Monitoring in support of estimated local palladium/PGM exposures

Depending on the outcome of risk characterisation for environmental exposure, monitoring may be required at some of the sites producing palladium substances in support of the site specific exposure assessments.

The current aquatic exposure estimates are based on information about the quantities of the Pd substances produced and available data on emissions from the site. Where possible this information is combined with site specific information on the dilution occurring upon release of the material into the local environment. Numerous assumptions are made in order to arrive at the exposure estimates, and further refinement would be possible if the actual concentrations resulting in the local environment were to be determined by direct measurement.

Monitoring points

In terms of refinement to the environmental risk assessment, the most important environmental compartments for monitoring are the receiving water, following mixing of the effluent discharge, and the receiving water sediment. Monitoring undertaken at these points may be used to override, or validate, the predicted environmental concentrations calculated in the site specific exposure assessments. It may also be valuable to undertake monitoring at other sampling points such as the wastewater effluent discharge from the site, the influent and effluent of the municipal STP, and the receiving water upstream of the discharge. Monitoring of the wastewater effluent discharge from the site may be used to refine the site specific exposure assessment (particularly where the LoD has been used to estimate annual discharges via waste water), and due to the higher concentrations present the likelihood of reliable detection of palladium may be greater than in receiving waters if analytical sensitivity is an issue[1]. Monitoring of the influent and effluent of the municipal STP may also be used to refine the site specific exposure assessment, and would provide additional information on the removal efficiency of palladium during wastewater treatment at a municipal STP. Monitoring of the receiving water upstream of the discharge would provide information on background levels of palladium in surface waters, and allow the addition of palladium due to the site to be identified should there be a measureable background concentration in the receiving waters.

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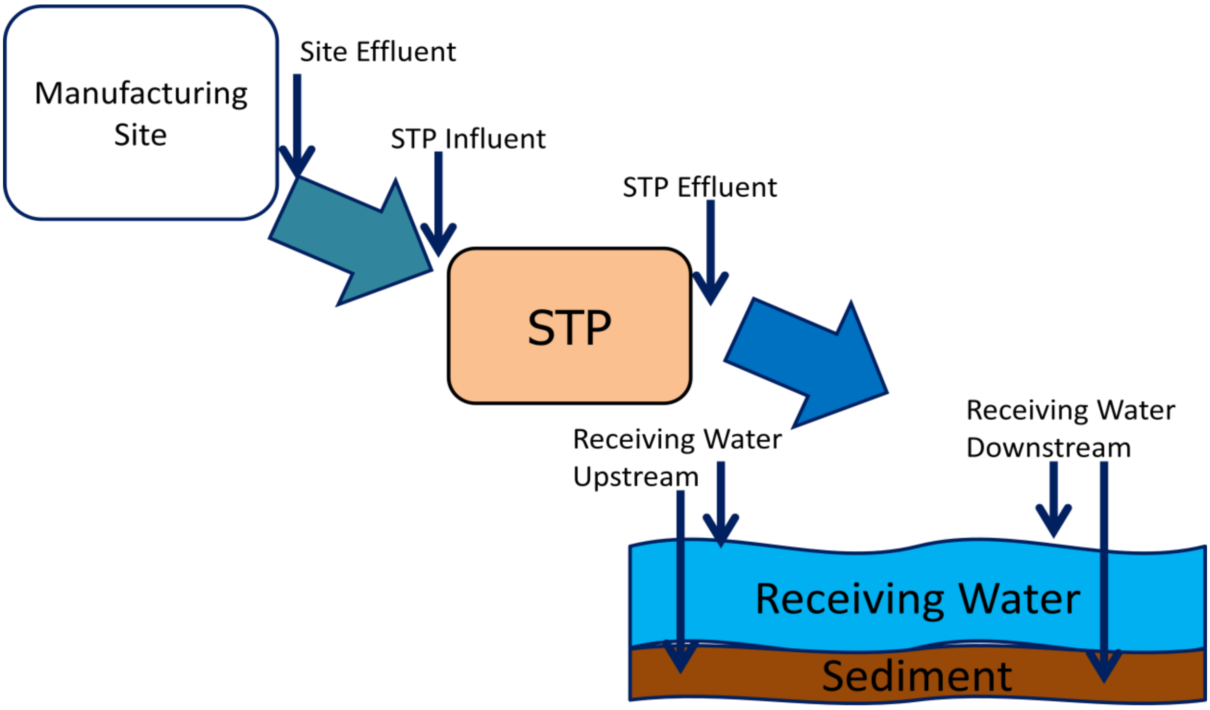
[1] It should be noted that samples of wastewaters may contain greater quantities of potentially interfering materials, resulting in reduced analytical sensitivity



Schematic of sampling locations for monitoring of environmental exposures at production sites

It is recommended that all of the sampling points included in the monitoring programme are sampled every time that sampling is undertaken, although lower sampling frequencies may be justified for the less important sampling points (e.g. upstream in the receiving water, site effluent, and STP influent and effluent).

Sampling frequency and representativeness of data

One of the most important aspects of the monitoring programme is to ensure that the resulting measurements are able to reliably represent the concentrations occurring at the sampling points, including the variability which occurs due to seasonal variation or process operations at the site. In order to achieve this representativeness samples need to be collected repeatedly over a relatively prolonged period of time, at a frequency which is able to reflect any variability in the conditions.

Variation in conditions may arise from the processes undertaken at the site (i.e. continuous or batch processes), other activities undertaken at the site (which may also contribute to loadings of the metal of interest or may affect the flow of wastewater from the site), variability of the influent flow to the municipal STP (due to other dischargers in the vicinity) and also variability in the conditions of the receiving water (e.g. high and low flows due to seasonal and climatic factors).

Prolonged monitoring programmes are therefore of much greater value than occasional spot samples, and it is recommended that monitoring programmes are undertaken for a minimum of six months. The most appropriate frequency of sample collection will depend upon the occurrence of relevant operations being performed at the site and will be different for sites which operate continuously compared to sites where processing of the relevant substances is performed intermittently.

It would be appropriate to perform regular sampling at a site that is operated continuously on a weekly, fortnightly, or monthly basis. The frequency of sampling could be adjusted according to the duration of the monitoring programme (i.e. more frequent samples for a shorter duration programme, e.g. weekly over 6 months or monthly over two years). In addition to these routine samples it would also be valuable to include a number of additional samples to enable duplication of some samples and to take some samples at more frequent intervals (e.g. daily samples over a one week period). This would provide information on the short term variability in concentrations which may not be reflected in samples collected over longer time periods. This would also enable particular conditions to be targeted, for example both high and low flow conditions in the receiving water which may not be included in weekly, fortnightly or monthly samples.

Sediment samples do not need to be measured with the same frequency as aqueous samples because they tend to integrate exposures over much longer time periods. Sediment samples may only need to be collected and analysed every three to six months over a period of between one and three years. However, due to the high spatial variability that often occurs in sediments it is typically necessary for several replicate samples to be collected from different locations within the sediment. It is possible for the replicate samples to be bulked together prior to analysis in order to reduce the number of analyses and to provide an average concentration of palladium in the local sediments. Alternatively, each sample can be analysed separately and this approach will provide additional information on the spatial variability of palladium concentrations in the local sediments. An average concentration can then be calculated from the individual samples.

Analytical requirements and monitoring parameters

The primary objective of the monitoring programme is the measurement of palladium in aqueous and sediment samples (ideally in both the total and dissolved forms). In addition, the measurement of a number of other chemical parameters may be beneficial, although they are currently not used in the quantitative risk assessment due to the limited understanding of the environmental fate and behaviour of palladium. These additional parameters are pH, dissolved organic carbon (DOC), calcium (or hardness), and conductivity.

It has also been confirmed that the majority of laboratories will be able to perform analysis for other PGMs at the same time as palladium at minimal additional cost.

From WFD guidance:
For the determination of dissolved metal concentrations water samples have to be passed through a membrane filter of 0.45 µm pore size. In principle and if possible, this filtration should be done in the field to prevent changes during transportation and subsequent storage due to adsorption processes etc. It is essential to ensure that filters are clean and to pre-clean them, if necessary. In addition, filters should be pre-washed with small sample volumes before collecting the filtrate for metal analysis. If possible (in the light of health and safety instructions), the filtrate shall be acidified with nitric acid to ensure that the pH is less than 2. For more information consult the respective substance guidance sheets and the methods referred to therein.

There is no requirement for palladium monitoring under the Water Framework Directive, as this metal has not been identified as either a priority substance or a specific pollutant. However, it is recommended that the requirements for sample collection and an adequately sensitive analytical method are followed as general good practice.

The target LoDs for the parameters of interest are detailed in Table 1, below. The target LoDs have been arbitrarily rounded down to 1 ng l^{-1} for water and 1.5 µg kg^{-1} for sediment in order to ensure generation of more robust data when measuring low concentrations of Pd (i.e. in close proximity to the PNECs).

Table 1 Target LoDs for the parameters of interest

Analyte	Target LoD
Pd (freshwater)	0.001 µg l^{-1}
Pd (sediment)	1.5 µg kg^{-1}
Pd (effluents)	0.01 µg l^{-1}
pH	range pH 4 to 9
DOC	0.2 mg l^{-1}
Total Hardness	2 mg l^{-1}
Alkalinity	3 mg l^{-1}
TSS	1 mg l^{-1}
Total Extractable metals (Cd, Cu, Ni, Pb, Zn); Sediments	0.1 mg kg^{-1}

Sampling Locations

All sampling locations must be recorded and reproducible, and should ideally be clearly marked so that samples are always taken from the same place.

The sampling point must provide safe access to collect the sample.

Receiving Water (Upstream)

Samples should be taken a short distance (e.g. 100 m) upstream of the discharge, in a steadily flowing region and away from the bank (e.g. 1 to 2 m) where practical.

Receiving Water (Downstream)

Samples must be taken far enough downstream of the discharge to allow mixing of the discharge and receiving water. It is recommended that the samples are taken from a location approximately 10 channel widths downstream of the discharge (i.e. 100 m downstream for a 10 m wide channel) and on the same side of the river as the discharge, unless other local information indicates that an alternative location would be more appropriate. Samples should be taken in a steadily flowing region and away from the bank (e.g. 1 to 2 m) where practical.

Discharge

Effluent discharge samples should be taken close to the middle of the channel in a region of high flow.

Additional Information

- The sample should have a specific identification record and be clearly marked
- The date, time, and sample collectors name should be recorded.
- Information on the flow rates of the river and discharge (qualitative, e.g. high, medium, low) and weather conditions should be recorded at the time of taking each sample.

- The processes operating at the site may also need to be recorded, especially if the site operates batch processes.

Sample Collection

- Sample containers should be pre-washed prior to use, and should be rinsed with the sample twice before filling with the final sample.
- Containers may be attached to a pole to enable samples to be taken away from the bank where sample collection is from the river bank.
- Sample containers should be completely filled with the sample before sealing.
- Samples should be refrigerated for storage and transport.
- Filtration will be required for dissolved palladium (and other dissolved metals if measured)
- Filtered samples should be taken as subsamples of whole water samples where matched total and dissolved concentrations are to be measured

Analysis

Filtered receiving water samples must be analysed for palladium, it may also be appropriate to include other metals in the same analysis as multiple element techniques are routinely used for metals analysis.

Analysis of both total and dissolved metal concentrations is recommended, although the PEC and PNEC values are calculated as dissolved concentrations. Analysis of both total and dissolved palladium concentrations would provide information on palladium partitioning, and allow site specific partition coefficients to be derived for the sites assessed.

Other PGMs

As metal concentrations are usually determined by multi-element techniques the additional cost of including analyses of other metals in the same samples can be relatively small. Given this it is recommended that consideration be given to including the analysis of other precious metals in the same samples (at least those metals which are relevant to operations at the site in question). It may also be useful to include analysis of other trace metals which are also in use, or likely to be present, at the site.

Essential
- Pd (total), Pd (dissolved)

Desirable
- Rh, Pd, Ag, Ru, Pt, Au, etc. as appropriate for the site concerned.

Supporting Parameters

There is currently no bioavailability correction available for palladium substances in any media, although the collection of bioavailability-related supporting parameters (listed below) may be of value for assessments of other metals at the site.

Essential for bioavailability correction (e.g. Ni, Zn, Pb, Cu, Mn...)
- pH, DOC, hardness

Useful

- Temperature, Alkalinity, suspended solids

Sediments

Parameter values that should be determined for sediment samples are listed below:

Essential

Pd (total)

Desirable *(in order of priority)*

Total Organic Carbon
Grain Size
Total Extractable Metals: Rh, Pd, Ag, Ru, Pt, Au
(Cd, Cu, Pb, Ni, Zn, Fe, Mn)
Acid Volatile Sulfide
Simultaneously Extracted Metals: Rh, Pd, Ag, Ru, Pt, Au
(Cd, Cu, Pb, Ni, Zn, Fe, Mn)

Sediment Pore Water:

Essential

Pd (dissolved)

Desirable *(in order of priority)*

pH
Dissolved Organic Carbon
Dissolved Metals: Rh, Pd, Ag, Ru, Pt, Au
(Cd, Cu, Pb, Ni, Zn, Fe, Mn)

General Issues

Collecting some of the non-routine samples (i.e. additional duplicate samples twice and daily samples on two separate weeks for continuously operating sites) relatively early in the monitoring programme will provide a greater amount of information on the palladium exposure concentrations at an earlier stage in the process.

The sampling plan should include some flexibility to ensure that samples can be collected under the range of different conditions which the site experiences over the period of the sampling programme, i.e. to include both high and low flow conditions in the receiving water.

Where river flows are recorded nearby on the river (i.e. with no major tributaries between the sampling point and gauging station) it may be possible to link the samples to the flow rate of the river at the time of sampling. This may assist in better understanding of the variation in exposures that may occur due to variations in river flow.

Provisional costing for sampling and analytical programme

Analytical costs for site sampling programmes

Sampling of receiving water bodies (both freshwater & marine) should be undertaken for analysis of both total and dissolved palladium. It is anticipated that the sample collection will be undertaken by the companies operating the sites.

From the quote for costing returned by a range of laboratories, ESG have been selected on the basis of cost and their reported analytical performance meeting the target LoDs (detailed in Table 1) and their ICP-MS method being UKAS accredited. The costs for analysis at ESG are detailed in Table 2 below;

Table 2 Method performance and associated costs of Pd analysis by ESG

Matrix	Parameter	Method	LoD; LoQ from lab (ng/L unless stated)	Cost (€ per sample)	Additional metals (€ per sample)	Comments
Freshwater	Pd	ICP-MS[a]	4; N.R.	30[b]	5.50[c]	[a]ICP-MS or ICP-AES depending on element for additional metals analysis [b] Minimum order charge of €116; Additional surcharge for quick turnaround if required; Price does not include VAT [c] No indication whether additional standards or method verification would be needed
Wastewater (requiring digestion)	Pd	ICP-MS[a]	400 ng/kg; N.R.	64[b]	5.50[c]	
Sediment	Pd	ICP-MS	5000 ng/kg; N.R.	64[b]	5.50[c]	

Sampling of STPs

Current exposure assessments assume that the behaviour of palladium during sewage treatment plant (STP) treatment can be estimated from information on partitioning to suspended particulate matter, and is controlled by partitioning to organic carbon. Currently no specific information exists regarding the fate of palladium during municipal sewage treatment. The most appropriate means of estimating the fraction of palladium released in the effluent is from direct monitoring of the influent and effluent at an STP. There are currently no reliable methods for estimating this behaviour, although there is no specific requirement to provide this information under REACH. This represents a significant uncertainty in the current exposure assessments.

It is recommended that a monitoring programme be undertaken at three STPs which are receiving discharges from palladium operations to monitor total and dissolved palladium in both the influent and effluent. Variations in the operating conditions at different plants mean that the partitioning behaviour of a metal between the sludge and effluent phases can differ considerably, and an average removal efficiency needs to be calculated.

ExCAL have provided a quote of €402 per person per day plus any incurred expenses for the sampling programme. An overall estimate of cost would be provided on provision of site locations. However, an estimate of costs for sampling of the three STPs based on €402 per person per day, would be a minimum of ~€1200 plus expenses for each round of sampling. Assuming that this took place twice this would equate to ~€2400 for STP sampling alone. Costs for analysis of samples (undertaken by ESG) are estimated at €488 for analysis of wastewater and solid samples for each STP visit based on 3x influent, 3x effluent each time and solid sludge analysis x2 on each visit. This would equate to an overall analytical costs of ~€2900 for this part of the monitoring programme; giving a total cost of ~€5300 plus expenses and transport costs. It is anticipated that this cost would be shared by all member companies manufacturing palladium and palladium compounds.

Table 3 Analysis costs from sampling at STPs

Task	Number	Cost (€)	Total Cost (€)
Sediment Sampling	1	402	402
Analysis of influent samples (total)	3	30	90
Analysis of influent samples (dissolved)	3	30	90
Analysis of effluent samples (total)	3	30	90
Analysis of effluent samples (dissolved)	3	30	90
Analysis of solid sludge samples (total)	2	64	128
TOTAL for sampling and analysis (per visit)			*890*
TOTAL (2 sampling regimes at 3 STPs)			**5340**
Optional:			
Other PGM metals for influent and effluent samples	6	5.50*	33 per metal
Other PGM metals for soil sludge samples	2	5.50*	11 per metal
Supporting parameters			
DOC/TOC	8	8.38	67.04
pH	8	2.76	22.08
Hardness	6	8.38	50.28
Alkalinity	6	6.90	41.4
TSS	6	2.76	16.56
TOTAL for optional parameters			*241⌖*
* 5.50 extra per metal ⌖cost per STP visit based on analysis of one additional PGM			

Sediment sampling programme across Europe

It is preferable that all sediment samples are taken in the same way and it is therefore recommended that one company is used to take sediment samples from all sites across Europe that are producing palladium and/or palladium compounds and require refinement of the site specific risk assessment for the aquatic compartment. ExCAL have quoted €402 per person per day plus any incurred expenses (i.e. travel and accommodation) for the sampling of STPs or sediments (an additional cost would be the cost of transporting samples to ESG for analysis).

Additionally, NIVA have been contacted about sampling the site in Norway. They have quoted €6,222 for the sampling of sediments, the analysis of samples for pH, DOC, hardness, alkalinity and suspended solids, and the shipping of sediments samples to the appropriate laboratory for Pd analysis from both the upstream and downstream sampling locations at the one Norwegian site only (this would be undertaken twice over a six month period).

Example sample programmes

Continuously Operating Site

- It is anticipated that water samples would be taken by site personnel (sediment samples to be taken by ExCAL)
- Sampling programme conducted over one year
- Routine weekly or fortnightly samples of receiving water (downstream), i.e. 26-52 samples from each sampling point in total over the duration of the monitoring programme. Minimum analysis total and dissolved Pd (site effluent optional but desirable if current discharge is based on LoD)
- Routine samples of receiving water (upstream) collected every four weeks, i.e. 13 samples in total. Minimum analysis total and dissolved Pd.
- Routine samples collected in duplicate on two occasions during the year (indicates variability between samples). Minimum analysis total and dissolved Pd.
- Additional daily samples of site effluent and receiving water (downstream) collected for between 5 and 7 days during two different times of the year (provides information on short term variability). Minimum analysis total and dissolved Pd.
- Sediment samples collected in triplicate on two occasions during the year. Minimum analysis total Pd.

Table 4, below, tabulates the estimated minimum costs of performing each task of the monitoring programme at a continuously operating site. It has been assumed that the analysis of effluent samples would not require digestion. If digestion is required, there will be additional costs associated with analysis (see Table 2).

Table 4 **Minimum estimated costs of continuously operating site monitoring program**

Task	Number	Cost (€)	Total Cost (€)
Sediment Sampling	2	402	804 plus expenses
Analysis of sediment samples	6[a]	64	384
Analysis of weekly (fortnightly) downstream receiving water samples for total Pd	52 (26)	30	1560 (780)
Analysis of weekly (fortnightly) downstream receiving water samples for dissolved Pd	52 (26)	30	1560 (780)
Analysis of upstream receiving water samples for total Pd	13	30	390
Analysis of upstream receiving water samples for dissolved Pd	13	30	390
Analysis of duplicate samples for total Pd	8[b]	30	240
Analysis of duplicate samples for dissolved Pd	8[b]	30	240
Analysis of daily sample of site effluent and receiving water for total Pd taken over 5 days (7 days)	20[c] (28[c])	30	600 (840)
Analysis of daily sample of site effluent and receiving water for dissolved Pd taken over 5 days (7 days)	20[c] (28[c])	30	600 (840)
TOTAL			**6768 (5688)**
Optional parameters:			
Analysis of site effluent samples for total Pd	52 (26)	64	3328 (1664)
Analysis of site effluent samples for dissolved Pd	52 (26)	64	3328 (1664)
Other PGM metal	52 (26)	5.50*	286 (143)
Supporting parameters			
DOC (in all aqueous samples)	93 (75)	8.38	779.34 (628.50)
pH (in all aqueous samples)	93 (75)	2.76	256.68 (207.00)
Hardness (in all aqueous samples)	93 (75)	8.38	779.34 (628.50)
Alkalinity (in all aqueous samples)	93 (75)	6.90	641.70 (517.50)
TSS (in all aqueous samples)	93 (75)	2.76	256.68 (207.00)

Key;
a; Analysis of triplicate samples on two occasions
b; Samples taken in duplicate on two occasions, cost for analysis of both duplicates
c; Cost of analysis of both receiving water and effluent samples on both sampling occasions

Note: All sampling costs are per person per day plus any incurred expenses.
*; 5.50 per additional metal per sample.

Site Operating Batch Processing

- It is anticipated that water samples would be taken by site personnel (sediment samples to be taken by ExCAL)
- Sampling programme conducted over one year
- Routine samples receiving water (downstream) taken during palladium processing operations (~30 times per year); site effluent optional but desirable if current discharge is based on LoD
- Routine samples of receiving water (both upstream and downstream) taken monthly, regardless of operating conditions
- Routine samples collected in duplicate on one occasion each for both daily and monthly samples (indicates variability between samples)
- Sediment samples collected in triplicate on two occasions during the year

The minimum estimated costs of performing the sampling program at sites operating batch processing are detailed in Table 5.

Table 5 Minimum estimated costs of batch processing sites sampling program.

Task	Number	Cost (€)	Total Cost (€)
Sediment Sampling	2	402	804 plus expenses
Analysis of sediment Samples	6[a]	64	384
Analysis of downstream receiving water samples during processing operations for total Pd	30[b]	30	900
Analysis of downstream receiving water samples during processing operations for dissolved Pd	30[b]	30	900
Analysis of monthly samples for total Pd	12[c]	30	360
Analysis of monthly samples for dissolved Pd	12[c]	30	360
Analysis of duplicate daily samples (total and dissolved)	4	30	120
Analysis of duplicate monthly samples (total and dissolved)	4	30	120
TOTAL			**3948**
Optional:			
Analysis of site effluent samples for total Pd	30 (12)	64	1920 (768)
Analysis of site effluent samples for dissolved Pd	30 (12)	64	1920 (768)
Other PGM metal	62 (92)	5.50*	341 (506)
Supporting parameters			
DOC	62 (92)	8.38	519.56 (770.96)
pH	62 (92)	2.76	171.12 (253.92)
Hardness	62 (92)	8.38	519.56 (770.96)
Alkalinity	62 (92)	6.90	427.80 (634.80)
TSS	62 (92)	2.76	171.12 (253.92)

Task	**Number**	**Cost (€)**	**Total Cost (€)**
Key; a; Analysis of triplicate samples on two occasions b; Analysis of 10 site effluent, 10 STP influent, 10 STP effluent and 10 downstream receiving water samples c; Analysis of 12 site effluent, 12 STP influent, 12 STP effluent, 12 U/S receiving water samples and 12 D/S receiving water samples Note: All sampling costs are per person per day plus any incurred expenses. *; 5.50 per metal per sample.			

Appendix

It is unlikely to be practical to measure the specific form of palladium present in the environment, so analyses are likely to be based on total concentrations of palladium in the samples analysed. The analytical method should be sufficient to be able to demonstrate that the resulting levels in the environment are safe (i.e. below the level of the PNEC). In order to be able to show this it is necessary for the limit of detection of the analytical technique to be sufficiently below the PNEC such that concentrations which are close to the level of the PNEC can be reported confidently.

For freshwaters the current (provisional) PNEC for Pd compounds is based on that for DDP: 0.013 µg l^{-1} (13 ng l^{-1} Pd). It is therefore possible that surface water monitoring downstream of discharges will not be sufficiently sensitive to be able to demonstrate that the levels of Pd in the environment are below the PNEC

The performance requirements of the analytical method are defined by the QA/QC Directive (Article 4) http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:201:0036:0038:EN:PDF:

1. *Member States shall ensure that the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50 % or below (k = 2) estimated at the level of relevant environmental quality standards and a limit of quantification equal or below a value of 30 % of the relevant environmental quality standards.*
2. *In the absence of relevant environmental quality standard for a given parameter, or in the absence of method of analysis meeting the minimum performance criteria set out in paragraph 1, Member States shall ensure that monitoring is carried out using best available techniques not entailing excessive costs.*

This indicates that the Limit of Quantitation (LoQ) should ideally be no higher than 3.9 ng l^{-1} (Pd), and that the uncertainty should be no more than 50% for a concentration of 13 ng l^{-1} (Pd) in order for the analytical method to be adequate to quantify Pd concentrations at the level of the current PNEC for freshwaters. For sediment the current (provisional) PNEC is 14.5 µg kg^{-1}; LoQ should ideally be no higher than 4.35 µg kg^{-1} (Pd), and that the uncertainty should be no more than 50% for a concentration of 14.5 µg kg^{-1} (Pd) in order for the analytical method to be adequate to quantify Pd concentrations at the level of the current PNEC for freshwater sediments.

During T/D testing of precious metals and their compounds a LoQ of 0.1 µg l^{-1} (100 ng l^{-1}) was achieved by the CANMET analytical laboratory in Canada. This LoQ is 25 times higher than the sensitivity required for reliable determination of concentrations close to the provisional PNEC. It was therefore uncertain as to whether a similar or improved LoQ could be achieved by a routine testing laboratory although recent Pd analyses performed by the Fraunhofer Institute for studies associated with PMRC activities have achieved a Limit of Detection (LoD) of 0.002 µg l^{-1}, and an LoQ of 0.006 µg l^{-1} (i.e. 2 ng L^{-1} for LoD and 6 ng L^{-1} for LoQ).

It is therefore likely that some refinement of analytical methodology for the analysis of Pd in aqueous environmental samples will be required.

Laboratory capabilities for palladium analysis

A number of laboratories have been contacted to provide details on their capabilities and costs regarding analysis of palladium in freshwater and sediments. A summary of their responses is provided below, with more detailed information provided on the following pages:

Table 1 **Summary of parameters to be analysed and laboratory quotes for analysis of freshwater, sediment porewater and sediments.**

Laboratory	Matrix	Parameter	Target LoD[2]	Method	LoD; LoQ from lab (ng/L unless stated)	Cost (€ per sample)	Additional metals (€ per sample)	Comments
Fraunhofer	Freshwater	Pd	0.001 µg l^{-1}	ICP-MS	4; N.R.	65[a]	5[b]	[a] Minimum of 20 samples [b] Additional metals standards would need to be purchased (€ 300 - 400 per std) and method verification performed (€ 500 per metal) prior to analysis [c] Based on a minimum batch of 4 samples
	Sediment	Pd	1.5 µg kg^{-1}	ICP-MS	800; N.R.	350[c]	5[b]	
Plymouth University	Freshwater and STP effluents	Pd	0.001 µg l-1 freshwater, 0.01 µg l^{-1} effluents	ICP-MS	100; 150	52[d]	No extra cost[e]	[d] €520 per batch of 10 samples [e] For Pt and Rh only [f] To achieve an LoD of <10 ng/L a pre-concentration method would be need which is not routinely performed [g] €700 per batch of 5 samples
	Sediment	Pd	1.5 µg kg^{-1}	ICP-MS	1000 ng/kg; 1500 ng/kg[f]	140[g]	No extra cost[e]	

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[2] Target LoDs have been arbitrary rounded down to 1 ng l^{-1} for water and 1.5 µg kg^{-1} for sediment in order to ensure generation of more robust data when measuring low concentrations of Pd (i.e. in close proximity to the PNECs).

Laboratory	Matrix	Parameter	Target LoD[2]	Method	LoD; LoQ from lab (ng/L unless stated)	Cost (€ per sample)	Additional metals (€ per sample)	Comments
ESG	Freshwater	Pd	$0.001\ \mu g\ l^{-1}$	ICP-MS[h]	4; N.R.	30[i]	5.50[j]	[h] ICP-MS or ICP-AES depending on element for additional metals analysis [i] Minimum order charge of €116; Additional surcharge for quick turnaround if required; Price does not include VAT [j] No indication whether additional standards or method verification would be needed
	Wastewater (requiring digestion)	Pd	$0.01\ \mu g\ l^{-1}$	ICP-MS[h]	400 ng/kg; N.R.	64[i]	5.50[j]	
	Sediment	Pd	$1.5\ \mu g\ kg^{-1}$	ICP-MS	5000 ng/kg; N.R.	64.00[i]	5.50[j]	
ExCAL	Freshwater	pH	range 4 to 9	N.R.	N.R.; N.R.	2.76[k]	N.A.	[k] Based on 24 samples [l] Plus additional cost of €6.90 per sample for sample preparation
	Freshwater	DOC	$0.2\ mg\ l^{-1}$	N.R.	N.R.; N.R.	8.38[k]	N.A.	
	Freshwater	Total Hardness	$2\ mg\ l^{-1}$	N.R.	N.R.; N.R.	8.38[k]	N.A.	
	Freshwater	Alkalinity	$3\ mg\ l^{-1}$	N.R.	N.R.; N.R.	6.90[k]	N.A.	
	Freshwater	TSS	$1\ mg\ l^{-1}$	N.R.	N.R.; N.R.	6.90[k]	N.A.	
	Sediment porewater	pH	range 4 to 9	N.R.	N.R.; N.R.	2.76[k,l]	N.A.	
	Sediment porewater	DOC		N.R.	N.R.; N.R.	8.38[k,l]	N.A.	
	Sediment	Total Extractable metals (Cd, Cu, Ni, Pb, Zn)	$0.1\ mg\ kg^{-1}$	ICP-MS/GC-MS	N.R.; N.R.	82.8[k]	N.A.	

Laboratory	**Matrix**	**Parameter**	**Target LoD[2]**	**Method**	**LoD; LoQ from lab (ng/L unless stated)**	**Cost (€ per sample)**	**Additional metals (€ per sample)**	**Comments**
	Sediment	Pd	1.5 $\mu g\ kg^{-1}$	ICP-MS	4000 ng/kg; N.R.	55.2[k]	N.A.	
	Sediment	Acid Volatile Sulfide and Simultaneously Extracted Metals	0.1 $mg\ kg^{-1}$	ICP-MS/GC-MS	N.R.; N.R.	138.00[K]	N.A.	
NIVA	Freshwater	pH	range 4 to 9	N.R.	N.R.; N.R.	6222[m]	N.A.	[m] Price quoted is for sampling of sediment, analysis of samples, and transport of samples for Pd analysis on two occasions within a year from the Norwegian sampling site only
	Freshwater	DOC	0.2 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	Total Hardness	2 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	Alkalinity	3 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	TSS	1 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
Cascade	Freshwater	pH	range 4 to 9	N.R.	N.R.; N.R.	~20000[n]	N.A.	[n] Indicative price quoted is for sampling of sediment, analysis of samples for specified determinands on two occasions within a year.
	Freshwater	DOC	0.2 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	Total Hardness	2 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	Alkalinity	3 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	
	Freshwater	TSS	1 $mg\ l^{-1}$	N.R.	N.R.; N.R.		N.A.	

Key: N.R. = Not reported; N.A. = not applicable

The UK Environment Agency's National Laboratory Service was contacted but they confirmed that they do not perform palladium analysis.

Fraunhofer Institute have performed palladium analysis for the ongoing ecotoxicity tests, utilising an ICP-MS method. For river water samples, acidified with nitric acid, very low LoQs can be achieved; however, an LoQ of <4 ng l^{-1} cannot be guaranteed as the LoQ is calculated daily based on the signal:noise ratio results of the calibration. Sediment samples will require *aqua regia* extraction prior to analysis to recover total palladium. Due to the chloride in the *aqua regia* causing interferences LoQs of <0.8 µg l^{-1} for sediment samples cannot be guaranteed using the current equipment. However, Fraunhofer are in the process of installing a new ICP-MS with the capability to filter out a significant portion of the interfering ions, via the use of a cut-off filter, and therefore, the LoQ for *aqua regia* extracts may be further reduced). Quantification of Pd in water samples is costed at ~ € 65 per sample, with a minimum order of €1300 i.e. 20 samples. For sediment samples digestion and quantification will cost €350 per sample, with a minimum order of €1400 (or 4 samples). Additionally, method verification in the respective matrices including quality assurance and quality control samples will cost €1500 but there is a 20% reduction if this is performed to non-GLP standards.

Fraunhofer also confirmed that it is possible to analysis other PGMs in parallel. However, they do not currently undertake analyses of these metals and the standards would need to be purchased (€300 – 450 per metal standard) and method verification performed (€500 per metal). After verification, the additional analysis would cost €5 per metal per sample. Due to this analysis not currently being routinely performed, accurate LoDs could not be provided as they are based on the results of the daily calibration, although they are anticipated to be in the range of 10 ng l^{-1}.

Three UK laboratories performing UKAS-accredited palladium analysis were identified from the UKAS directory, although of these only one (Environmental Scientifics Group, ESG) uses ICP-MS for the analysis. Analytical information has been received from this company indicating an anticipated LoD of 4 ng l^{-1} for freshwater, 400 ng l^{-1} for wastewater, and 5 µg kg^{-1} for sediment. The wastewater and sediment samples would undergo (non-UKAS accredited) digestion prior to analysis. River water sample analysis cost ~€30.00 per sample (excluding VAT), and for waste water and sediment sample digestion and analysis would be ~€64.00 per sample (excluding VAT), with a minimum order charge of ~€116.00. Additionally, there is a fast turn-around surcharge ranging from + 25% for one week to +100% for 24 hours, if required. It has also been confirmed by ESG, that they can also perform parallel analysis of other PGMs during Pd analysis, this would incur an extra cost of ~€5.50 per sample per extra metal. ESG have not stated in the quote that any additional standards would need to be purchased, or that any additional method validation would be needed.

Plymouth University are also able to perform palladium analysis; however, the indicative LoD for analysis of river waters and STP effluents is relatively high at < 0.1 µg l^{-1}, with an LoQ of <0.15 µg l^{-1}. The actual LoD/LoQ would be determined by calibration of the instrument on the day of analysis. Additionally, the LoD for STP effluents may be even higher, in proportion to the dilution factor if sample dilution is required prior to analysis. For sediment samples indicative LoD and LoQ values of < 1 µg kg^{-1} and < 1.5 µg kg^{-1} were provided, with the actual LoD and LoQ calculated on the day of analysis based on the calibration. During discussions with Plymouth University, it was stated that pre-concentration of samples prior to analysis would be required to achieve a LoD of < 10 ng l^{-1}. This is not something that they have performed previously meaning that a method would need to be validated before undertaking analysis.

For water samples analysed in triplicate costs would typically be ~€520 per batch of 10 samples, or ~€700 per batch of 5 samples for sediment analysis. Plymouth University have indicated that they would provide quantification of platinum and rhodium concentrations at no extra cost when analysing for palladium.

It is proposed that sampling of sediments is undertaken twice a year and ideally, that this task should be performed by the same company at each site[3]. ExCAL Ltd., Cascade consulting, ALS, and the Norwegian Institute for Water Research (NIVA), have been contacted regarding their capability to perform this work and to provide indicative costs.

ExCAL have indicated that they would be interested in performing this sampling work and that they could also perform Pd analysis by ICP-MS. ExCAL have returned a quote for sampling activities of €402 per person per day plus any expenses (an overall estimate of cost would be provided on provision of site locations). They have also quoted prices for pH, DOC, total hardness, alkalinity, and TSS determination in river water samples of €2.76[4], €8.28[2], €8.28[2], €6.90[2] and €6.90[2] per sample, respectively, based on a total of 24 samples. The costs for determination of pH and DOC in sediment pore water are the same as for river waters. However, there would be an additional cost of €6.90[2] per sample for sample preparation of sediment pore water samples. For analysis of the sediment samples ExCAL have quoted €55.20 per sample for analysis of Pd, and €138.00[2] for analysis of acid volatile sulphide (AVS) and simultaneously extracted metals, based on a total of 24 samples. With regards to achieving the requested LoDs/LoQs, ExCAL stated that they would adjust the amount of sediment or acid used during the extraction to meet a 4 µg kg^{-1} detection limit. In order to achieve limits of quantification below this level, an impracticably large sample size would need to be extracted, and differentiation between a positive signal and background interference would be difficult. ExCAL also stated that they would perform all analysis in triplicate and to the appropriate UK Environment Agency guidance (*pers. coms.* Prigmore 2013).

An estimated indicative quote of ~ €23,000[2] has been provided by Cascade for the sampling of all the sites twice in a year. This is an indicative quote, as due to the confidential nature of the sampling sites, only the general area of the sites have been provided to the potential contractors rather than the exact locations. Cascade has stated that if selected for this sampling task they would further refine the quote when additional site location information is available to them. Additionally, the indicative costing provided by Cascade does not include the transportation of the samples to the selected laboratory.

NIVA have quoted €6,222[5] for the sampling of sediments, the analysis of samples for pH, DOC, hardness, alkalinity and suspended solids, and the shipping of sediments samples to the appropriate laboratory for Pd analysis from both the upstream and downstream sampling locations at the one Norwegian site only (this would be undertaken twice over a six month period). If NIVA are selected for sampling of the Norwegian site, a second consultancy would also need to be commissioned for sampling the other sites.

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[3] NB. A number of consultancies expressed reservations about including Norway in the sampling programme so a Norwegian organisation (NIVA) were contacted to provide a costing for undertaking sampling at the one site in Norway only.

[4] The quote received was in GBP, costs have been converted to € on the basis of an exchange rate of 1:1.15 GBP: €. Therefore, the actual price in € may change.

[5] The quote received was in NOK, costs have been converted to € on the basis of an exchange rate of 0.12:1 NOK: €. Therefore, the actual price in € may change.

Summary of reporting requirements

Criteria	**Requirement**
Analyte	Once per method
Method	Once per method
Units	Once per method
Limit of Quantitation	Once per method (but may need to be reported on a daily basis by some laboratories)
Blank concentration	Once per method
Recovery	Once per method
Accuracy	Once per method
Reproducibility	Once per method
Sample Collection	Once per sampling location
Value reported	Each result
Location	Each sampling location
Date	Each sample
Compartment	Each sample
Sampling frequency & pattern	Sampling programme
Proximity of discharge	Sampling programme
Discharge emission pattern & volume	Sampling programme
Flow and dilution	Sampling programme
Treatment for <LoQ	Sampling programme