments after amendment with acid washed sand (Zhang et al. 2012). According to EU TGD (2011, p.150), the geometric mean is calculated when multiple reliable data are available for the same species and endpoint. Because OC was not measured after amendment with acid washed sand and the estimated OC (0.14 %) falls below the recommended range for OC normalization (0.2-10 %; Simpson et al. 2013, p.12), where other physical and chemical factors influence the partitioning process for hydrophobic organics (Batley et al. 2002), this effect datum is considered R3 and is not used for EQS_{sed} derivation⁷.

⁴ *Anabaena flosaquae, Chironomus acutus, Chironomus riparius, Chironomus tentans, Chironomus yoshimatsui, Chironomus dilutus, Craticula accomoda, Diporeia spp, Elodea spp, Fragilaria rumpens, Glyceria maxima, Gomphonema parvulum, Hexagenia spp, Hyalella azteca, Lumbriculus variegatus, Mayamaea fossalis, Myriophyllum aquaticum, Myriophyllum spicatum, Pseudokirchneriella subcapitata, Pseudomonas putida, Sellaphora minima, Tubifex tubifex.*

⁵ "Although the immobilized algal beads showed slower growth than free cells, growth of algae cells in the beads was high enough to be valid for an appropriate toxicity test." p. 21 EFSA, effect assessment on sediment organisms.

⁶ "Algal, Growth Inhibition Test. The EC50 from this 72-h algae test is considered an acute value, the NOEC or EC10 a chronic value." (EC, 2011) p. 136

⁷ EU TGD p.150, point 3. « If an effect of test conditions is expected to be the cause of variation in toxicity values (hardness of test water, life stage of the test animal, etc.), averaging of data per species should not be performed. »

Proposed SQC (EQS_{sed}) for Diuron



Table 5 Sediment effect data collection for diuron. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Casado-Martinez et al. 2017). Data assessed as not relevant and not reliable is in grey font. Abbreviations: n. a. = not available.

Group	Species	Test compound	Administration of tested substance	Equilibration time	Endpoint	Test duration	Effect concentration	Value [mg /kg d.w.]	Normalized value [mg /kg OC d.w.]	Normalized value 5 % OC [mg /kg d.w.]	Nominal/ measured exposure concentration	Sediment type	Validity	Comments	Reference
Algae	<i>Raphidocelis subcapitata</i>	Diuron	spiked into the sediment	1 month	Growth inhibition, measured as cell yield	72 h	NOEC	0.55	39.29	1.96	Measured	Natural freshwater sediment, clay 29 %, OC 1.4 %	R2, C1	Effect concentration from non-shaking flasks as being more relevant for sediment assessment	Zhang et al. (2012)
Algae	<i>Raphidocelis subcapitata</i>	Diuron	spiked into the sediment	1 month	Growth inhibition, measured as cell yield	72 h	NOEC	0.15	-	-	Measured	Mixture of 10 % of natural sediment and 90 % sand; no sediment characterization performed	R3, C1		Zhang et al. (2012)



4.1 Graphic representation of effect data

There is not enough effect data for benthic organisms from spiked sediment toxicity tests for graphic representation. According to effect data for pelagic organisms, primary producers are more sensitive than invertebrates and vertebrates (Ecotox Centre 2016), which is in agreement with the mode of toxic action of diuron.

The representation of chronic NOECs for benthic organisms exposed through spiked diuron in waters (Fig. 1; effect data available in Appendix II) also shows that primary producers are more sensitivity than insects (NOEC > 4000 $\mu\text{g/L}$) and crustaceans ($\geq 60 \mu\text{g/L}$). Lambert et al. (2006) reported NOECs of 0.5 and 50 ng/L for relative growth rate for the rooted macrophytes *Myriophyllum spicatum* and *Apium nodiflorum*, respectively, suggesting that rooted macrophytes might be the most sensitive sediment-relevant effect data, although these conclusions should be taken with care because effect data is either not relevant (macrophytes) or not assignable (all other effect data).

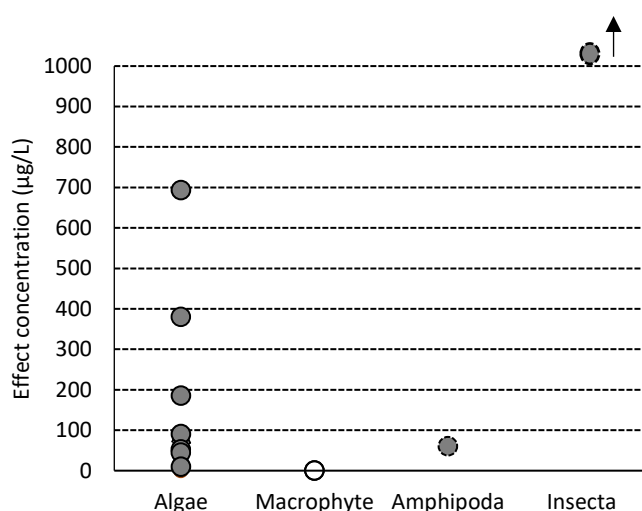


Figure 1 Graphical representation of chronic effect data from spiked water toxicity tests with diuron for relevant benthic organisms. According to data, algae and macrophytes seem to be the most sensitive species. Empty dots: not reliable data; grey dots: not assignable data; dotted line: unbounded NOEC.

4.2 Comparison between marine and freshwater species

No effect data is available for marine spiked sediment toxicity tests.

4.3 Overview of the most sensitive relevant and reliable long-term study

Zhang et al. 2012:

- Species: *Raphidocelis subcapitata* (formerly known as *Pseudokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*)).
- Origin: Algae culture collection of Wuhan Institute of Hydrology.
- Experimental sediment: two types of sediment S1 and S2 for exposure were prepared. S1 is a natural freshwater sediment with 1.4 % OC and 29 % clay, 66 % silt and 5 % sand. Sediment was analyzed for all metals and OC content. S2 was prepared by mixing S1 with 10 % weight of acid-washed sand, no further information is provided for S2.
- Spiking and equilibration time: according to the spiking procedure from US EPA (2001) and Simpson et al. (2004). Diuron-spiked sediments were prepared at eight nominal concentrations. The required volume of the stock solution (10000 mg/L, Shanghai Pesticide



Research Institute, 98 mg/L) was added directly to the 400 g fresh sediment at a sediment to water ratio of 4:1. Then the sediment was mixed thoroughly for 2 h, equilibrated for 24 h, and neutralized to pH 7 with NaOH. The spiked sediments were finally held in the dark at 4°C for a month to equilibrate, and their pH values were checked every day and adjusted if necessary to pH 7.

- Overlying water: US EPA medium without EDTA.
- Overlying water quality: determination of pH, dissolved oxygen and diuron concentrations in overlying water at day 0 and day 3.
- Bioassays: 72 h exposure test. 3 to 4 days old culture of *R. subcapitata* culture was immobilized on 4 % alginate and CaCl₂ beads. Eight different nominal concentrations of diuron were tested: 0, 0.4, 0.8, 1.6, 3.2, 6.3, 12.5, 25, and 50 mg/kg (dry weight) for sediment S1, and 0, 0.25, 0.5, 1, 2.5, 5, 10, and 20 mg/kg (dry weight) for sediment S2. The test was carried out in six replicates for each concentration treatment, three replicates used to determine cell yield after 72 h exposure and the other three replicates to determine pH, dissolved oxygen, and diuron in overlying water and sediment on day 0 and day 3. Each treatment concentration was tested in 6 replicates containing 10 beads (5X10⁴ cells/bead) per replicate. Algae growth determined after 72 h of exposure at 24 ± 1°C under continuous illumination (4000 lux, cool white fluorescence) in a thermostatic incubator. Test performed without shaking the flasks and shaking the flasks twice a day. Incubation of test media without shaking is preferred for whole-sediment toxicity testing as being more environmentally realistic of whole-sediment exposure.
- Test controls: blank control (sediment control) and solvent controls (trace methanol, <0.1 %) always tested alongside the test sediments.
- Test endpoint: inhibition of algal growth measured as algae cell concentration with cell yields used as the endpoint. Cell yields determined by counting algal cells on a hemocytometer under a microscope. Variability of the algal counting (*n* = 3) was less than 15 %.
- Statistics: Fitting for a dose-response curve with four-parameter logistic equation. NOEC determined by one way ANOVA (*p*<0.05) on mean measured environmental concentrations on day 0 and day 3. No post-hoc test performed.

→ Data are accepted as R2, C1. Effect data from non-shaking tests are used because they are considered more environmentally relevant compared to shaking tests.

5 Derivation of QS_{sed}

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 2011). Thus, in the following, the appropriateness of the deterministic approach (AF-Method), the probabilistic approach (SSD method) and the EqP approach were examined.

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

Only one effect datum from spiked sediment toxicity tests is available, for the algae *R. subcapitata* from Zhang et al. (2012).

The following considerations apply for the selection of the assessment factor:

- For the selection of the assessment factor to derive the AA-EQS_{AF} for surface waters, the TGD (EC 2011 p. 37) specifically says “*The algal growth inhibition tests of the base set is, in principle, a multigeneration test. However, for the purposes of applying the appropriate assessment factors, the EC50 is treated as a short term toxicity value. The NOEC from this test may be used*



as an additional NOEC when other long-term data are available. In general an algal NOEC should not be used unsupported by long term NOECs of species of other trophic levels. However if the short term algal toxicity test is the most sensitive of the short term tests, the NOEC from this test should be supported by the result of a test on a second species of algae.”

- According to Table 5.1 (TGD for EQS), an AF of 100 should be applied to a single long-term NOEC or EC10, irrespective of the trophic / taxonomic group to which the test organism belongs.
- According to uncertainties in the study (see section 9.1), it is proposed to increase the AF from 100 to 1000.

In view of these elements, an assessment factor of 1000 is proposed, and the resulting $QS_{sed,AF}$ must be compared with the QS_{sed} derived using the EqP method⁸. The application of the AF method to the only relevant and reliable (R2/C1) NOEC is:

$$QS \left(\frac{mg}{kg} \right) = \frac{\text{lowest EC10 or NOEC}}{1000}$$

$$QS_{sed,AF} \left(\frac{mg}{kg} \right) = \frac{39.29 \frac{mg}{kg - OC}}{1000} = 39.29 \left(\frac{\mu g}{kg - OC} \right)$$

This $QS_{sed,AF}$ is equal to 1.96 $\mu g/kg$ d.w. for a sediment with 5 % OC or 0.39 $\mu g/kg$ d.w. for a sediment with 1 % OC. A sediment with 1 % OC is considered a worst case scenario in Switzerland.

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/EC₁₀s, from different species covering at least eight taxonomic groups (EC (2011), 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-QS) has been proposed by the European Commission which sets a value of 0.2 $\mu g/L$ for the protection of pelagic species (EC 2005). In 2016, the Ecotox Centre revised the quality criteria according to the availability of new effect data for the years 2005-2016. This update performed in accordance with the TGD provides an AA-EQS of 0.07 $\mu g/L$ (Ecotox Centre 2016). The AA-EQS proposed by the Ecotox Centre is used in the application of the EqP because it takes into consideration the most recent published data and uses the statistical approach (SSD) compared to the AA-EQS from the EU dossier (based on the AF).

⁸ EU TGD (EC 2011, p.96): « If only results from short-term tests with sediment-dwelling organisms are available, an assessment factor of 1000 is applied to the lowest reliable value. In situations where only short term test data is available a QS should also be derived using the Equilibrium Partitioning approach ».



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 (ECHA 2017, p. 143) 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.”

A review of K_{OC} values compiled from different reports (see Appendix I and Table 1) derived from batch-equilibrium and field studies plus K_{OC} estimated from the K_{OW} using the equation for phenylureas as required by EU TGD (EC 2011, p. 172) resulted in a geometric mean of 339 l/kg. This K_{OC} value is used in the application of the EqP model.

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 a standard sediment according to the EU TGD with 5 % OC (EC 2011). As 5 % OC might not be representative for sediment in Switzerland, calculation was made as well for a worst case scenario considering measurement on total sediment with 1 % OC (approx. 10th percentile of OC content in Swiss Rivers).

6.4 Derivation of $QS_{sed,EqP}$

For the derivation of $QS_{sed,EqP}$, the partition coefficient between water and sediment has been estimated as the fraction of organic carbon multiplied by organic carbon partition coefficient ($K_p=f_{OC} \cdot K_{OC}$) as proposed by Di Toro et al. (1991) for nonionic organic chemicals. Di Toro et al. (1991) considered that, for sediment with an organic fraction higher than 0.2 %, organic carbon is the main driver for chemical sorption.

The calculated $QS_{sed,EqP}$ is 0.35 $\mu\text{g}/\text{kg}$ d.w. for a sediment with 1 % OC and 1.30 $\mu\text{g}/\text{kg}$ d.w. for 5 % OC (Table 6).

The application of the additional AF of 10 to derive the $QS_{sed,EqP}$ is not justified according to a $K_{ow} < 5$ (Table 1), which presumes not extra uncertainty due to uptake through ingestion.

Table 6 $QS_{sed,EqP}$ derived from the geometric mean of K_{OC} values with the AA-EQS for water derived by the Ecotox Centre of 0.07 $\mu\text{g}/\text{L}$ (Ecotox Centre 2016). The partition coefficient solid-water sediment ($K_{p_{sed}}$) is estimated for a sediment with 1% and 5 % OC (standard EU TGD sediment).

Sediment with	K_{OC} [L/kg]	$K_{p_{sed}}$ [L/kg]	$K_{sed-water}$ [m^3/m^3]	$QS_{sed,EqP}$ [$\mu\text{g}/\text{kg}$ ww]	$QS_{sed,EqP}$ [$\mu\text{g}/\text{kg}$ d.w.]
1 % OC	339	3.39	2.50	0.13	0.35
5 % OC	339	16.95	9.28	0.50	1.30

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

No mesocosm study that provides effect concentrations of diuron on benthic communities exposed to spiked sediment is available that can be used to derive a QS_{sed} .

Although there are also no mesocosm studies that could be used to derive reliable NOEC values for AA-EQS derivation (Ecotox Centre 2016), several mesocosms studies are available that can be used as supportive information for the plausibility of the safety factors selected in QS derivations. Relevant for the sediment compartment, Knauert et al. (2010) exposed the rooted macrophytes *Elodea canadensis*, *Myriophyllum spicatum* and *Potamogeton lucens* to 5 $\mu\text{g}/\text{L}$ diuron (98.4 %) in overlying water in



mesocosm studies comprising a sediment layer. Significant reduction on photosynthetic efficiency of all three macrophytes was observed after 5 days of exposure, but macrophytes recovered and no significant effects were observed neither on photosynthesis nor growth at the end of the exposure (34 days).

8 Toxicity of degradation products

According to APVMA (2011), diuron metabolites resulted as more mobile than the parent compound in sorption/desorption studies with soils following US EPA Guidelines: DCPMU is moderately adsorbed to soils according to K_{OC} values ranging from 572 to 4989, m-CPDMU has K_{OC} values ranging from 40 to 323 and for PDMU from 33 to 138. According to a log K_{OC} ranging from 2.75 to 3.69, DCPMU may also likely partition to sediment, which is in agreement with measured environmental concentrations (section 2.6).

No sediment toxicity data are available for these compounds. However, m-CPDMU and DCPMU have shown to exert toxicity to the algae *Scenedesmus subspicatus* exposed through the water phase, with EC50 of 246 and 18.4 $\mu\text{g/L}$ respectively in the same order of magnitude as toxicity of the parent compound, and low toxicity for DCPMU with EC50 of 5660 $\mu\text{g/L}$ (APVMA 2011).

9 EQS_{sed} proposed to protect benthic species

The different QS values from each derivation method included in the EU TGD (EC 2011) are summarized in Table 7. According to the EU TGD, the most reliable extrapolation method for each substance should be used (EC 2011, p. 39).

Table 7 QS_{sed} derived according to the three methodologies stipulated in the EU-TGD and their corresponding AF. All concentrations expressed as $\mu\text{g/kg d.w.}$.

Generic QS_{sed}	Derived value 1 % OC	Derived value 5 % OC	AF
$QS_{sed,field}$	-	-	-
$QS_{sed,SSD}$	-	-	-
$QS_{sed,AF}$	0.39	1.96	1000
$QS_{sed,EqP}$	0.35	1.30	-
Proposed EQS_{sed}	0.39	1.96	-

9.1 Uncertainty analysis

The $QS_{sed,EqP}$ is in line with the $QS_{sed,AF}$ derived by applying an AF of 1000 to the NOEC from spiked sediment toxicity tests using the microalgae *R. subcapitata*. The AF of 1000 seems justified taking into consideration the following uncertainties:

- The only effect datum from spiked-sediment toxicity test is considered reliable and relevant with restrictions, given the algal beads have a diameter of approx. 4 mm and contains approx. 52000 cells. Algae that are not at the surface of the bead might not be in close contact with diuron applied to the sediment.
- No additional chronic NOEC is available from spiked sediment toxicity tests for another microalgae species as recommended for surface water AA-EQS development.
- Effect data from spiked water toxicity tests for sediment-relevant organisms (Fig. 1) suggest that the most sensitive taxonomic group might be that of rooted macrophytes, although this conclusion is based on non-reliable (R3) effect data and results are not fully in agreement with results from mesocosm exposures (Knauert et al. 2010).



- No effect data for the degradation products of diuron in sediment is available although DCPMU and m-CPDMU have shown to be persistent in this environmental compartment, present at concentrations as high as that of the parent compound, and exert similar toxicity to microalgae.

Taking into consideration the recommendations from the EU TGD and the remaining uncertainties, an EQS_{sed} for diuron of 0.39 µg/kg d.w. for 1 % OC representative of a worst case for Swiss sediments is proposed.

10 References

- APVMA, 2011. Diuron Final Review Report (No. ISBN: 978–1–922188–08–3). Australian Pesticides and Veterinary Medicines Authority, Kingston, Australia.
- Batley, G.E., Burton, G.A., Chapman, P.M., Forbes, V.E., 2002. Uncertainties in sediment quality weight of evidence assessments. *Human Ecol. Risk Assess.* 8, 1517-1547.
- Bockting, G.J.M., van de Plassche, E.J., Struijs, J., Canton, J.H., 1993. Soil-water partition coefficients for organic compounds (No. 679101013). National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.
- Backhaus, T., Faust, M., Scholze, M., Gramatica, P., Vighi, M., Grimme, L.H., 2004. Joint algal toxicity of phenylurea herbicides is equally predictable by concentration addition and independent action. *Environ. Toxicol. Chem.* 23, 258–264.
- Casado-Martinez, M. C., Mendez-Fernandez, L., Wildi, M., Kase, R., Ferrari, B. J. D., Werner, I., 2017. Incorporation of sediment specific aspects in the CRED evaluation system: recommendations for ecotoxicity data reporting. SETAC Europe 27th Annual Meeting, Brussels.
- Chiaia-Hernandez, A.C., 2014. Temporal records of organic contaminants in lake sediments, their bioconcentration and effect on *Daphnia* resting eggs. ETHZ, Zürich.
- Crommentuijn, T., Kalf, D.F., Polder, M.D., Posthumus, R., van de Plassche, E.J., 1997. Maximum Permissible Concentrations and Negligible Concentrations for pesticides (No. 601501002). RIVM, Bilthoven, the Netherlands.
- Crommentuijn, T., Sijm, D., de Bruijn, J., van Leeuwen, K., van de Plassche, E., 2000. Maximum Permissible and Negligible Concentrations for some organic substances and pesticides. *J. Environ. Manag.* 58, 297-312.
- Di Toro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10, 1541–1583.
- Doppler, T., Mangold, S., Wittmer, I., Spycher, S., Comte, R., Stamm, C., Singer, H., Junghans, M., Kunz, M., 2017. Hohe PSM- Belastung in Schweizer Bächen. *Aqua and Gas* 46, 11.
- Dores, E.F.G.C., Spadotto, C.A., Weber, O.L.S., Carbo, L., Vecchiato, A.B., Pinto, A.A., 2009. Environmental behaviour of metolachlor and diuron in a tropical soil in the central region of Brazil. *Water. Air. Soil Pollut.* 197, 175–183.
- EC, 2005. Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 13 Diuron CAS-No. 330-54-1. Final Version. Brussels.
- EC, 2010. ESIS (European Chemical Substances Information System). Joint Research Center - Institute for Health and Consumer Protection, European Commission (EC) <http://ecb.jrc.ec.europa.eu/esis/>.
- EC, 2011. Technical Guidance (TGD) For Deriving Environmental Quality Standards, Common Implementation Strategy for the Water Framework Directive (2000/60/EC).
- EC DAR, 2005. Draft Assessment Report (DAR) for Diuron - public version- Initial Risk Assessment Provided by Rapporteur Member State Denmark for the Existing Active Substance Diuron of



- the Second Stage of the Review Programm Referred to in Article 8(2) of Council Directive 91/414/EEC (No. Volume 1).
- ECHA, 2017. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.7b: Endpoint specific guidance (No. ECHA-17-G-10-EN). European Chemicals Agency, Finland.
- EC RAR, 2018. Renewal Assessment Report, Diuron, Volume 3 - B.2 Physical and Chemical Properties (p. 12).
- Ecotox Centre, 2016. EQS - Vorschlag des Oekotoxenzentrums für: Diuron (p. 40). Dübendorf: Ecotox Centre EAWAG-EPFL. Retrieved from <http://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/>
- EFSA, 2015. Scientific Opinion on the Effect Assessment for Pesticides on Sediment Organisms in Edge-of-field Surface Water: Effect Assessment on Sediment Organisms. EFSA J. 13, 4176.
- Finizio, A., Vighi, M., Sandroni, D., 1997. Determination of n-octanol/water partition coefficient (Kow) of pesticide critical review and comparison of methods. Chemosphere 34, 131–161.
- Hauzenberger, I., Trimbacher, T., Weiß, S., 2015. Erste Österreichische Fallstudie Zu Antifoulingwirkstoffen In Der Umwelt (No. REP-0530). Umweltbundesamt GmbH Spittelauer Lände 5, 1090 Wien/Österreich.
- Karickhoff S. W., Carreira L. A., Hilal S. H., 2009. SPARC v.4.5 online calculator. Version September 2009 release w4.5.1529-s4.5.1529, <http://sparc.chem.uga.edu/sparc/>.
- Knauer, K., Sobek, A., Bucheli, T.D., 2007. Reduced toxicity of diuron to the freshwater green alga *Pseudokirchneriella subcapitata* in the presence of black carbon. Aquat. Toxicol. 83, 143–148.
- Knauert, S., Singer, H., Hollender, J., Knauer, K., 2010. Phytotoxicity of atrazine, isoproturon, and diuron to submerged macrophytes in outdoor mesocosms. Environ. Poll. 158, 167-174.
- Lambert, S.J., Thomas, K.V., Davy, A.J., 2006. Assessment of the risk posed by the antifouling booster biocides Irgarol 1051 and diuron to freshwater macrophytes. Chemosphere 63, 734-743.
- Larras, F., Montuelle, B., Bouchez, A., 2013. Assessment of toxicity thresholds in aquatic environments: Does benthic growth of diatoms affect their exposure and sensitivity to herbicides? Sci. Total Environ. 463, 469-477.
- Mackay, D., Shiu, W. Y., Ma, K.-C., & Lee, C. L., 2006. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals (Taylor & Francis Group). 6000 Broken Sound Parkway NW, Suite 300: CRC Press. Retrieved from <https://www.crcpress.com/Handbook-of-Physical-Chemical-Properties-and-Environmental-Fate-for-Organic/Mackay-Shiu-Ma-Lee/p/book/9781566706872>
- Mazzella, N., 2014. Pesticide-Méthode d'Analyse dans les Sédiments (Fiche No. MA-19). Aquaref.
- Moermond, C.T.A., Kase, R., Korkaric, M., Ågerstrand, M., 2016. CRED: Criteria for Reporting and Evaluating Ecotoxicity Data. Environ. Toxicol. Chem. 35, 1297–1309.
- Moncada, A., 2004. Environmental Fate of Diuron, Environmental Monitoring Branch, Department of Pesticide Regulation, Sacramento.
- Müller, A., Chiaia-Hernandez, A., Hollender, J., 2016. Exploring Temporal Trends of Pesticides in Lake Sediments by LC-HRMS. ETH Zürich, Zürich.
- Munz, N., Leu, C., Wittmer, I., 2013. Pesticides dans les Cours d'Eau Suisses – Aperçu de la Situation à l'Échelle Nationale.
- OFEV, 2016. SwissPRTR Pollutant Register [WWW Document]. Swiss Confed. URL <http://www.prtr.admin.ch/PublicWebSite/Abfrage.aspx?Lang=eng>.
- Peck, D.E., Corwin, D.L., Farmer, W.J., 1980. Adsorption-desorption of diuron by freshwater sediments. J. Environ. Qual. 9, 101–106.
- Simpson, S.L., Angel, B.M., Jolley, D.F., 2004. Metal equilibration in laboratory-contaminated (spiked) sediments used for the development of whole-sediment toxicity tests. Chemosphere 54, 597–609.
- Simpson, S.L., Batley, G.E., Chariton, A.A., 2013. Revision of the ANZECC/ARMCANZ Sediment Quality Guidelines. <https://doi.org/10.4225/08/5894c6184320c>
- University of Minnesota, 2010. UM-BBD Pathway Prediction System - Based On Structural Formula. <http://umbbd.msi.umn.edu/predict/>.



- US EPA, 2001. Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical manual. EPA-823-B-01-002. Washington, DC.
- US EPA, 2003. Reregistration Eligibility Decision (RED) for Diuron (p. 211). Washington DC 20460: U.S. Environmental Protection Agency.
- US EPA, 2008. EPI Suite™. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11 or insert version used]. United States Environmental Protection Agency, Washington, DC, USA.
- US EPA, 2016. AQUIRE: AQUatic toxicity Information Retrieval database [WWW Document]. URL <http://www.epa.gov/ecotox/>.
- Wang, P., Keller, A.A., 2009. Sorption and desorption of atrazine and diuron onto water dispersible soil primary size fractions. *Water Res.* 43, 1448–1456.
- Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A., 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments—A Review. *Appl. Geochem.* 18, 159–194.
- Wittmer, I., Junghans, H., Singer, H., Stamm, C., 2014. Micropolluant, Stratégie d'Évaluation pour les Micropolluants de Sources Non Ponctuelles. Etude Réalisée sur Mandat de l'OFEV. Eawag, Dübendorf.
- Zhang, L.-J., Ying, G.-G., Chen, F., Zhao, J.-L., Wang, L., Fang, Y.-X., 2012. Development and application of whole-sediment toxicity test using immobilized freshwater microalgae. *Environ. Toxicol. Chem.* 31, 377–386.



Appendix I. Experimentally derived log K_{oc} for soil and sediments

Log (K _{oc})	Cited in
1.38	Bockting et al. 1993
2.30	Bockting et al. 1993
2.65	Bockting et al. 1993
1.76	Bockting et al. 1993
2.31	Bockting et al. 1993
2.66	Bockting et al. 1993
1.80	Bockting et al. 1993
2.31	Bockting et al. 1993
2.67	Bockting et al. 1993
1.80	Bockting et al. 1993
2.32	Bockting et al. 1993
2.68	Bockting et al. 1993
1.80	Bockting et al. 1993
2.32	Bockting et al. 1993
2.68	Bockting et al. 1993
1.84	Bockting et al. 1993
2.33	Bockting et al. 1993
2.69	Bockting et al. 1993
1.90	Bockting et al. 1993
2.33	Bockting et al. 1993
2.69	Bockting et al. 1993
1.93	Bockting et al. 1993
2.33	Bockting et al. 1993
2.70	Bockting et al. 1993
1.97	Bockting et al. 1993
2.33	Bockting et al. 1993
2.73	Bockting et al. 1993
1.98	Bockting et al. 1993
2.34	Bockting et al. 1993
2.73	Bockting et al. 1993
1.99	Bockting et al. 1993
2.35	Bockting et al. 1993
2.74	Bockting et al. 1993
2.02	Bockting et al. 1993
2.35	Bockting et al. 1993
2.75	Bockting et al. 1993
2.03	Bockting et al. 1993
2.36	Bockting et al. 1993
2.75	Bockting et al. 1993
2.04	Bockting et al. 1993
2.36	Bockting et al. 1993
2.75	Bockting et al. 1993
2.06	Bockting et al. 1993
2.36	Bockting et al. 1993



Log (K _{oc})	Cited in
2.76	Bockting et al. 1993
2.08	Bockting et al. 1993
2.39	Bockting et al. 1993
2.76	Bockting et al. 1993
2.09	Bockting et al. 1993
2.40	Bockting et al. 1993
2.77	Bockting et al. 1993
2.10	Bockting et al. 1993
2.40	Bockting et al. 1993
2.77	Bockting et al. 1993
2.10	Bockting et al. 1993
2.41	Bockting et al. 1993
2.78	Bockting et al. 1993
2.10	Bockting et al. 1993
2.41	Bockting et al. 1993
2.78	Bockting et al. 1993
2.11	Bockting et al. 1993
2.45	Bockting et al. 1993
2.79	Bockting et al. 1993
2.13	Bockting et al. 1993
2.46	Bockting et al. 1993
2.79	Bockting et al. 1993
2.13	Bockting et al. 1993
2.46	Bockting et al. 1993
2.80	Bockting et al. 1993
2.13	Bockting et al. 1993
2.47	Bockting et al. 1993
2.80	Bockting et al. 1993
2.15	Bockting et al. 1993
2.48	Bockting et al. 1993
2.81	Bockting et al. 1993
2.15	Bockting et al. 1993
2.49	Bockting et al. 1993
2.81	Bockting et al. 1993
2.15	Bockting et al. 1993
2.49	Bockting et al. 1993
2.81	Bockting et al. 1993
2.16	Bockting et al. 1993
2.49	Bockting et al. 1993
2.81	Bockting et al. 1993
2.16	Bockting et al. 1993
2.50	Bockting et al. 1993
2.82	Bockting et al. 1993
2.17	Bockting et al. 1993
2.51	Bockting et al. 1993
2.83	Bockting et al. 1993



Log (K _{oc})	Cited in
2.18	Bockting et al. 1993
2.51	Bockting et al. 1993
2.85	Bockting et al. 1993
2.19	Bockting et al. 1993
2.52	Bockting et al. 1993
2.85	Bockting et al. 1993
2.19	Bockting et al. 1993
2.52	Bockting et al. 1993
2.85	Bockting et al. 1993
2.19	Bockting et al. 1993
2.52	Bockting et al. 1993
2.86	Bockting et al. 1993
2.20	Bockting et al. 1993
2.53	Bockting et al. 1993
2.86	Bockting et al. 1993
2.21	Bockting et al. 1993
2.56	Bockting et al. 1993
2.86	Bockting et al. 1993
2.21	Bockting et al. 1993
2.56	Bockting et al. 1993
2.87	Bockting et al. 1993
2.21	Bockting et al. 1993
2.56	Bockting et al. 1993
2.87	Bockting et al. 1993
2.21	Bockting et al. 1993
2.56	Bockting et al. 1993
2.87	Bockting et al. 1993
2.22	Bockting et al. 1993
2.58	Bockting et al. 1993
2.88	Bockting et al. 1993
2.22	Bockting et al. 1993
2.59	Bockting et al. 1993
2.93	Bockting et al. 1993
2.22	Bockting et al. 1993
2.59	Bockting et al. 1993
2.93	Bockting et al. 1993
2.23	Bockting et al. 1993
2.59	Bockting et al. 1993
2.94	Bockting et al. 1993
2.23	Bockting et al. 1993
2.59	Bockting et al. 1993
2.94	Bockting et al. 1993
2.23	Bockting et al. 1993
2.60	Bockting et al. 1993
2.96	Bockting et al. 1993
2.25	Bockting et al. 1993



Log (K _{oc})	Cited in
2.61	Bockting et al. 1993
3.00	Bockting et al. 1993
2.26	Bockting et al. 1993
2.63	Bockting et al. 1993
3.00	Bockting et al. 1993
2.27	Bockting et al. 1993
2.63	Bockting et al. 1993
3.06	Bockting et al. 1993
2.27	Bockting et al. 1993
2.64	Bockting et al. 1993
3.08	Bockting et al. 1993
2.27	Bockting et al. 1993
2.64	Bockting et al. 1993
3.14	Bockting et al. 1993
2.30	Bockting et al. 1993
2.65	Bockting et al. 1993
3.24	Bockting et al. 1993
2.57	Crommentuijn et al. 1997
2.54	Crommentuijn et al. 1997
2.95	Crommentuijn et al. 1997
2.89	Crommentuijn et al. 1997
2.21	Crommentuijn et al. 1997
2.44	Crommentuijn et al. 1997
2.91	Crommentuijn et al. 1997
2.27	Crommentuijn et al. 1997
2.16	Crommentuijn et al. 1997
2.93	Crommentuijn et al. 1997
3.03	Crommentuijn et al. 1997
2.37	Crommentuijn et al. 1997
2.23	Crommentuijn et al. 1997
3.16	Crommentuijn et al. 1997
3.22	Crommentuijn et al. 1997
3.19	Crommentuijn et al. 1997
3.16	Crommentuijn et al. 1997
3.16	Crommentuijn et al. 1997
3.18	Crommentuijn et al. 1997
2.50	Crommentuijn et al. 1997
2.59	Crommentuijn et al. 1997
3.00	Crommentuijn et al. 1997
2.83	Crommentuijn et al. 1997
2.66	Crommentuijn et al. 1997
2.68	Crommentuijn et al. 1997
2.66	Crommentuijn et al. 1997
2.64	Crommentuijn et al. 1997
2.87	Crommentuijn et al. 1997
2.98	Crommentuijn et al. 1997



Log (K_{oc})	Cited in
2.88	Crommentuijin et al. 1997
2.67	Crommentuijin et al. 1997
3.18	Crommentuijin et al. 1997
3.16	Crommentuijin et al. 1997
3.08	Crommentuijin et al. 1997
2.68	Crommentuijin et al. 1997
3.23	Crommentuijin et al. 1997
3.75	Crommentuijin et al. 1997
3.34	Crommentuijin et al. 1997
3.19	Crommentuijin et al. 1997
3.56	Crommentuijin et al. 1997
2.95	Crommentuijin et al. 1997
2.65	Wang and Keller 2009
2.52	Wang and Keller 2009
2.58	Wang and Keller 2009
2.53	Wang and Keller 2009
2.60	Wang and Keller 2009
3.13	Wang and Keller 2009
2.73	Wang and Keller 2009
2.39	Wang and Keller 2009
2.45	Wang and Keller 2009
3.17	Wang and Keller 2009
2.34	Wang and Keller 2009
2.68	Wang and Keller 2009
2.90	Wang and Keller 2009
2.62	Wang and Keller 2009
2.73	Wang and Keller 2009
2.67	Wang and Keller 2009
2.33	Wang and Keller 2009
2.53	Wang and Keller 2009
2.82	Wang and Keller 2009
2.67	Wang and Keller 2009
2.94	Mackay et al. 2006
2.68	Mackay et al. 2006
3.03	Mackay et al. 2006
2.82	Mackay et al. 2006
2.66	APVMA 2011
2.62	APVMA 2011
2.76	APVMA 2011
2.69	APVMA 2011
2.41	estimated from K_{ow}
2.54	geometric mean
223	Number of data



Appendix II. Effect data on benthic organisms exposed through the dissolved phase

Summary of effect data available for benthic organisms exposed through the water phase to diuron (spiked water) as in Ecotox Centre dossier. Data assessed for reliability but considered not relevant for the derivation of EQS_{sed}.

Group	Species	Test compound	Administration of tested substance	Endpoint	Test duration	Effect concentration	Value [µg /L]	Nominal/ measured exposure concentration	Comments	Validity	Reference
Algae	<i>Craticula accommoda</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	185	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Sellaphora minima</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	693	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Mayamaea fossalis</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	91	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Encyonema silesiacum</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	90	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Gomphonema parvulum</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	53	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Fragilaria capucina var vaucheriae</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	21	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Ulnaria ulna</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	24	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Fragilaria rumpens</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	0.76	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Nitzschia palea</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	380	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Achnanidium minutissimum</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	45	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Cyclotella meneghiniana</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as chlorophyll a	96 h	EC10	27	Not stated, but measured concentrations > 80 % nominal	Benthic growth mode	R4	Larras et al. 2013
Algae	<i>Raphidocelis subcapitata</i>	Diuron 99.5 % purity	Spiked water	Growth inhibition, measured as cell yield	72 h	NOEC	9.4	Measured	Growth as algal beads 4% alginate	R2	Zhang et al. 2012
Insect	<i>Chironomus riparius</i>	Diuron 79.2 % purity	Spiked water	Mortality	21 d	NOEC	> 4000	NA	Considered "not well-grounded" by EC 2005	R4	Cited in EC 2005
Crustacean	<i>Hyalella azteca</i>	Diuron 79.2 % purity	Spiked water	Mortality, growth	21 d	NOEC	≥ 60	NA		R4	Cited in EC 2005

Proposed SQC (EQS_{sed}) for Diuron



Rooted macrophyte	<i>Myriophyllum spicatum</i>	Diuron > 99 % purity	Spiked water	Relative growth rate, dry weight	14 d	NOEC	0.0005	Not stated		R3	Lambert et al. 2006
Rooted macrophyte	<i>Apium nodiflorum</i>	Diuron > 99 % purity	Spiked water	Relative growth rate, dry weight	14 d	NOEC	0.05	Not stated		R3	Lambert et al. 2006