SUMMARY OF THE DERIVATION OF PREDICTED NO EFFECT CONCENTRATIONS (PNECS) FOR PALLADIUM SUBSTANCES

DRAFT REPORT TO THE PRECIOUS METALS AND RHENIUM CONSORTIUM FROM WCA

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EXECUTIVE SUMMARY

Ecotoxicity data are available for palladium dinitrate, tetramminepalladium hydrogen carbonate, dihydrogen tetrachloropalladate, diamminedichloropalladium (DDP) and Palladium di (4-oxopent-2-en-2-oate). The results for these substances show that diamminedichloropalladium is the most toxic palladium substance, when results are expressed as concentrations of palladium. In general the toxicity of metal compounds is considered to be due to the metal ions in solution, and the coordinating ligands or counter-ions are not expected to influence the toxicity unless they are themselves toxic. However, for palladium substances this does not appear to be the case, with chloro complexes being more toxic.

The approach that is applied for deriving predicted no effect concentrations (PNECs) for palladium substances assumes that the palladium present in the environment has the potential to be in the most toxic form, which is diamminedichloropalladium. The generic PNECs for all palladium substances are therefore derived based upon the ecotoxicity data for diamminedichloropalladium.

The PNECs derived for each relevant compartment are presented in the table below.

PNEC	Units	PNEC	PNEC derivation method
Freshwater	µg/L	0.027	Lowest NOEC of 1.33 µg/L Pd with an assessment factor of 50
Intermittent releases	Not required		
Freshwater sediment	mg/kg dwt	0.274	Lowest NOEC of ≥27.4 mg/kg Pd dwt, with an assessment factor of 100
Marine water	µg/L	0.0027	Lowest NOEC of 1.33 µg/L Pd with an assessment factor of 500
Marine sediment	mg/kg dwt	0.0274	Lowest NOEC of ≥27.4 mg/kg Pd dwt, with an assessment factor of 1000
Soil	mg/kg dwt	0.027	Equilibrium partitioning based on a freshwater PNEC of 0.027 µg/L Pd
Microorganisms	mg/L	1.46	EC10 from an ASRIT study of 14.59 mg/L Pd, with an assessment factor of 10
Secondary poisoning	Requirement to be reviewed following completion of toxicology testing		

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1 INTRODUCTION

1.1 Approach to PNEC derivation for palladium substances

The derivation of PNECs is required for the chemical safety assessment (CSA) of substances manufactured or imported in quantities from 10 tonnes per annum upwards. For each tonnage level standard data requirements have been specified in REACH (Annex VII-X, in conjunction with annex XI), but REACH also requires that any other relevant hazard information that is available (i.e. from other available tests and non-test methods) is taken into account.

Ecotoxicity data are available for palladium dinitrate, tetramminepalladium hydrogen carbonate, dihydrogen tetrachloropalladate, diamminedichloropalladium (DDP) and Palladium di (4-oxopent-2-en-2-oate). The results for these substances show that diamminedichloropalladium is the most toxic palladium substance, when results are expressed based on palladium concentration. In general the toxicity of metal compounds is considered to be due to the metal ions in solution, and the coordinating ligands or counter-ions are not expected to influence the toxicity unless they are themselves toxic. However, for palladium substances this does not appear to be the case, with chloro complexes being more toxic.

The approach that is applied for deriving predicted no effect concentrations (PNECs) for palladium substances assumes that the palladium present in the environment has the potential to be in the most toxic form, which is diamminedichloropalladium. The generic PNECs for all palladium substances are therefore derived based upon the ecotoxicity data for diamminedichloropalladium.

2.2 Toxicity data

As part of the REACH registration process the following testing was commissioned at Fraunhofer and LAUS, for DDP:

- Short-term toxicity testing on aquatic invertebrates – OECD 202
- Growth inhibition study on aquatic plants – OECD 201
- Short-term toxicity testing on fish – OECD 203
- Daphnia reproduction study – OECD 211
- Sediment-water chironomid test – OECD 218
- Activated sludge respiration inhibition test (ASRIT) – OECD 209

The results from the above tests are presented in the Table 1.1.

Table 1.1 Available ecotoxicity data for diamminedichloropalladium

TEST	RESULT (as DDP)	RESULT (as Pd)
Short-term *Daphnia magna* [static test, results based on mean measured concentrations]	48-h EC50 = 69.91 µg/L DDP (95% confidence interval not determined)	48-h EC50 = 35.19 µg/L Pd (95% confidence interval not determined)
Algal growth inhibition *Pseudokirchneriella subcapitata* [results based on mean measured concentrations]	72-h EC50 Yield = 4.03 µg /L DDP (95% confidence interval 3.58-4.85 µg /L DDP) 72-h EC50 Growth Rate = 5.88 µg /L DDP (95% confidence interval 5.27-6.22 µg /L DDP) 72-h NOEC Growth Rate & Yield = 2.64 µg /L DDP	72-h EC50 Yield = 2.03 µg /L Pd (95% confidence interval 1.8-2.44 µg /L Pd)72-h EC50 Growth rate = 2.96 µg /L Pd (95% confidence interval 2.65-3.13 µg /L Pd) 72-h NOEC Growth rate & Yield = 1.33 µg /L Pd
Short-term fish *Oncorhynchus mykiss* [semi-static test, results based on geometric mean measured concentrations]	96-h EC50 = 306 µg/L DDP (95% confidence interval 203-443 µg/L DDP)	96-h EC50 = 154 µg/L Pd (95% confidence interval 102-223 µg/L Pd)
Daphnia magna reproduction [semi-static, results based on time weighted average of mean measured concentrations]	21-d NOEC = ≥28.39 µg/L DDP	21-d NOEC = ≥14.3 µg/L Pd
Sediment-water chironomid test with *Chironomus riparius* [static test, results based on arithmetic mean measured concentrations]	28-d NOEC = ≥ 54.3 mg DDP/kg dw 28-d EC10 and EC50 = >54.3 mg DDP/kg dw (95% confidence interval not determined)	28-d NOEC = ≥27.4 mg Pd/kg dw 28-d EC10 and EC50 = >27.4 mg Pd/kg dw (95% confidence interval not determined)
ASRIT [activated sludge taken from domestic sewage treatment plant]	3-h EC50 = 61 mg/L DDP (95% confidence interval 59-63 mg/L DDP) 3-h EC10 = 29 mg/L DDP (95% confidence interval 28-30 mg/L DDP) 3-h NOEC = 18 mg/L DDP	3-h EC50 = 30.71 mg/L Pd (95% confidence interval 30-32 mg/L Pd) 3-h EC10 = 14.6 mg/L Pd (95% confidence interval 14.1-15.1 mg/L Pd) 3-h NOEC = 9.07 mg/L Pd

The PNECs detailed in the following sections have been derived following the guidance provided in ECHA (2008)[1].

[1] ECHA 2008 Guidance on information requirements and chemical safety assessment Chapter R.10: Characterisation of dose [concentration]-response for environment.

2 PNEC DERIVATION

2.1 Freshwater compartment

Acute EC50 values are available for fish, *Daphnia* and algae for DDP. In addition, NOECs are available from a chronic *Daphnia* reproduction study and a 72-hour algal growth inhibition study. In the case of algae studies, which are in effect multi-generation studies, it is generally accepted that a 72-hour (or longer) EC10 or NOEC value may be considered as a long-term result.

The NOEC from the *Daphnia* reproduction study is ≥14.3 µg/L Pd, and the NOEC from the algal study is 1.33 µg/L Pd (growth rate and yield). An assessment factor is therefore applied to the lowest NOEC, 1.33 µg/L Pd, in order to derive the freshwater PNEC. An assessment factor of 50 is applied to this value in accordance with the REACH guidance, as two long-term NOECs are available from two different trophic levels (*Daphnia* and algae).

This results in:

$$\mathbf{PNEC_{freshwater}} = \frac{\mathbf{1.33\ \mu g/L}}{\mathbf{AF\ 50}} = \mathbf{0.027\ \mu g/L\ Pd}$$

In the acute ecotoxicity tests with DDP, fish were 52 times less sensitive than algae, and invertebrates were 12 times less sensitive than algae. The acute to chronic ratio for algal exposure to DDP is 2.2, and the acute to chronic ratio for invertebrates (*Daphnia*) is at least 2.5. An acute to chronic ratio of more than 10 would be required for fish to be more sensitive than invertebrates in chronic exposures, and an acute to chronic ratio of over 100 would be required for fish to be of comparable sensitivity to algae in chronic exposures. It may therefore be appropriate to consider applying an assessment factor of 10, rather than 50, to the NOEC derived from the algal study, despite no chronic fish data being available. It is likely that if waiving of the chronic fish study were agreed, an alternative study would be required on an alternative test organism. Given the apparent sensitivity of plants to palladium and DDP, tests on alternative algal species or higher aquatic plants (e.g. *Lemna spp.*) may provide suitable alternatives. At this stage a site-specific monitoring programme is being conducted for all sites with a risk characterisation ratio (RCR) close to 1. If, following this programme, some sites still have an RCR above 1 for freshwater it may be appropriate to consider whether the PNEC can be refined further at that stage.

2.2 Marine water compartment

Where only data for freshwater algae, crustaceans and fish are available, a higher assessment factor than that for the derivation of $PNEC_{freshwater}$ is applied, to reflect the greater uncertainty in the extrapolation from the freshwater to the marine environment. Therefore an assessment factor of 500 is applied on the lowest NOEC from the relevant available toxicity data (72-h NOEC freshwater alga).

This results in:

$$\mathbf{PNEC_{marinewater}} = \frac{\mathbf{1.33\ \mu g/L}}{\mathbf{AF\ 500}} = \mathbf{0.0027\ \mu g/L\ Pd}$$

2.3 Intermittent releases

Intermittent releases are defined as occurring infrequently, i.e. less than once per month and for no more than 24 hours. If an intermittent release scenario is identified, only short-term effects are considered for the aquatic ecosystem. It is unlikely that releases from any of the sites producing palladium substances would be considered as being intermittent, therefore this PNEC is not required for palladium substances. The $PNEC_{freshwater}$ is used in the risk assessment.

2.4 Microorganisms in sewage treatment plants (STP)

Since chemicals may cause adverse effects on microbial activity in STPs it is necessary to derive a $PNEC_{microorganisms}$. An assessment factor of 10 is applied to the NOEC or EC10 of an activated sludge respiration inhibition test.

This results in:

$$\mathbf{PNEC_{microorganisms}} = \frac{\mathbf{14.6\ mg/L}}{\mathbf{AF\ 10}} = \mathbf{1.46\ mg/L\ Pd}$$

2.5 Freshwater Sediment compartment

The information requirement for a chronic sediment toxicity study appears in Annex X of REACH, and as such does not need to be filled for any of the palladium substances. However, a 28-day sediment-water chironomid test was conducted with DDP in order to refine the sediment PNEC. The NOEC from this study was ≥27.4 mg/kg Pd dwt. The NOEC is unbounded as this was the highest concentration that could be achieved in the sediment without also spiking the overlying water. As higher sediment concentrations could not be tested the unbounded NOEC is used to derive the PNEC. An assessment factor is applied to the NOEC in order to derive the PNEC sediment. According to the REACH guidance an assessment factor of 100 is applied when one long-term NOEC is available.

This results in:

$$\mathbf{PNEC_{sediment,FW}} = \frac{\mathbf{27.4\ mg/kg\ dwt}}{\mathbf{AF\ 100}} = \mathbf{0.274\ mg/kg\ Pd\ dwt}$$

2.6 Marine water Sediment compartment

The PNEC for marine sediment is derived based on the NOEC from the chronic freshwater sediment study, with an assessment factor of 1000 applied.

This results in:

$$\mathbf{PNEC_{sediment,SW}} = \frac{\mathbf{27.4\ mg/kg\ \ dwt}}{\mathbf{AF\ 1000}} = \mathbf{0.0274\ \ mg/kg\ Pd\ dwt}$$

2.7 Terrestrial (soil) compartment

In cases where no reliable toxicity data are available for the terrestrial environment, a $PNEC_{soil}$ can be calculated according to the equilibrium partitioning concept based on a $PNEC_{water}$ and a reasonable worst-case soil: water distribution coefficient (K_D) (Eq.R16-7). In the case of palladium there are no reliable data for the partitioning of palladium between soil and soil porewater and the median K_D value derived for sediment has been applied, making the appropriate adjustment for the difference in organic carbon content between suspended sediment and a standard soil, in order to provide an indication of the likely range of the $PNEC_{soil}$ for palladium.

This method should be considered as a screen for identifying substances requiring further testing. For organic non-ionic chemicals, adsorption/desorption processes are often based on octanol-water partition coefficients (Kow) and the assumption that all adsorption is related to the organic matter. This approach cannot be used to describe the partitioning of metal compounds in the various environmental compartments. Consequently, the distribution of metals between the aqueous phase and soil/sediment/suspended matter should be preferentially described on the basis of measured soil/water, sediment/water and suspended matter/water equilibrium distribution coefficients:

$K_D = Cs / Caq$

Cs = total concentration of test substance in the solid phase (mg/kg)

Caq = concentration of test substance in aqueous phase (mg/L).

The terms K_D and K_P are often used interchangeably to define the partitioning behaviour of substances. The term K_D is used in the metal specific guidance, whereas the term K_P is used in the general guidance. This approach can be taken if information is available regarding the concentrations of metal in both the solid and aqueous phases for the partitioning studies, and allows the calculation of the partition coefficient in L/kg. However, in many cases the results of experiments are reported only as partition coefficients and the data used to derive them are not available. It should be noted that it is the unitless partition coefficient (m^3/m^3) which is used to estimate PNEC values by equilibrium partitioning.

In the absence of specific partitioning data for each compartment, as is the case for Pd, it is considered to be more appropriate to estimate partition coefficients for other compartments based on the partitioning of Pd in the compartment for which information is available (suspended sediment). This approach assumes that organic matter is primarily responsible for the partitioning behaviour of Pd in environmental systems and the following equation is used to estimate a organic carbon partition coefficient (K_{OC}):

$K_D = F_{OC} \times K_{OC}$ [Eq R16-6]

F_{OC} is the weight fraction of organic carbon in the compartment (kg/kg)

K_{OC} is the organic carbon – water partition coefficient

Where log K_{OC} is known it is possible to back-calculate an equivalent log K_{OW} value according to generic QSAR relationships established for estimating log K_{OC} from log K_{OW}. Performing this back calculation for Pd results in an equivalent log K_{OW} value of 7.075; and this can then be used to estimate the partitioning of Pd in all environmental compartments including its fate in a sewage treatment plant. This also allows calculations to be performed in EUSES, as this programme requires a log K_{OW} value (amongst other key properties of organic chemicals) to be entered in order for it to run.

There are 15 K_D values for palladium reported in the literature for a variety of fresh and estuarine waters (see table below). The experiments all used analytical grade standards (assumed to be Pd metal dissolved in 1 or 1.2 M HCl).

Table 2.1 K_D values for palladium

Sediment Type	Salinity	Kd value (L/kg)	log Kd	Reference
River	NA	555.55	2.74	Turner et al. 2006
River	NA	882.35	2.95	
River	NA	882.35	2.95	
River	0.10	3000	3.48	Cobelo-Garcia et al. 2008
River	0.10	3500	3.54	
River	0.10	5000	3.70	
River	0.10	5000	3.70	
River	0.10	5000	3.70	
River	0.10	5500	3.74	
Estuarine	1.30	6000	3.78	
Estuarine	4.53	7000	3.85	
Estuarine	10.09	7000	3.85	
Estuarine	13.85	7000	3.85	
Estuarine	25.09	8000	3.90	
Seawater	33.63	16280	4.21	

K_D values for palladium range from 555 L/kg to 16,280 L/kg, with equivalent log K_D values of 2.7 and 4.2. The K_D values derived for fresh and estuarine waters are considerably lower than those derived in seawater. As there is a clear effect of salinity on the K_D values calculated for palladium, the K_D value of 16,280 (equivalent log K_D 4.21), which is derived from an experiment performed in seawater, was excluded from the calculation of the median value for use in the derivation of the $PNEC_{sediment}$.

The median Kd-value must be used in the exposure assessment and effect assessment of the CSA (ECHA 2008)[2]. Median values of partition coefficients are used in risk assessment in order to avoid any over, or under, emphasis of the potential risks to different environmental compartments. For organic chemicals typically a single value would be derived according to an estimation method (e.g. OECD 121), which avoids the uncertainty associated with direct measurement of this parameter and the need to represent typical or average conditions.

This results in:

$$\mathbf{PNEC_{soil}} = \frac{\mathbf{0.027\,\mu g/L\ x\ 1500\ m^3/m^3}}{\mathbf{1700\,kg/m^3}} = \mathbf{0.024\ mg/kg\,Pd\,wwt\,(0.027\,mg/kg\ \ dwt)}$$

This method should be considered as a screen for identifying substances requiring further testing. If the outcome of the equilibrium partitioning method results in a $PEC_{soil}/PNEC_{soil}$ ratio greater than 1, then it will be necessary to refine the assessment. This could be by refining the exposure modelling, conducting further chronic toxicity tests with aquatic organisms to refine the $PNEC_{freshwater}$, or as a final step conducting toxicity tests with soil organisms. Site-specific exposure assessments have been conducted for sites manufacturing palladium substances, and no RCRs are greater than 1 for the soil compartment.

2.8 Secondary poisoning

An assessment of secondary poisoning only needs to be made if the substance being registered is classified as "Very Toxic (T+) or Toxic (T) or harmful (Xn) with at least one of the risk phrases R48 "Danger of serious damage to health by prolonged exposure", R60 "May impair fertility", R61 "May cause harm to the unborn child", R62 "Possible risk of impaired fertility", R63 "Possible risk of harm to the unborn child", R64 "May cause harm to breastfed babies"[3]. Toxicology testing is ongoing for palladium substances and an assessment of whether a PNEC oral needs to be derived will be conducted on completion of this testing.

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[2] ECHA 2008 Guidance on information requirements and chemical safety assessment Appendix R.7.13-2: Environmental risk assessment for metals and metal compounds

[3] ECHA 2010 Guidance on information requirements and chemical safety assessment Chapter R.16: Environmental Exposure Estimation

3 CONCLUSIONS

PNECs for palladium substances were derived based on ecotoxicity results for diamminedichloropalladium, expressed as concentrations of palladium. These PNECs cover all palladium substances.

The PNECs that have been derived for each compartment are presented in Table 3.1 below.

Table 3.1 PNECs derived for palladium

PNEC	Units	PNEC	PNEC derivation method
Freshwater	µg/L	0.027	Lowest NOEC of 1.33 µg/L Pd with an assessment factor of 50
Intermittent releases	Not required		
Freshwater sediment	mg/kg dwt	0.274	Lowest NOEC of ≥27.4 mg/kg Pd dwt, with an assessment factor of 100
Marine water	µg/L	0.0027	Lowest NOEC of 1.33 µg/L Pd with an assessment factor of 500
Marine sediment	mg/kg dwt	0.0274	Lowest NOEC of ≥27.4 mg/kg Pd dwt, with an assessment factor of 1000
Soil	mg/kg dwt	0.027	Equilibrium partitioning based on a freshwater PNEC of 0.027 µg/L Pd
Microorganisms	mg/L	1.46	EC10 from an ASRIT study of 14.59 mg/L Pd, with an assessment factor of 10
Secondary poisoning	Requirement to be reviewed following completion of toxicology testing		

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