

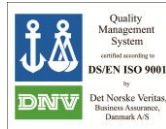


Risk characterization of nickel in sediments



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Risk characterization of nickel in sediments

Draft report

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1 Introduction

The effect of nickel and nickel compounds to sediment organisms was evaluated in the preparation of the European Union Risk Assessment Report (RAR) which was discussed finally at TC NES III '07. The overall conclusion from the meeting was a request to the Danish rapporteur and the Nickel Industry to develop a resolution to the conclusion i) based on a refinement of the derived Predicted No Effect Concentration (PNEC) for sediment organisms based on additional information on the effect of nickel to sediment organisms and revise the risk characterisation sediments based on available data.

It was further recognized that there was insufficient time to finalize the conclusion i) program under the ESR program, which would mean that the responsibility for delivering the outcome of the conclusion i) research would fall to Industry under the REACH legislation. The program included an evaluation of spiking methods, long-term testing of 9 benthic species in two sediment types and assessment of the toxicity in 8 sediment types representing a range from high to low bioavailability sediments.

The work on the conclusion i) of the Nickel risk assessment under the Existing Substances Regulation (ESR) program has since 2007 been followed by a formal regulatory oversight committee established by TC NES and chaired by the Danish EPA. The committee has taken the responsibility overseeing the resolution of the conclusion i) in the transitional period between ESR and REACH. This report presents a preliminary characterisation of risks of nickel to sediment organisms of the production and use of nickel in industry sectors based on currently available recent data on release and emission to the water environment.

2 Objective

It is the main objective of this report to document the overall pattern and scale of potential risks to sediment organisms from emission of nickel and nickel compounds from industrial activity in EU. This is done by characterisation of the risks to sediments exposed to discharges from industries within the sectors of nickel producers and nickel downstream users. The characterisation is made for industry sectors and sites where discharge data have been updated due to the REACH registration of nickel in 2010. This means that sectors where only old data were available (i.e. approx. 10 years old) have been excluded. However, the sectors with recent data are included in this report and represent the vast majority of the applied tonnage of nickel in EU today.

It is moreover the aim to demonstrate how the refinement of the assessment at a specific site can be done applying a tiered approach where bioavailability of nickel in the sediment is considered. The tiered approach starts with a realistic worst case scenario using a default PNEC_{sed} value and default values for Predicted Environmental Concentration (PEC) estimation, followed by iterations based on bioavailability considerations using default values and at the highest tier based on site specific measurements. The possible iterative refinement of the risk characterization is demonstrated using an anonymized real life case study.

3 Methods

The environmental exposure assessment, effect assessment and risk characterization of nickel and nickel compounds was reported in the European Union Risk Assessment Report (European Commission 2008). The report covered industry sectors producing and using nickel and nickel compounds including nickel metal, nickel sulfate, nickel chloride, nickel dinitrate, and nickel carbonate. The present report presents an update of the characterization of risks of nickel to the sediment

compartment and covers nickel producers and the downstream use sectors where data were updated by the Nickel Institute in 2009-2011. Based on these data the consultant team from Arche and DHI has generated an updated preliminary risk characterisation for the sediment compartment.

The emission data for the individual sites included:

- Average values of measured nickel concentration in effluent (after treatment locally or in municipal STP).
- Measured average daily waste water volume emitted
- Dilution factor based on measured effluent volume and local river flow, or by use of default dilution factor (DF). When the DF could not be calculated a default DF of 10 was used for rivers and DF of 100 for discharge to sea. In cases where there was a high dilution factor (>1000) but no specific value could be estimated an DF = 1000 was used.

Measured values for sediment concentrations were only obtained for one site (see the case in section 5 of this report. The local sediment concentrations were estimated from the local concentration in the water compartment ($PEC_{wat,tot}$) at each site (local concentration) assuming equilibrium partitioning as expressed by a $Kp_{ss} = 26,303 \text{ L/kg}$ ($= 6,577 \text{ m}^3/\text{m}^3$), which corresponds to the 50th percentile of the partitioning coefficients of suspend solids for EU waters. This approach was also applied in the EU RAR (Commission, 2008). Equilibrium partitioning is used to estimate the sorption of nickel to the sedimentation of particulate matter from the water column to the sediments, and does not take the bioavailability in the sediment compartment into account.

The estimated concentration of nickel in the surface water after dilution ($C_{wat,tot}$) was thus estimated as:

$$PEC_{wat,tot} = C_{eff} \times \frac{V_{ww}}{V_{river}} + C_{reg}$$

Where the C_{eff} is the average nickel concentration in the effluent after treatment; V_{ww} is the average waste water emitted per day and V_{river} is the average river flow; and C_{reg} is the regional background concentration of nickel.

The local and regional sediment concentration PEC_{sed} was estimated based on the $PEC_{wat,tot}$:

$$PEC_{sed} = PEC_{wat,tot} \times Kp_{ss}$$

Where the Kp_{ss} is the equilibrium partitioning coefficient as defined above.

The data used for the preliminary risk characterisation for the sediment compartment presented in this report are based on the data reported from industry and data gaps were bridged by use of default values or assumptions. It is therefore possible to refine the estimates for the individual sites by using measured values instead of default values applied in these expressions.

As example the available data for the stainless steel industry is summarized below.

Table 1: Data availability for the stainless steel sector.

Parameter	Data availability (out of a total of 23 sites)
Effluent mean volume (V_{ww} ; m ³ /day)	18 measured 5 not determined
Nickel concentration in effluent after treatment (C_{eff} , mg/L)	20 measured 3 not determined
Dilution factor (DF)	9 estimated (range 3.1 - 316) 8 by default DF = 10 (discharge to river) 2 by default DF = 100 (discharge to sea) 4 by default = 1000 (discharge to large rivers)
Regional nickel concentration (C_{reg})	9 by measured background values by country 13 by default freshwater conc. (2.9 µg/L) 1 by default seawater conc. (0.3 µg/L)

Note: the level of detail of the site specific data on nickel concentrations in the effluent after on-site treatment and the estimated dilution factors (non-default values) vary but are generally not very detailed. Note that background concentrations by country (PEC sed regional) are based on the average background concentration for the country in which the site is situated. The default background concentration is based on the average for EU countries where background surface water concentrations were available (Commission, 2008).

The report covers new sites as well as sites previously referenced in the EU RAR. Sectors without new data since the data collection in 2000-2003 for the EU RAR (Commission 2008) have been omitted from the current report, because this would most probably not reflect the current situation due to changes in production and environmental releases, closing of sites and opening new sites. Thus the present report contains a preliminary assessment of the following sectors:

- Nickel refining/production
- Stainless steel production
- Ferro-nickel production
- Nickel chemical production
- Nickel Plating
- Catalysts
- Battery producers
- Ceramics production

These sectors account for in total over 75% of the use of nickel in the EU (Nickel Institute, 2008) Due to lack of recent data the following sectors that were represented in the EU RAR (Commission 2008) are not covered by this report:

- Multiple steel product manufacturers
- Nickel alloy production
- Steel production and foundry
- Metal product manufacturers
- Recycling

A description of the industries and activities within the individual sectors is found in the EU RAR section 3.1.3.4 (Commission 2008).

The data coverage, i.e. the number of sites where data are available compared to the number of known sites in EU, are listed below. The figures on the total number of sites in EU are based on the

information from the RAR supplemented with more recent knowledge when available. The estimated coverage gives an indication of the uncertainty of the evaluation of the industrial sectors in this report.

In addition to the coverage the percentage of the total release from the sectors presented in the table below is roughly calculated. This calculation is based on the assumption that the sites where data are available represent the whole sector. For chemical production, plating industry and ceramics the total number of sites are however unknown. For these sectors the estimation is based on the assumed minimum number of sites, i.e. 18 sites¹ for chemical production, 800 plating sites¹ and 10 ceramic production¹ sites in EU. Note that this calculation leads to an maximum estimate of the *coverage* of these industrial sectors but to minimum release estimates.

Table 2: Data coverage of the individual sectors. Estimated contribution of each sector to the total release from the sectors mentioned in this table.

Sector	Data coverage Number responding companies/ expected number of EU compa- nies	Remarks	Approximate per- centage of total release from all of the industrial sec- tors evaluated in this report
Nickel production	7/7	Full coverage	2.1
Stainless Steel pro- duction	19/23	Good coverage	51 ²
Ferro-nickel pro- ducers	1/1	Full coverage	22
Nickel chemical production	11/>18	EU RAR mentions 18 EU sites. The actual number is likely to be higher	3.2
Nickel plating	12/ >800	Low coverage	21
Catalysts production	13/13	Full coverage	0.3
Battery production	3/7	Medium coverage	0.1
Ceramics production	2/>10	Unknown number of EU sites	0.0

The derivation of PNEC values for freshwater sediment is discussed in details in the report: *Development of PNEC sediment of nickel for the freshwater environment* (ARCHE, 2011). The report includes as well a description of the development of predictive models for bioavailability and chronic toxicity of nickel in freshwater sediments. The relationships between chronic Ni toxicity and sediment parameters were evaluated in order to identify main determinants for the bioavailability of nickel in sediment: Acid Volatile Sulfides (AVS); Organic Carbon (OC), iron (oxy)hydroxides and Cation Exchange Capacity (CEC). Due to co-variance none of the sediment parameters could be singled out as being the predominant parameter. However, AVS and iron were significant parameters for bioavailability correction, whereas models based on organic carbon and CEC normalizations were deemed inappropriate due to a low correlation with the observed chronic toxicity (ARCHE 2011). In the present report the bioavailability normalization for nickel in sediments has been illustrated by using real world AVS concentrations which are typically encountered in European freshwater sediments systems. The examples cover from the 10th to 90th percentiles of the AVS distribu-

¹ Estimated by the Nickel Institute in 2012

² One very large site contributes with approx. 30% of the release from all sectors and 76% of the release from the stainless steel sector

tion typically encountered in the EU (i.e 0.64-61.52 $\mu\text{mol/g}$ dry wt for the 10th and 90th percentiles, respectively).

4 Results

This section presents the RCR³ for the sediment compartment based on the predicted environmental concentration for sediment: (PEC total; mg/kg dry weight), which is calculated as the regional background plus the estimated local contribution from the site. For each site the risk characterisation ratio for the sediment compartment is calculated ($\text{RCR} = \text{PEC total} / \text{PNEC}$) under a number of different set of assumptions.

Firstly the RCR is calculated using a generic approach for the individual sites based on the Realistic Worst Case (RWC) PNEC values for the sediment compartment different application factors, i.e. PNEC derived using $\text{AF} = 1, 1.5; 2; \text{ or } 3$, corresponding to $\text{PNEC} = 94; 63; 47; \text{ or } 31 \text{ mg/kg d.w.}$

Secondly the implication on the RCR of a reduced bioavailability of nickel is presented using a generic approach for calculation of the bioavailability and $\text{AF} = 2$. The lower bioavailability at increasing levels of AVS results in corresponding lower RCR values at the individual sites. A series of scenarios are calculated representing for each individual site and sector the corrected RCR values of AVS that are relevant for the European freshwater sediments systems, i.e. at the 10th, 50th and 90th percentile values represented by $\text{AVS} = 0.64; 7.75; \text{ and } 61.52 (\mu\text{mol/g d.w.})$, corresponding to bioavailability corrected $\text{PNEC} = 56, 118; \text{ and } 155 \text{ mg/kg dw}$

Section 5 of this report presents a flexible optional refinement approach for

- Refinement of PEC local sediment i.e. by using more sophisticated exposure data (based on refined exposure data of the receiving surface water or alternatively using measured sediment total exposure data) and/or
- Refinement of PNEC local sediment by employing site specific bioavailability normalization by use of site specific AVS information.

It is noted that for implementing each refinement approach it may be warranted to increase the current guidance on issue like:

- Measurement of representative regional and local (site specific) metal (nickel) concentrations in surface water, and sediment,
- Measurement of a representative local K_p to organic matter and or K_d for sediment (local)
- Measurement of representative local AVS and SEM data.

³ RCR: Risk Characterization Ratio = $\text{PEC}_{\text{sed}} / \text{PNEC}_{\text{sed}}$. When $\text{RCR} > 1$ risk is indicated and implementation of Risk Management Measures warranted which can lower the exposure of sediments e.g. decreased environmental emission. If the RCR is based on PEC_{sed} and/or PNEC_{sed} which can be refined, an $\text{RCR} > 1$ indicates *potential* risk and that refinement is warranted.

4.1.1 Generic Risk characterization of the sediment compartment compared to the surface water compartment taking variation in bioavailability and different AFs into account

The figures below are comparing values of RCR for the water phase with the RCR for the sediment compartment on three selected industrial nickel sectors. The analysis is performed to illustrate the extent to which it is possible based on currently available information to conclude that either the pelagic or the sediment compartment is the most sensitive one for chronic nickel toxicity, i.e. whether the RCR is highest for one or the other compartment. The data are based on an AF = 2 for both the RWC PNEC_{water} and the RWC PNEC_{sed}.

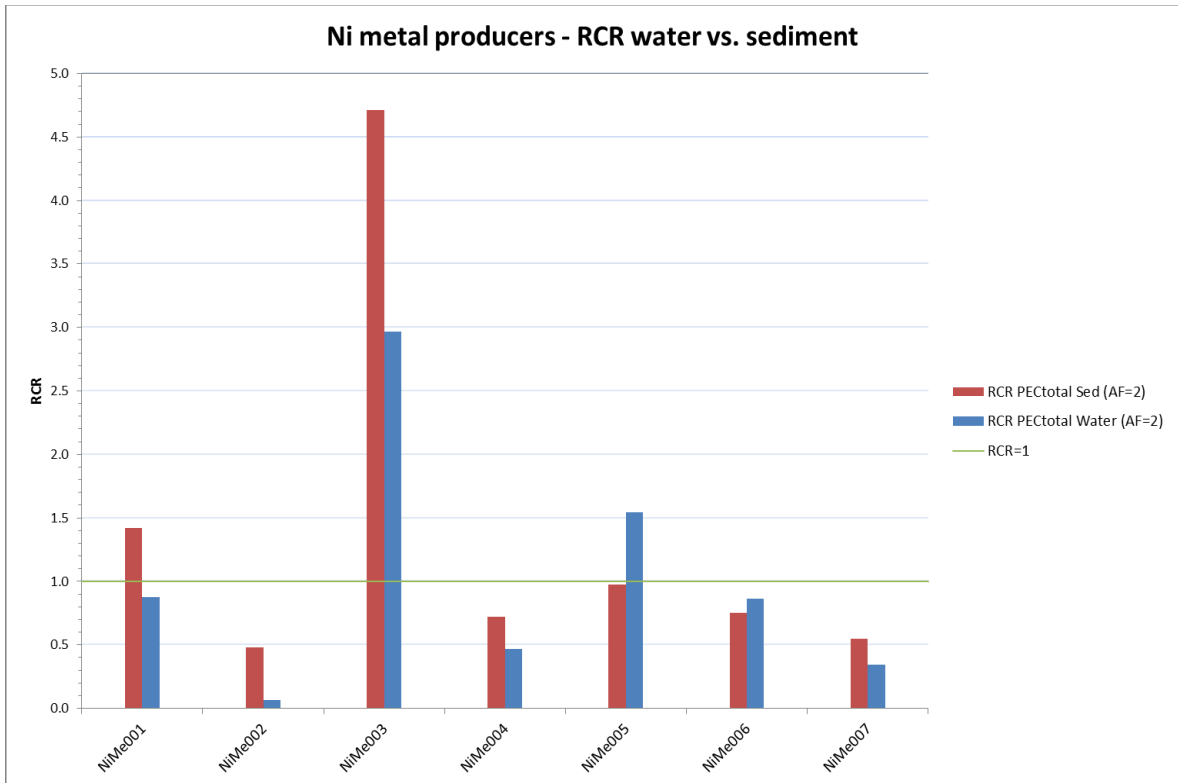


Figure 1: RCR values for water and sediment; Nickel producer sector.

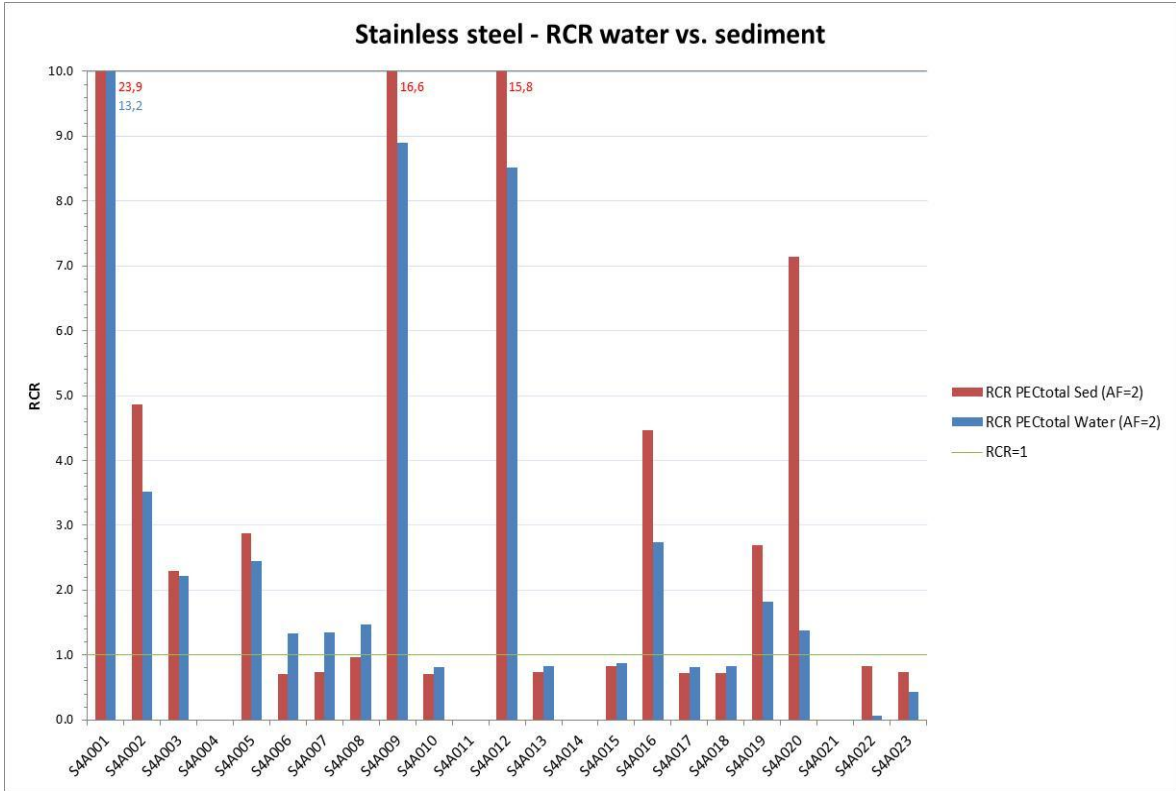


Figure 2: RCR values for water and sediment; Stainless steel sector.

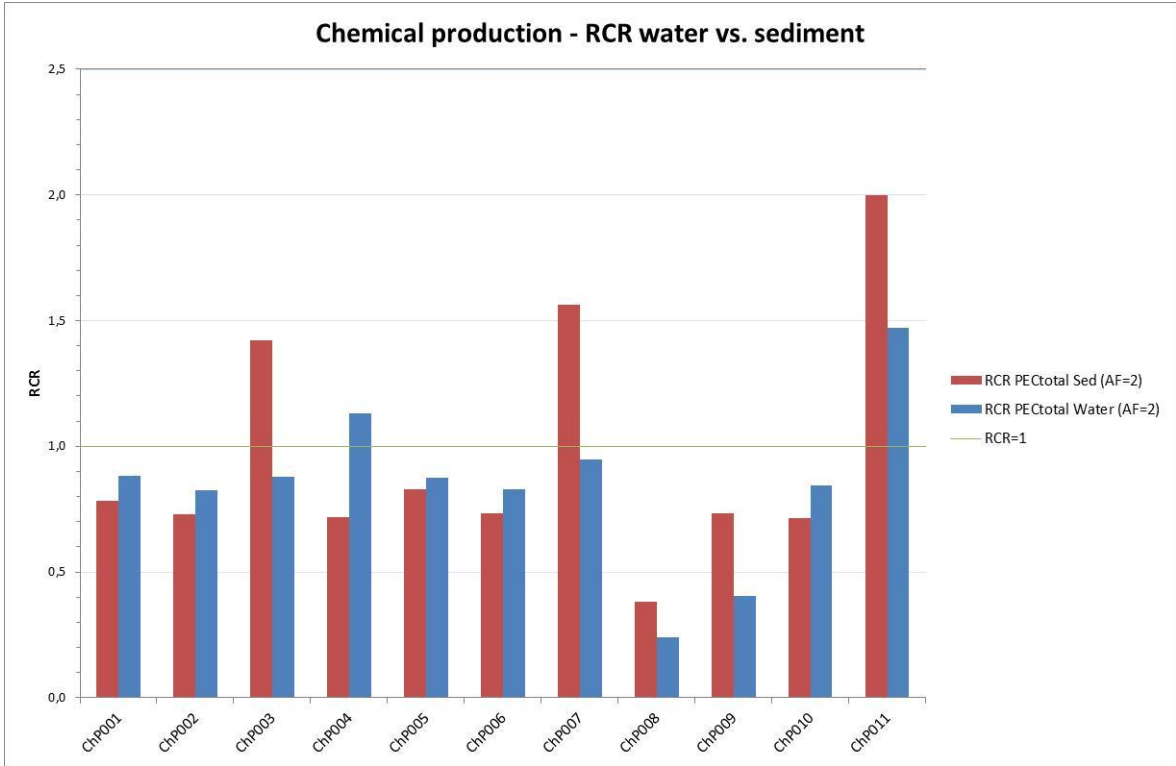


Figure 3: RCR values for water and sediment; Nickel chemical production sector.

For nickel metal producers the sediment RCRs ($RCR_{sed, total}$) are higher than the corresponding RCR for the water compartment ($RCR_{water, total}$) at 5 out of 7 sites. The $RCR_{sed, total} \geq 1$ at 2 sites, whereas the $RCR_{water, total} \geq 1$ at 2 sites out of a total of 7 in this industrial sector.

In the stainless steel sector the $RCR_{sed, total}$ is in general higher than $RCR_{water, total}$ at the sites with the highest RCR values. However at low RCR values around or below the $RCR = 1$ the opposite trend is seen, i.e. that the RCR for the water phase is generally higher than the RCR for sediments (at 8 of the 23 sites). Overall the $RCR_{sed, total}$ is higher than $RCR_{water, total}$ in 11 out of the 23 sites. Very high $RCR_{sed} \geq 10$ or more are observed at 3 sites, and 9 of 23 sites have $RCR_{sed, total}$ at or above 1.

For nickel chemical production the RCR_{sed} is higher than the RCR_{water} at 5 out of 11 sites, including those sites where very high RCR values were observed. At sites with RCR values around or below 1, the RCR for water is higher than for sediment at 6 out of 11 sites.

It should be noted that because the sediment concentration is estimated from the water concentration by assuming equilibrium partitioning the relation between the RCR for the water compartment vs. the sediment compartment is mainly determined by the ratio between $PNEC_{wat}$ and $PNEC_{sed}$ in those cases where the regional concentrations do not contribute significantly to PEC_{local} sediment. This is clearly the case for high RCR values above 1, where the RCR for sediments are generally higher than the RCR for the water compartment. However, at lower RCR values the regional background nickel concentration contributes more significantly to the PEC_{local} sediment. Therefore at low RCR values for water and sediment, the RCR for water is in some cases higher than the RCR for the sediment while at other sites the opposite is seen.

In conclusion from currently available data, which implies that the local sediment nickel concentrations are estimated from estimated surface water concentrations, it seems that the sediment compartment may have a higher sensitivity to chronic nickel toxicity than the pelagic compartment at high RCRs, but also that the two compartments may be of equal sensitivity at lower RCRs. However this conclusion is only provisional and tentative due to the limitations in the current available information especially regarding exposure. In order to conclude more definitively on the relative sensitivity of the sediment vs. the water compartment, representative site specific measured values of nickel concentration in surface water and local sediments as well as representative regional values are needed. Thus no firm general conclusion can be drawn based on the currently available data regarding whether the aquatic or sediment compartment is the most sensitive compartment to chronic nickel toxicity.

4.2 Risk characterization for sediments applying different AF values

In the examples below the RCR values for sediments applying different application factor (AF) values for derivation of PNEC for sediments ($PNEC_{sed}$) are presented for three selected industrial sectors nickel producers, stainless steel and nickel chemical production sectors. The three selected industrial sectors are estimated to cover 75 % of the total environmental release of all of the industrial sectors analyzed in this report.

The figures present the total concentration of nickel in the sediment compartment $PEC_{sed, total}$ as the sum of the regional background (brown) and the estimated local concentration (grey). The horizontal lines indicate the derived PNEC when different AF-values are selected. Note that a generic regional background concentration (i.e. 33.5 mg/kg for freshwater sediments and 16.1 mg/kg dry wt. for marine sediments) has been employed in most cases, i.e. where country specific background concentrations were not available.

Data for the other industrial sectors are found in the Appendix including data for PNEC values derived using an AF of 1; 1.5; 2 and 3.

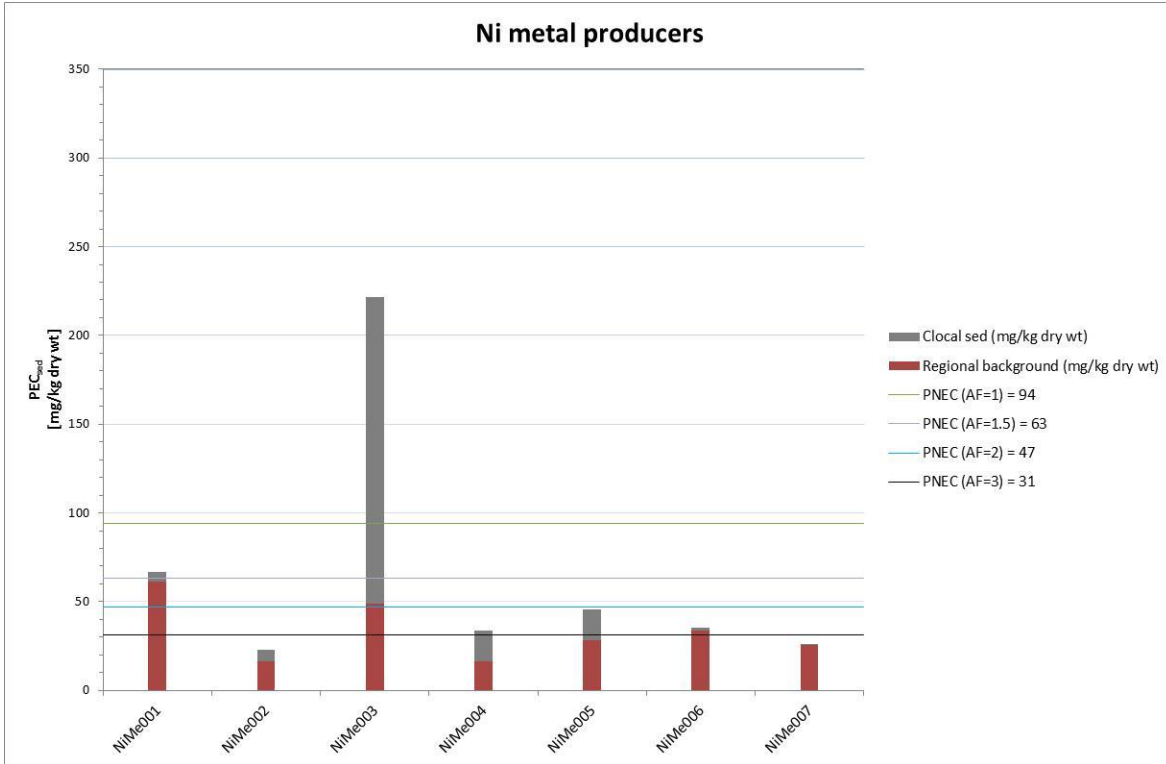


Figure 4: PEC in sediments compared to PNEC values derived by different application factors (AF); Nickel metal producer sector.

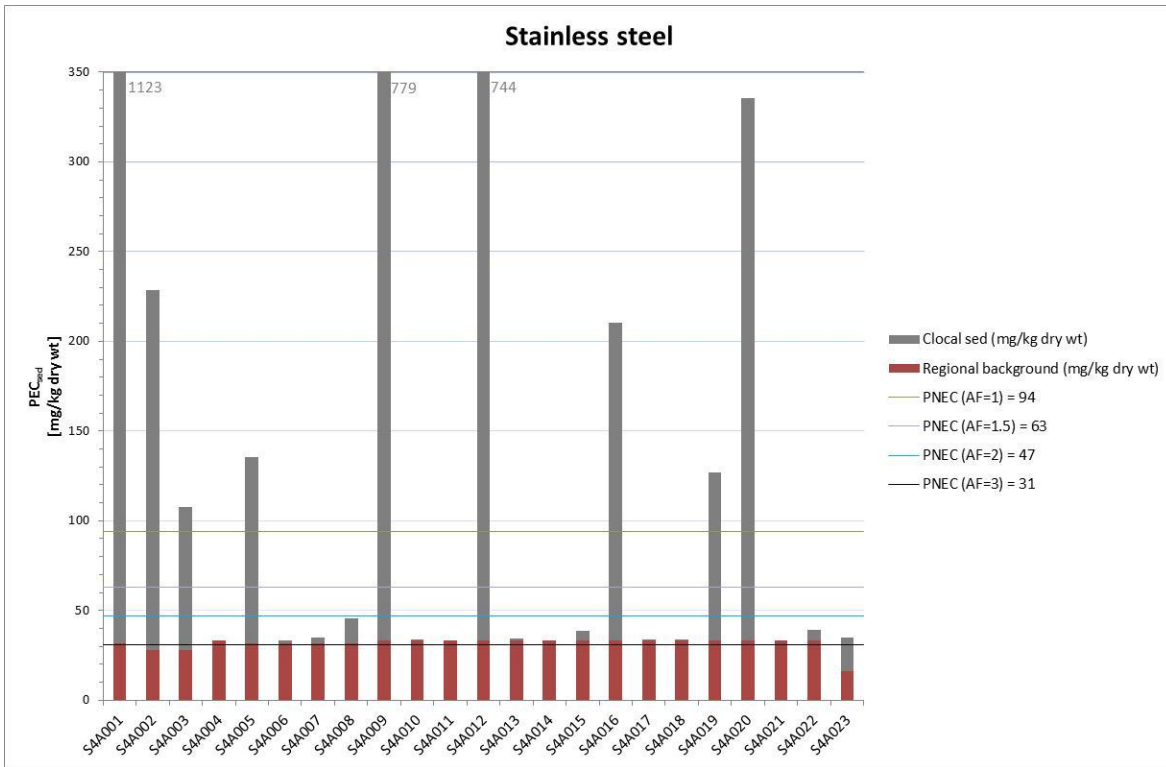


Figure 5: PEC in sediments compared to PNEC values derived by different application factors (AF); Stainless steel sector.

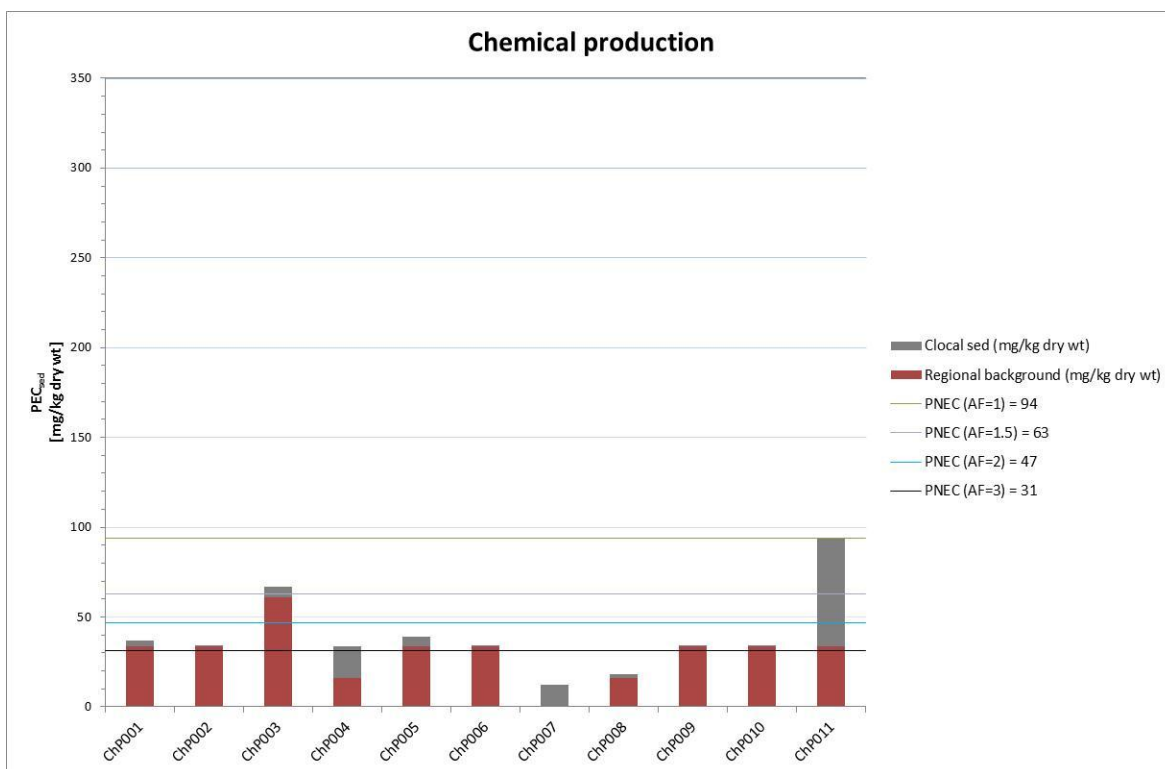


Figure 6: PEC in sediments compared to PNEC values derived by different application factors (AF); Nickel chemical production sector.

The results across all industrial sectors analyzed in this report are summarized in Table 3.

Table 3: Number of sites within the individual industrial sectors where RCR > 1 compared to the total number of sites in each sector.

Industrial Sector	No. of sites with RCR > 1 / total no. of sites			
	AF = 1	AF = 1.5	AF = 2	AF = 3
Nickel metal producers	1/7	2/7	2/7	5/7
Stainless Steel production	9/23	9/23	9/23	23/23
Ferro-nickel producers	0/1	1/1	1/1	1/1
Chemicals production	1/11	2/11	2/11	9/11
Nickel plating	4/12	4/12	6/12	11/12
Catalyst producers	2/10	4/10	4/10	10/10
Battery production	0/3	0/3	0/3	3/3
Ceramics production	0/2	0/2	0/2	2/2
No. of sites RCR>1/ total no. of sites	17/69	22/69	24/69	64/69

The PNEC derived using an AF = 3 (31 mg/kg dw) is in many cases lower than the generic regional background sediment concentration. It is noted, however, that the regional background concentrations employed here are average EU (default) or national values and that the background concentrations in the individual catchments and at the different sites can be very different from this average concentration. The implication of using an AF = 3 in relation to whether the total regional background concentration in sediments really are exceeded at the local sites thus need be evaluated against more comprehensive site specific exposure data.

However, based on the current generic estimations of total local sediment nickel concentrations (from local surface water concentrations, dilution factors and a generic adsorption coefficient) and generic regional sediment concentrations it seems that a potential risk is very often indicated near

regional background concentrations of nickel in sediments: Based on the available data the fraction of sites where a potential risk is indicated is very high (64/68 sites) when AF = 3 is employed. The number of sites where potential risk for the sediment compartment is indicated is however significantly lower when an AF = 2 is employed (24/69 sites). This number of sites with potential risk is even less when using either an AF of 1.5 (22/69 sites) or an AF of 1 (17/69 sites).

Overall it is not possible to compare nickel background concentrations at the local industrial sites with the $PNEC_{\text{sediment}}$ for these sites because of lack of site specific and relevant regional data concerning total nickel concentrations in the sediments. Hence it is currently not possible this way to use such a comparison in the overall evaluation of the appropriateness of the size of the AF to be selected to derive $PNEC_{\text{sed, total}}$ for nickel. The currently available data may however suggest that selection of an AF of 3 could result in RCRs above 1 in many cases even after having refined the basis for the RCR calculation by refining the exposure assessment and the bioavailability normalization, but that this may not be the case if an AF of 2 is selected (see also the following section).

4.3 Risk characterization considering the bioavailability of nickel in sediments

The bioavailability of nickel in sediments is correlated with a number of abiotic factors in the sediment, including AVS. The documentation for the use of AVS as parameter for estimating the bioavailability of nickel in freshwater sediments is discussed in details in ARCHE (2011). The figures in this section presents for different industry sectors the $PEC_{\text{sed, total}}$ for the individual sites compared to the PNEC values normalized for AVS in sediment ($PNEC_{\text{AVS normalized}}$) at different AVS levels spanning the different percentiles of AVS typically found in European fresh water sediments. This illustrates generically how the variation of AVS in sediments across EU may impact the site specific RCR sediment if taken into account for normalizing the $PNEC_{\text{sed}}$ values for bioavailability as proposed (cf. ARCHE 2011). Note that it was not possible to analyze the impact of such a bioavailability normalization in a sites specific manner because local and often also regional (background) AVS concentrations for regions (water sheds) where the sites are located are currently not available. However when local SEM and AVS measurements in addition to local and regional total nickel concentrations in sediments are available it is possible to obtain the most realistic risk estimate at the local site.

Table 4: AVS values in $\mu\text{mol/g dw}$ and corresponding approximate percentile of EU freshwater sediments.

	Representativeness of applied AVS level		
AVS ($\mu\text{mol/g dw}$)	0.64	7.75	61.52
Approximate percentile in EU	10 th	50 th	90 th

The presented figures are for nickel producers, stainless steel and chemical production. Data for the other sectors are found in the Appendix including data for PNEC values derived using AF at 1; 1.5; 2 and 3.

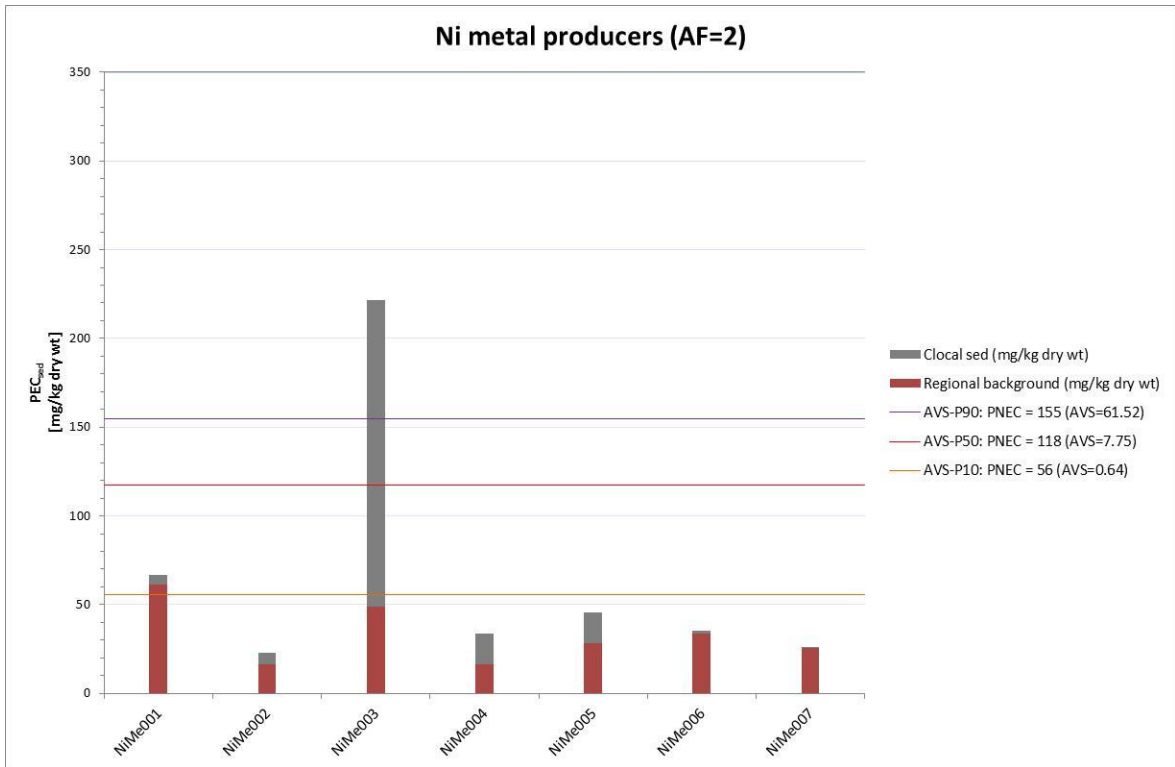


Figure 7: PEC sediments compared to AVS normalized PNEC values. Nickel producer sector.

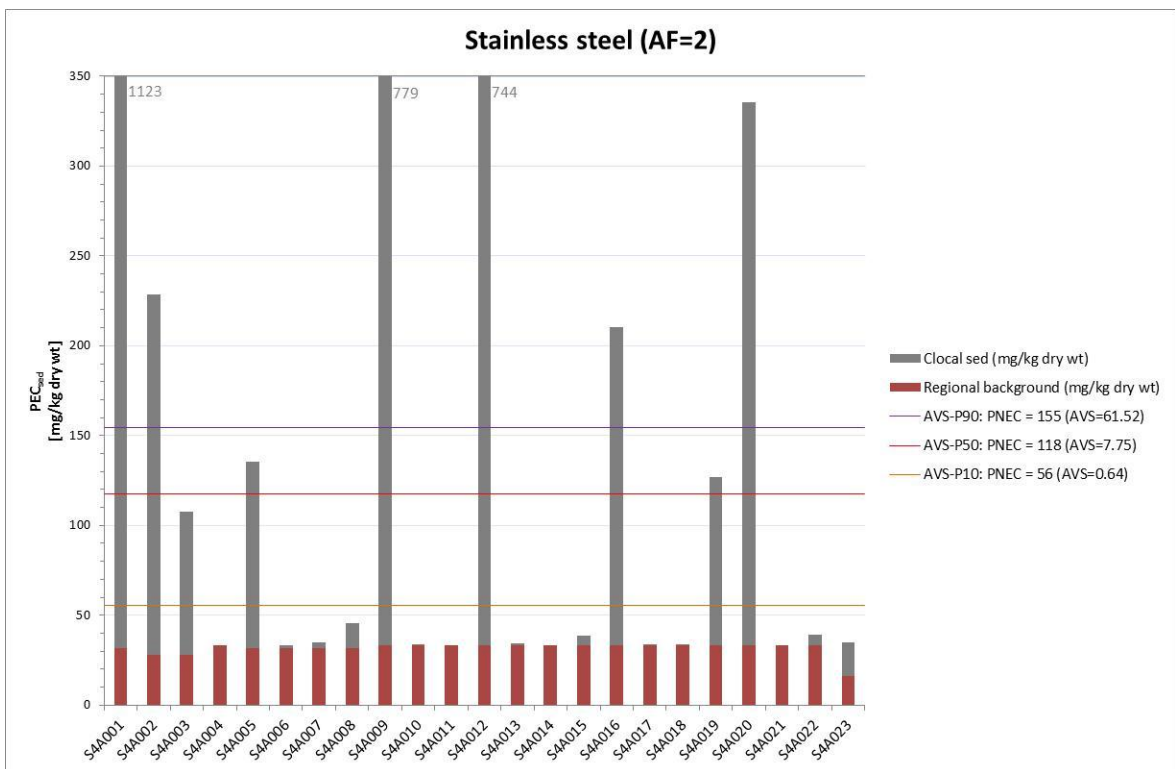


Figure 8: PEC sediments compared to AVS normalized PNEC values. Stainless steel sector.

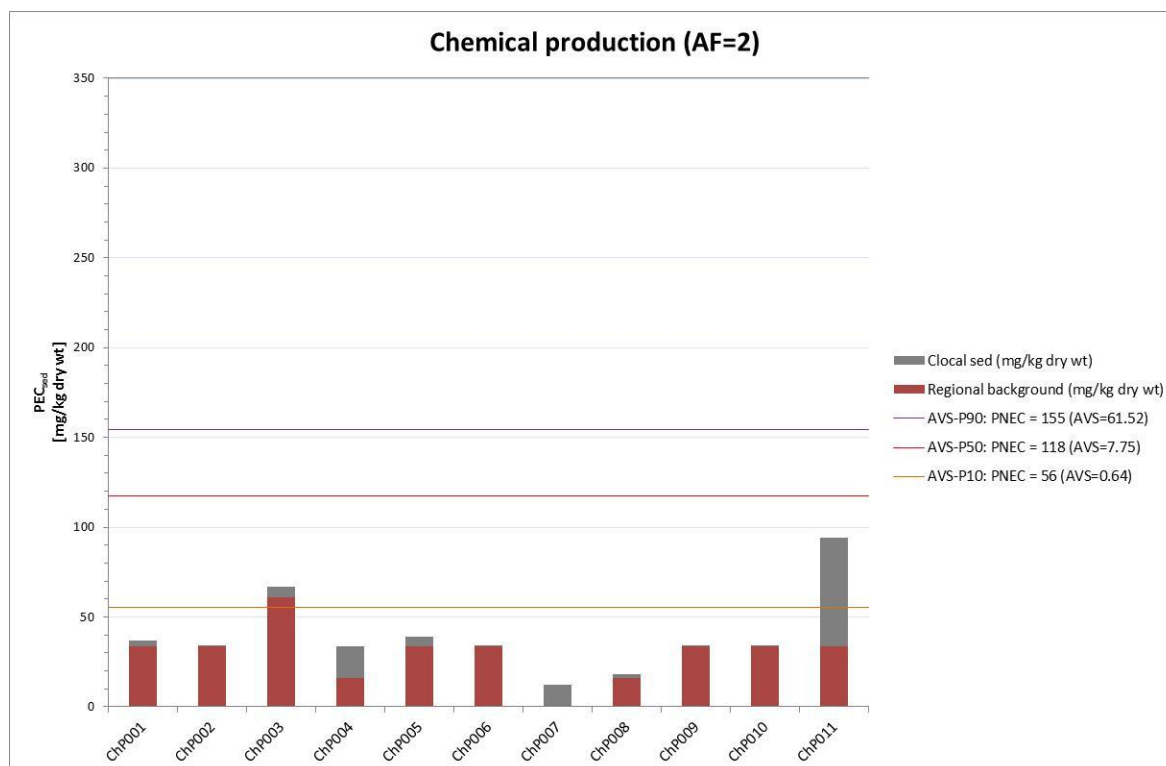


Figure 9: PEC sediments compared to AVS normalized PNEC values. Nickel chemical production sector.

Table 5: Number of sites within the industrial sectors where RCR > 1 compared to the total number of sites in the sector. Figures are shown for different levels of AVS. All observations are based on a PNEC derived using AF = 2. Similar tables for PNEC derived using AF = 1; 1.5; and 3 are found in the appendix.

AVS ($\mu\text{mol/g dw}$)	Number of sites with RCR > 1 / total observations at different AVS levels			
	0 AF=2	0.64 (P10)	7.75 (P50)	61.52 (P90)
Nickel metal producers	2/7	2/7	1/7	1/7
Stainless Steel production	9/23	9/23	8/23	6/23
Ferro-nickel producers	1/1	1/1	0/1	0/1
Chemicals production	2/11	2/11	0/11	0/11
Nickel plating	6/12	5/12	3/12	3/12
Catalyst producers	4/10	4/10	2/10	2/10
Battery production	0/3	0/3	0/3	0/3
Ceramics production	0/2	0/2	0/2	0/2
Number of sites where RCR > 1	24/69	23/69	14/69	12/69

The results show for example that for the nickel metal producers the number of sites with potential risk to sediments organisms (at AF = 2) decreases from 2 to 1 site out of 7 at the 50th percentile AVS levels of 7.75 $\mu\text{mol/g dw}$ and that one site remains with a potential risk to sediments even at the highest AVS levels.

For stainless steel production the number of sites where a potential risk is indicated is decreased from 9 to 6 out of the 23 sites but first at relatively high AVS levels.

For chemicals production the number of sites where a potential risk is indicated is reduced from 2 to 0 before the 50th percentile level with AVS-value of 7.75 µmol/g dw is reached.

Across the included industrial sectors the number of sites where a potential risk is indicated is reduced from 24 to 12 when applying up to 90th percentile AVS values occurring in EU sediments.

In conclusion, the application of bioavailability correction reduces the number of sites with a potential risk.

It is noted that this illustration of the impact of the proposed AVS based bioavailability normalization on the number of sites at potential risk has been done based on *estimated* local sediment concentrations and therefore also that the number of sites at risk is likely to be significantly lower if based on more advanced realistic site specific PEC local sediment values for nickel.

Furthermore it is from this analysis obvious that in a number of cases in certain of the evaluated industry sectors a refinement of the environmental emission and exposure assessment is warranted because even at high AVS-sediment concentrations in the local sediment (i.e. at site even with AVS concentrations > the 90th percentile of those observed in the EU) the RCR is exceeded. This applies to the following industrial sectors when an AF of 2 is used (c.f. also Table 5 on p. 14):

- nickel metal producers : 1 out of a total of 7 sites with exposure information
- stainless steel producers: 6 out of 23 sites with exposure information
- nickel plating : 3 out of 12 sites with exposure information
- Catalyst producers: 2 out of 10 sites with exposure information.

Finally because of the limited analysis (industrial sectors with no new exposure information have not been included) and the limited information available for many of the industrial sectors included in the analysis (c.f. Table 1 p. 4 and Table 2 p. 5), a firm conclusion cannot be drawn as regarding the number of sites where an improved environmental emission and exposure analysis is warranted. It is however from the information available estimated to be in a significant number of cases.

5 Overview possible refinement options to be used in the risk characterization for sediments

5.1 Overall framework

In general a risk characterization is conducted using a realistic worst case (RWC) scenario with a default PNEC and an estimated PEC based on measured or estimated (modeled) emissions to the water compartment. Several options, however, are available to refine the risk characterization and to get to a more realistic risk estimate. This may include simple refinements like collecting more sophisticated emission data, but can when potential risk is indicated be extended to include site specific total nickel sediment data and in fewer cases when needed be enhanced to include a full-blown bioavailability assessment for sediments by use of AVS modeling. The sequence of approach to take when refining the assessment should however not be fixed. Rather the actual choice of the refinement method will most likely be driven by factors such as cost-efficiency to reach the envisaged goal (demonstrating no risk for the sediment compartment, i.e. safe use). Table 6 provides

several options that when necessary could be used to calculate more realistically the risk at the local site. The table is not intended to suggest a hierarchical tiered approach but merely outlines the possible refinement options that can be applied in a flexible way.

Table 6: Overview possible refinement options and associated benefits, limitations.

Refinement Predicted Environmental Concentration (PEC)		
Refinement	Benefits	Limitations
Collect additional exposure data for the aquatic compartment	Reduces the uncertainty in deriving the PEC aquatic	EP method still needed to derive the sediment PEC Some data (e.g.) flow rate river and local Kd values are difficult to obtain
Collect additional exposure data for the sediment compartment	Reduces the uncertainty in deriving the PEC sediment	Historical measured sediment data are scarce and sometimes not Spatial and temporal variability should be taken into account when conducting new measurements
Refinement Predicted No Effect Concentration (PEC)		
Collect historical or new AVS data	Allows to normalize the PNEC for bioavailability	Availability of historical AVS data is limited AVS measurements is not a routine measurement
Collect local SEM-AVS data	SEM-AVS < 0 can be used as an indicator for absence of toxicity	SEM-AVS measurements are not routine measurements Spatial and temporal variability should be taken into account

The several refinement options are more detailed here below

Refinement option 1: Collect more sophisticated exposure/emission data for the aquatic compartment (surface water and sediment)

Typically a fixed dilution factor is applied to the effluent concentration of an STP in order to obtain the PEC surface water (by default assumed to be 10) (ECHA, 2010). Since this PEC local water, can be subsequently used in the derivation of the sediment PEC value by applying the Equilibrium Partitioning approach it could be worthwhile to conduct a more specific assessment. For example collecting data on effluent discharge rates and flow rate of the receiving surface water can be used to calculate the actual dilution factor after complete mixing. When considering the available dilution, account should be taken of the fluctuating flow-rates of typical receiving waters. The low-flow rate (or 10th percentile) should always be used. Where only average flows are available, the flow for dilution purposes should be estimated as one third of this average. It must be noted that with the assumption of complete mixing of the effluent in the surface water no account is taken of the fact that in reality in the mixing zone higher concentrations will occur. For situations with relatively low dilution factors this mixing-zone effect can be accepted. For situations with very high dilution factors,

however, the mixing zones may be very long and the overall area that is impacted by the effluent before it is completely mixed can be very substantial. Therefore, in case of site-specific assessments the dilution factor that is applied for calculation of the local concentration in surface water should never be greater than 1,000 (ECHA, 2010).

Next to the local conditions from the surface water around the point source information on the partitioning to suspended solids can be used to refine the assessment. In absence of a local K_d value, a default K_d value is typically extrapolated from a distribution of measured K_d values over all EU countries from where data are available or from the country at which the site is located. In the latter cases typically a median value is being used (ECHA, 2008). To avoid the use of such a default K_d value a possible refinement is to measure K_d in experiments conducted under local site conditions.

Refinement option 2: Collect measured data for the sediment compartment

Instead of refining the PEC water for use in an estimation of PEC_{sed} a more direct refinement is to use actual measured data in the sediment compartment. Since sediment organisms inhabit the top layer of a sediment the first 10-30 cm should be sampled using a dredge or core sampler. It should be noted that for assessing bioavailability parameters such as SEM-AVS the top 5 cm should preferentially be sampled using a core sampler (see also section 5.1).

Due to spatial heterogeneity it is recommended to make a composite sample from several samples taken from depositional zones.

Refinement option 3: Collect bioavailability parameters for the sediment compartment

Nickel bioavailability in sediments is governed by several sediment characteristics with AVS and iron as the predominant significant parameters mitigating nickel toxicity. ARCHE (2011) developed for the AVS parameter predictive bioavailability models that can be used to assess toxicity of nickel in freshwater sediments. If local sediment AVS data are not available alternatively use of iron concentrations in the sediment may be considered for use in a predictive bioavailability model for the assessment of chronic nickel toxicity in freshwater sediments (ARCHE 2011).

The generic PNEC reflects already conditions in which bioavailability of nickel in sediments can be considered high (low AVS and organic carbon) and could be used to screen out those case where nickel toxicity is unlikely to occur. However, the AVS content in the sediment tests used for the generic PNEC derivation did contain some AVS (approximately 10th percentile of the AVS encountered in the EU). Therefore are very sensitive areas with AVS concentrations in the sediment of less than the 10 percentile of that in EU sediments not covered by this approach. Therefore further considerations should be made on the need for refinement of the risk assessment even when a potential risk is not indicated, if it is likely or known that there is a very low AVS level in local sediments at the local site. However, it may also be noted that with those typical aerobic sediments binding to iron/manganese oxide may still play an important role in reducing the bioavailability of nickel

When a refinement has been decided which should include bioavailability normalization, representative local AVS measurements should be considered to provide data for normalizing the generic PNEC towards the AVS conditions prevailing at the site. In absence of actual measured SEM-AVS data, AVS data from past monitoring campaigns for the region of interest may be considered and used in a cautious way in this context. Proper justification should, however, be given (e.g. sediment type, iron content, organic carbon content) in order to assess the cautious nature of the value chosen to represent the local conditions .

Once an AVS concentration has been selected the available nickel bioavailability models should be used to derive the site specific AVS normalized PNEC (cf. ARCHE 2011). Note that these models were developed with natural test sediments containing background values of other metals (Cu, Cd, Pb, Zn, Hg) that have a higher affinity to bind with AVS than Ni. Therefore these bioavailability models inherently take the multi metallic nature of the SEM-AVS concept into account. The background values of the different metals in the sediments used to derive the bioavailability models were < 2mg/kg dry wt for Cd, < 10 mg/kg dry wt for Cu, < 50 mg/kg dry wt for Pb and between 38-64 kg for zinc. If substantially lower or higher background values are known or can be expected for these metals this should be taken into account in the assessment by subtracting the molar difference (background local site – background test sediment) from the selected AVS concentration.

The potential risks for the local site can subsequently be calculated from the PEC_{Total} and the $PNEC_{AVS\ normalized, site\ specific}$ (Eq-3)

$$RCR = \frac{PEC_{Total}}{PNEC_{AVS\ normalized, sitespecific}} \quad (Eq-1)$$

In case RCR indicate a potential risk the assessment can be further refined by using actual measured SEM-AVS concentrations (upstream and downstream of the site) for the site under investigations.

Care should be taken to collect sediment samples in the season where AVS concentrations are expected to be the lowest, i.e. spring season in order to preserve the cautious nature of the assessment. In this regard, SEM and AVS concentrations needs also to be collected in the top 5 cm of a sediment core sample since AVS exhibits a pronounced vertical concentration profile. (i.e. lowest concentrations in the top layer)

As a third and supplementary option it may be considered to take the SEM and AVS concentrations into account because the difference between these parameters can be used as an indicator for the absence of potential risks to sediment organisms (cf. ARCHE 2011):

$$\begin{aligned} SEM_{site\ specific} - AVS_{site\ specific} < 0, \text{ no risk} \\ SEM_{site\ specific} - AVS_{site\ specific} > 0, \text{ potential risk} \end{aligned}$$

In case SEM-AVS > 0 a further weight of analysis should be conducted

5.2 Case: Real life example of the use of the suggested tiered approach

Example: Incorporation of bioavailability in the risk characterization of Ni metal and chemical producer (Ni sulphate and Ni hydroxy carbonate)

A nickel metal and nickel chemical producing plant located in Finland reported measured SEM-AVS data. This site, encoded ChP003, has been selected as an example to demonstrate the way bioavailability refinements can be incorporated in the overall sediment risk characterization framework. For this example the RWC PNEC of 47 mg Ni/kg dry wt. (including an AF of 2) has been selected as benchmark. The option to measure bioavailability parameters as a refinement step as outlined above has been applied and the results are presented here below:

Generic approach: comparison modeled/measured data with RWC PNEC

In absence of bioavailability data modeled/measured total nickel concentrations need to be compared with the RWC PNEC of 47 mg/L (Table 7).

Table 7: Overview exposure data and risk characterization.

Site ChP003	C local	PEC regional	PEC total	Approach	PNEC	RCR
Sediment (mg/kg dry wt)	12,3	61,2	73,5	TIER 1	47	1,6

A potential risk for the sediment compartment is observed. It should be noted that the RWC PNEC is lower than the regional background.

Bioavailability refinement using historical AVS concentrations: comparison modeled/measured data with RWC PNEC normalized to a default AVS concentration likely to occur in the region.

Since a potential risk is identified a literature search was conducted to identify AVS measurements from past monitoring campaigns. in the river sediments or from rivers in the region with similar characteristics. For the current example earlier AVS measurements (2007) for the receiving river Kokemäenjoki (Harjavalta, Finland) are available revealing an AVS concentration of 7.9 $\mu\text{mol/g}$ dry wt. The RWC PNEC was subsequently normalized towards this AVS concentration yielding a PNEC normalized of 118 mg/kg dry wt (Table 8)

Table 8: Overview exposure data and risk characterization.

Site ChP003	C local	PEC regional	PEC total	Approach	PNEC normalized 10 th percentile AVS	RCR
Sediment (mg/kg dry wt)	12,3	61,2	73,5	TIER 2	118	0,62

Using the available AVS concentration for the river it is unlikely that a risk will occur at the site (RCR < 1).

Bioavailability refinement using actual measured SEM-AVS data: site specific approach to calculate the actual risks

In the spring of 2010 actual SEM and AVS measurements were made upstream and downstream of the plant (Table 9). During this time window the AVS concentration is expected to be at the lowest and hence the assessment represents realistic worst- case conditions.

Table 9: Overview exposure data and risk characterization.

Sediment ($\mu\text{mol/g}$ dry wt.)	SEM Cu	SEM Pb	SEM Cd	SEM Zn	SEM Ni	ΣSEM	AVS	SEM-AVS
Downstream	0.083	0.044	0.002	0.439	0.054	0.622	6.18	< 0 (toxicity not expected)
Upstream	0.268	0.047	0.004	0.456	0.316	1.1	48.8	< 0 (toxicity not expected)

The AVS concentration measured downstream the plant, i.e. $6.2 \mu\text{mol/g}$ dry wt. is similar to the value measured in 2007 (i.e. $7.9 \mu\text{mol/g}$ dry wt.). Upstream a higher AVS concentration and higher nickel contamination levels are measured. The SEM-AVS calculation taking into account all metals present at the site is smaller than 0 predicting the absence of metal induced toxicity and hence no local risk.

6 Conclusion

A preliminary risk characterization was performed of the chronic toxicity of nickel to sediment organisms for selected industrial sectors covering approximately 75 % of the use of nickel in the EU (2008 data).

The preliminary risk characterizations made in this report indicate that no final conclusions can be drawn based on the available data regarding whether the aquatic or sediment compartment is the more sensitive compartment to chronic nickel toxicity

The estimated sediment concentrations of nickel show that a PNEC derived by use of an AF = 3 gives a PNEC equal to or lower than the estimated nickel sediment background concentrations at most sites. The actual background concentrations will however in many cases will differ from the average national or regional values used in this assessment and that a refined assessment based on actual measured sediment concentrations may give another picture. Based on the available data on total nickel concentrations in nickel sediments with low AVS concentrations the number of sites where a potential risk is indicated is high (64 of a total of 69 sites) when AF = 3 is applied. If AF = 2 is applied, potential risk is indicated at 24 of 69 sites. For PNEC values derived using lower AF values the number of sites where a potential risk is indicated is reduced from 24 (AF=2) to 22 (AF = 1.5) and 17 (AF = 1).

If the bioavailability of nickel in sediments is also taken account of by applying a PNEC value normalized for AVS sediment concentration (ARCHE 2011), the number of sites where a potential risk is indicated (using a realistic worst case) is reduced with increasing AVS concentrations. Using an AF = 2, a potential risk is observed at 23 of 69 industrial sites at the lowest AVS concentration corresponding to 0.64 $\mu\text{mol/g dw}$ (= 10th percentile of AVS in freshwater sediments in EU). This number of sites is decreased to 12 sites where a potential risk is indicated at a high AVS value of 61.52 $\mu\text{mol/g dw}$ (= 90th percentile of AVS in EU freshwater sediments).

The results of this preliminary risk characterization indicates that assessments of risk at the individual local sites emitting nickel to freshwater systems could in many cases benefit from a refinement of

- The estimated PEC_{sed} , e.g. from measurements determining the actual dilution factor or measurements of the sediment concentration.
- Use of bioavailability corrected PNEC values and supplementary use of Simultaneously Extracted Metals (SEM) and AVS approach.

In accordance with this, a flexible approach is suggested for refinement of site specific assessment of the risk of nickel to the freshwater sediment compartment. The approach starts with a realistic worst case (RWC) scenario calculating RCR using a default PNEC and an estimated PEC based on estimated or measured emission data. Considerations should be made to replace any estimated emissions by measured data and apply relevant local K_d values and dilution factors or representative measured nickel concentrations in the sediments at the local and regional scale. In a further refinement step the bioavailability may be accounted for by using cautiously set default, or existing or new regional values for sediment AVS concentrations. As a most sophisticated step specifically measured site specific values for SEM and AVS may be used. The presented real life case illustrates that the approach may be an effective approach to refine a site specific assessment of nickel where a realistic worst case indicates a potential risk in sediments.

7 References

ARCHE 2011: M. Vangheluwe , F. Verdonck: Development of a PNEC sediment of nickel for the freshwater environment. Final report, August 2011.

Commission, 2008: European Union Risk Assessment Report. NICKEL. CAS No: 7440-02-0. EINECS No: 231-111-4. RISK ASSESSMENT

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

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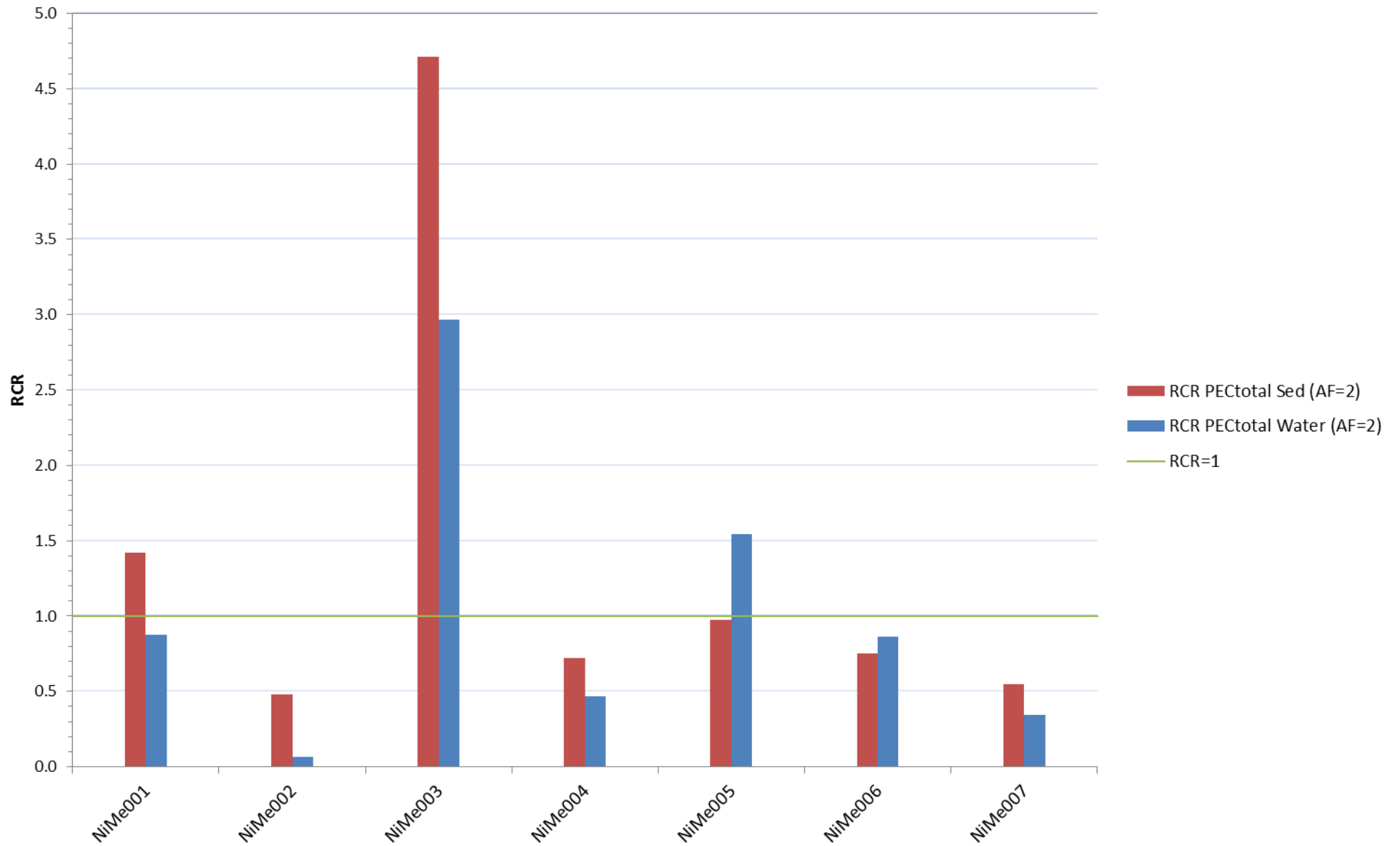
Vangheluwe M., Verdonck F., Heijerick D., Shtiza A., Burtin A., Taulbee K., Boucard T., Mäkinen J. and Gonzales E., 2008. Acid volatile sulphide survey of large river and/or lake sediments in the United Kingdom (England and Wales) Spain and Finland in 2007. Final report September 2008.

Nickel Institute. 2008. Nickel in Society, lasting value, innovative solutions. Brochure by the Nickel Institute.

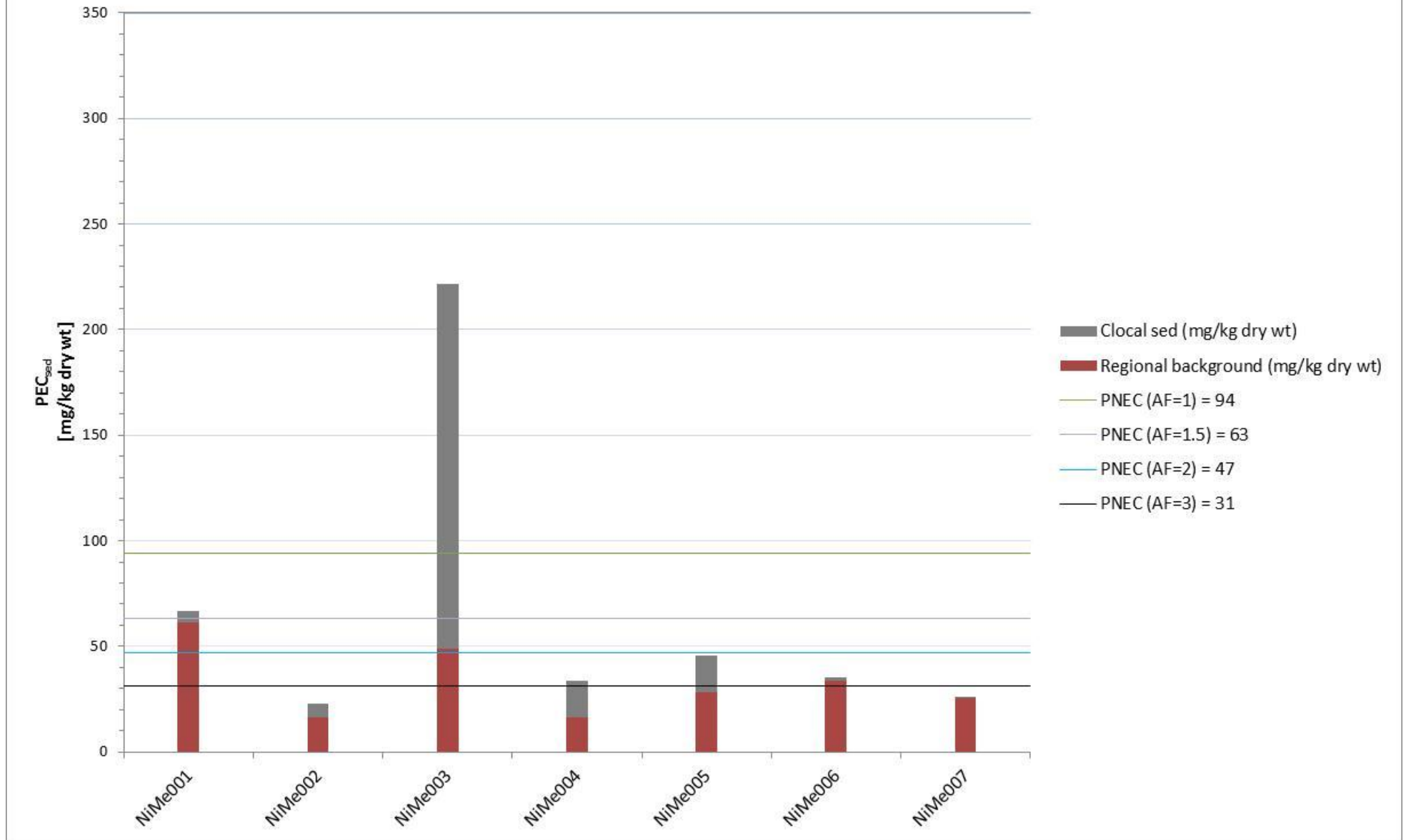
8 Appendix 1: Graphs covering all sectors included in the report

The graphs include the calculations presented and discussed in section 4. Results are shown for all sectors included in the present report.

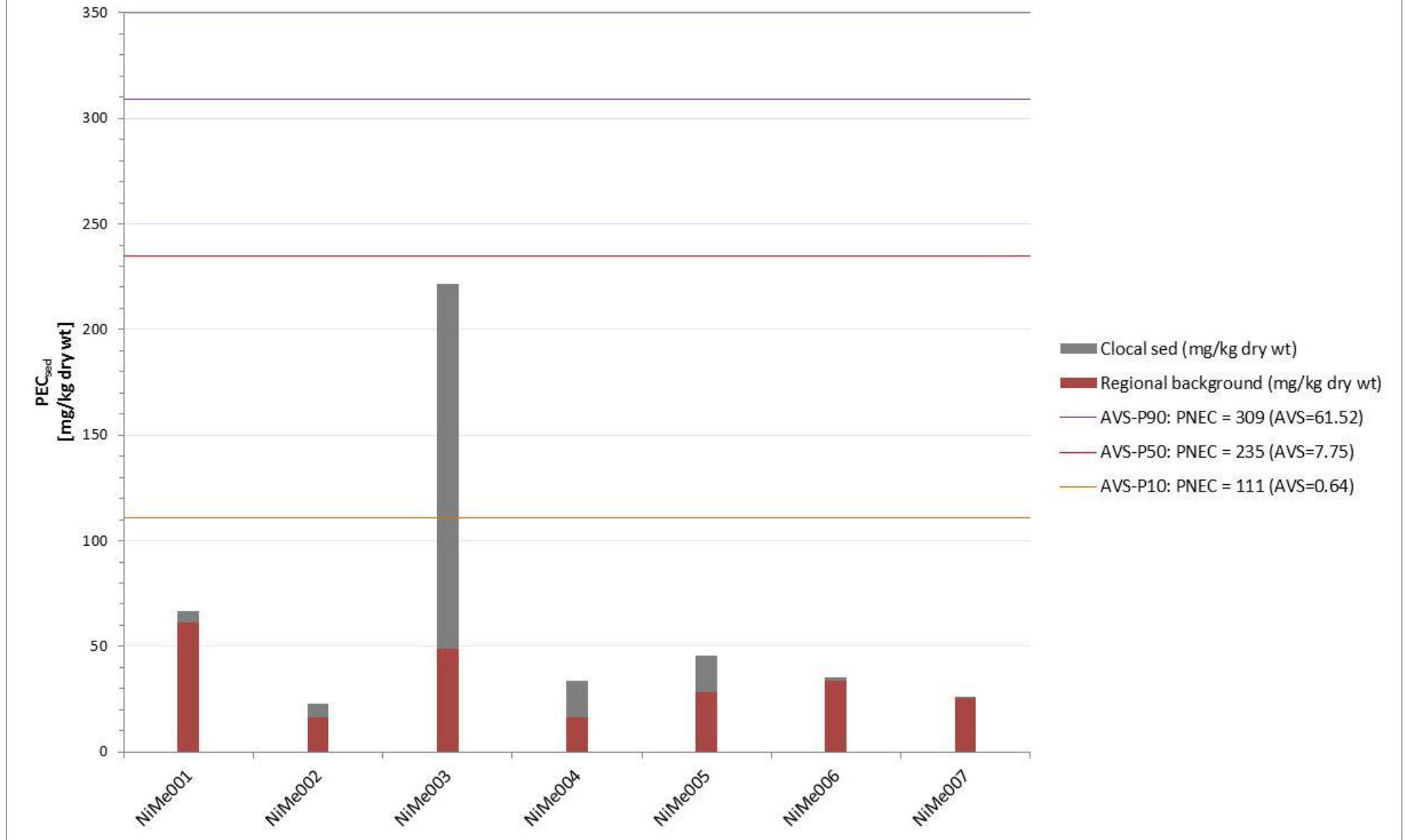
Ni metal producers - RCR water vs. sediment



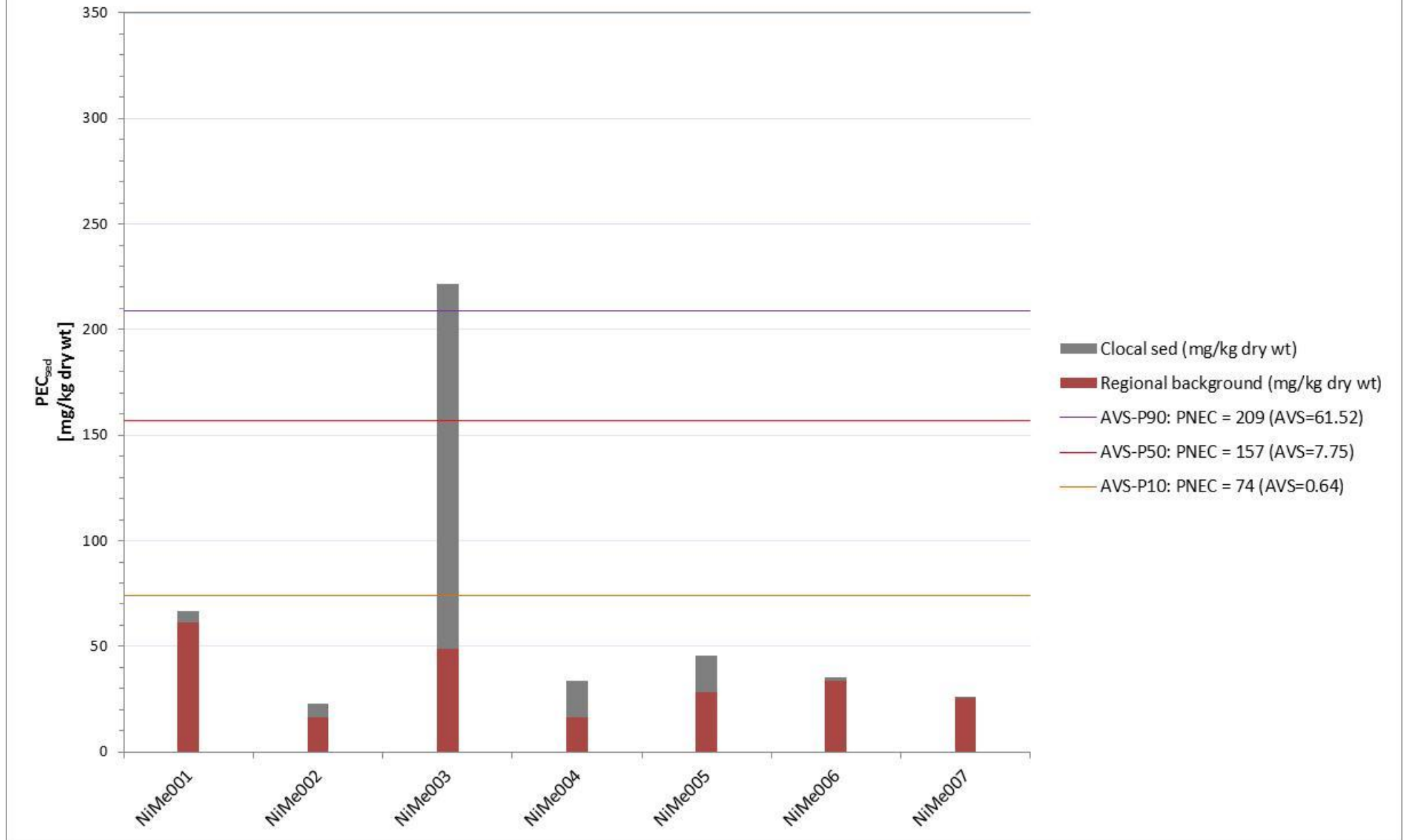
Ni metal producers



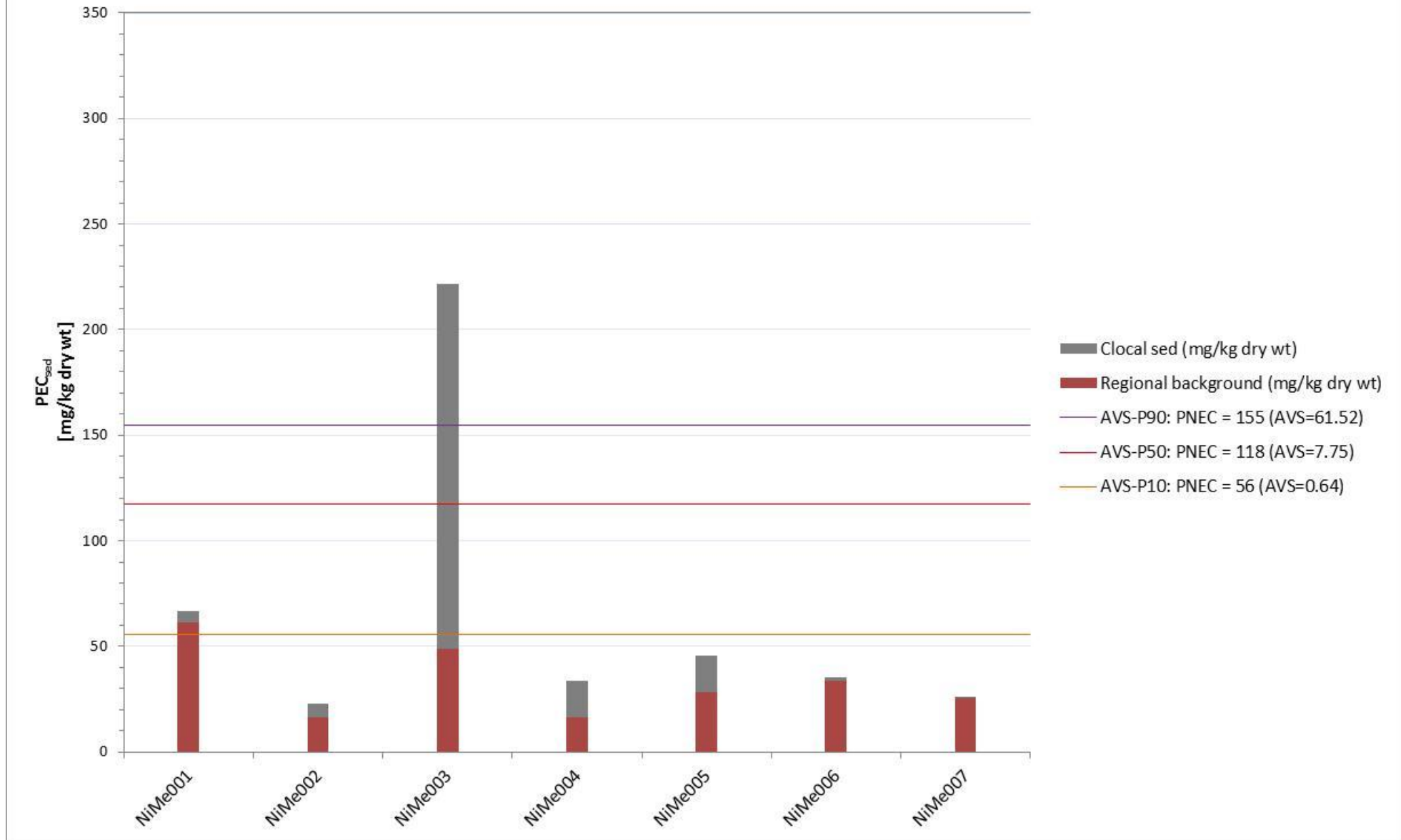
Ni metal producers (AF=1)



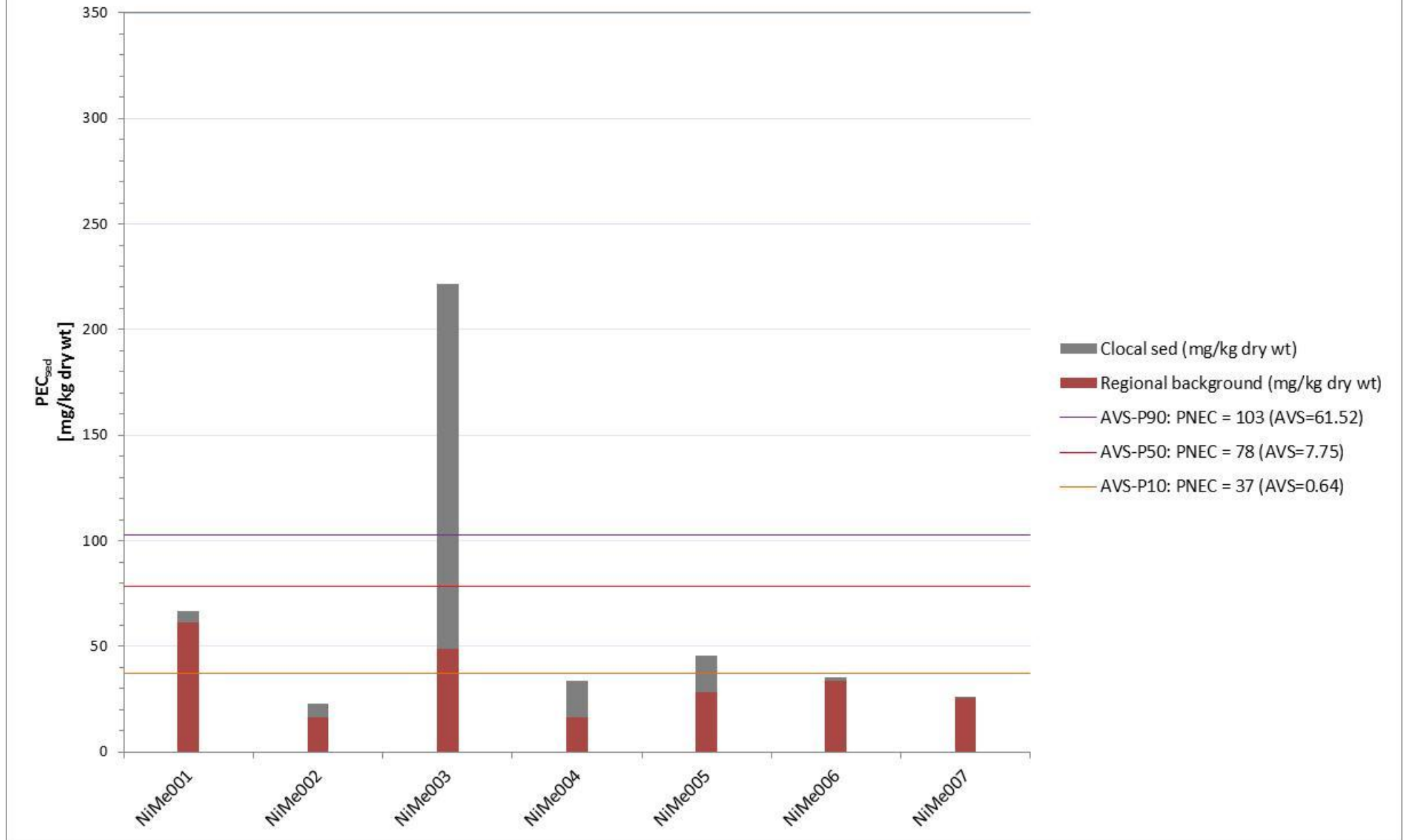
Ni metal producers (AF=1.5)



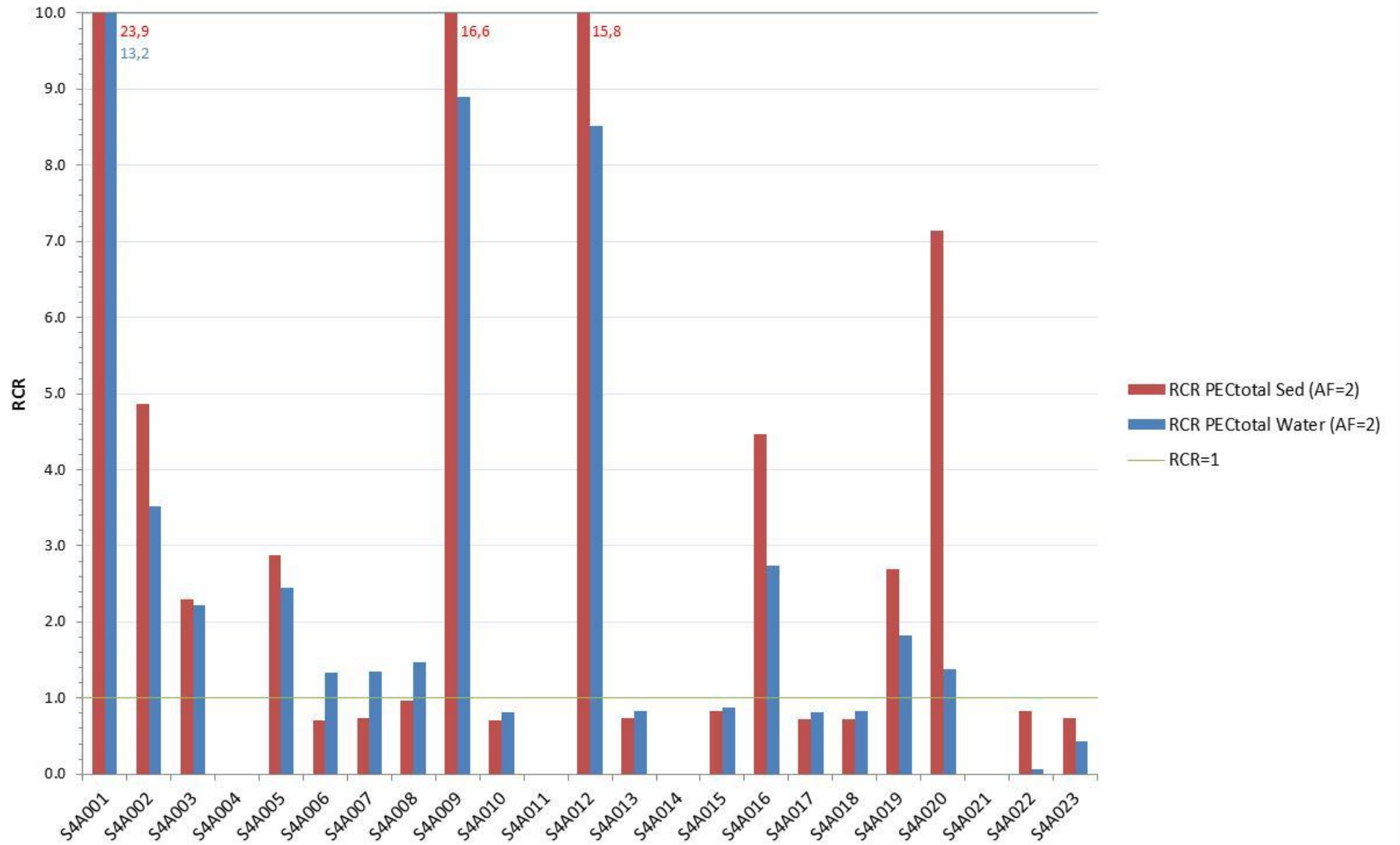
Ni metal producers (AF=2)



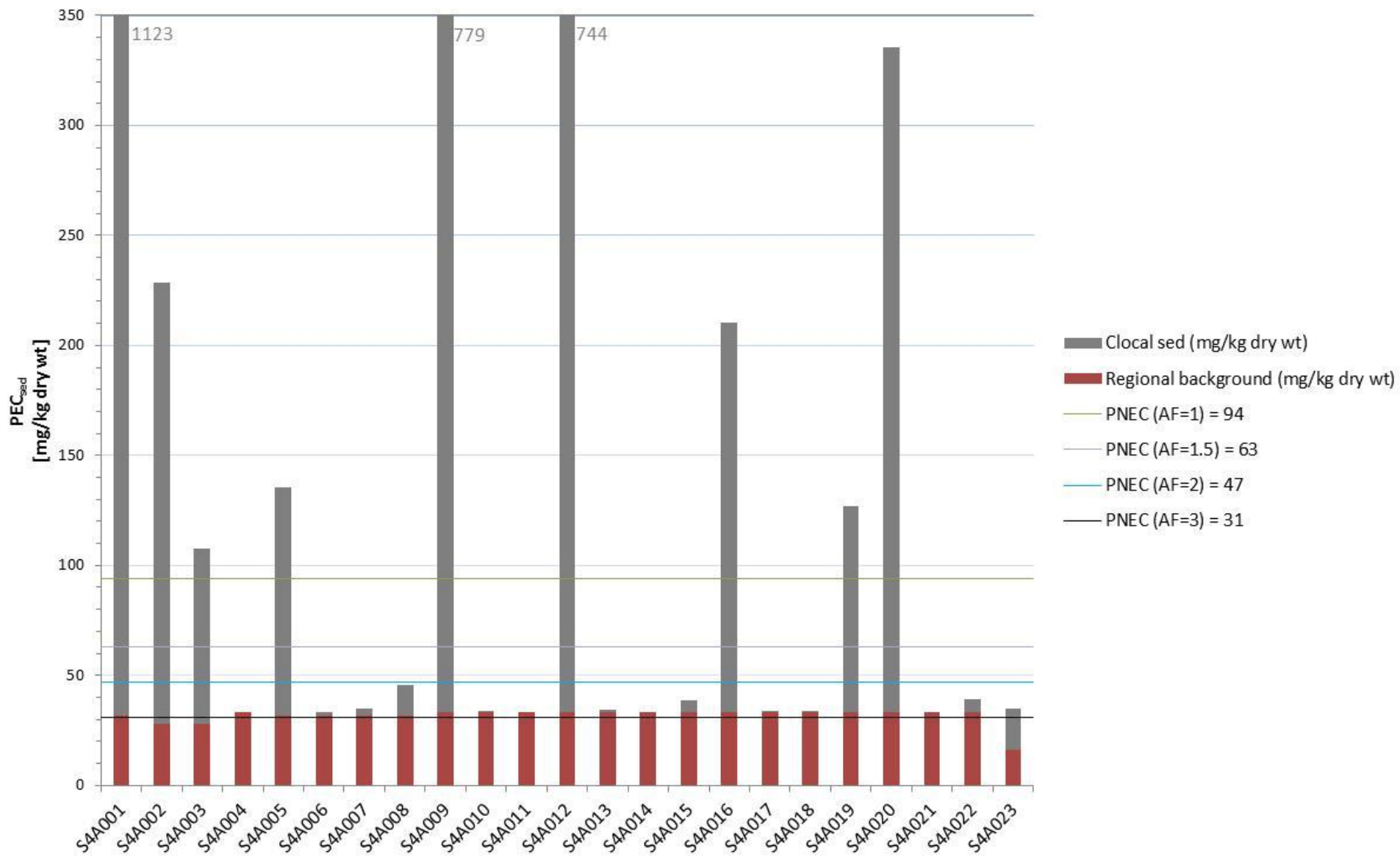
Ni metal producers (AF=3)



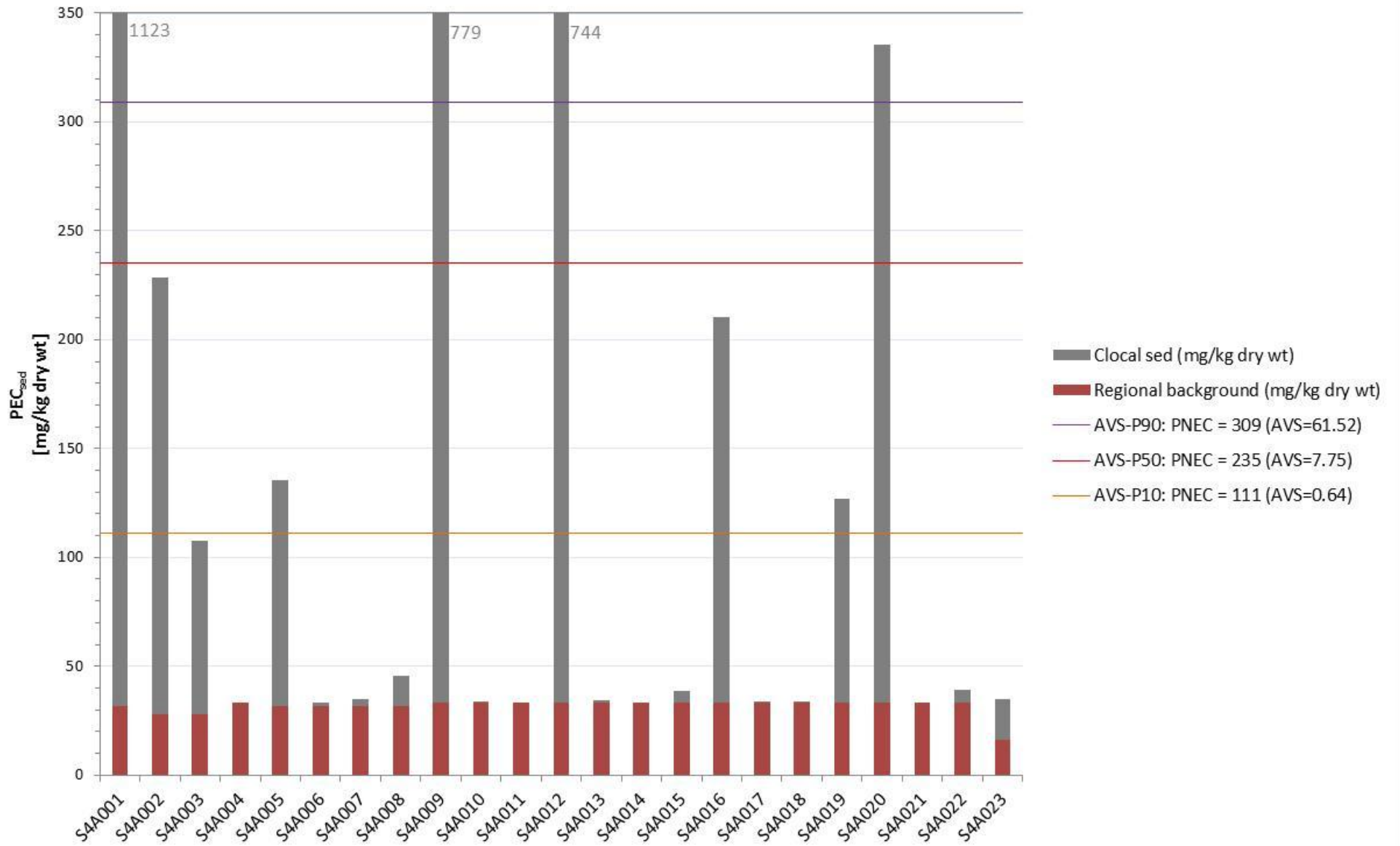
Stainless steel - RCR water vs. sediment



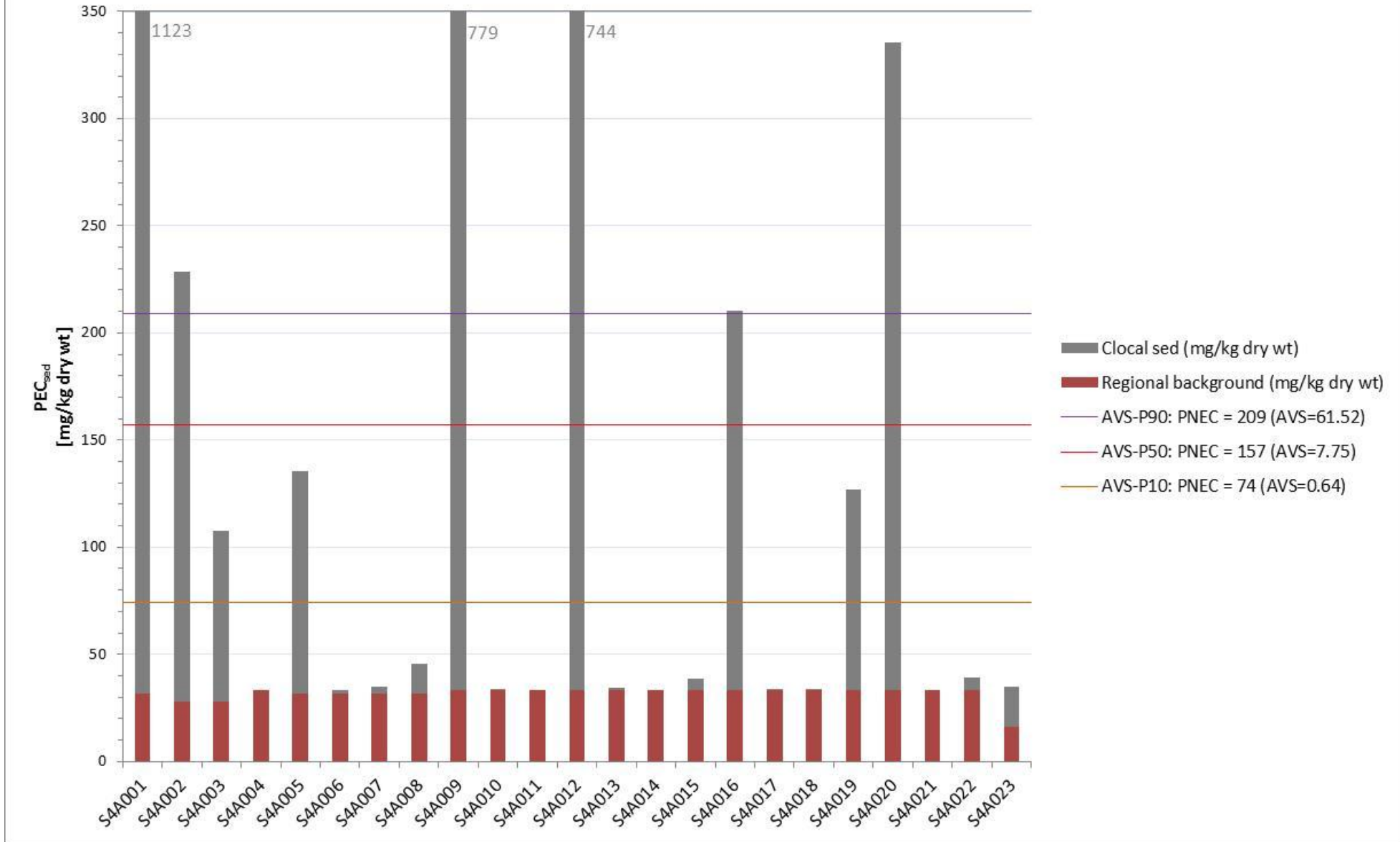
Stainless steel



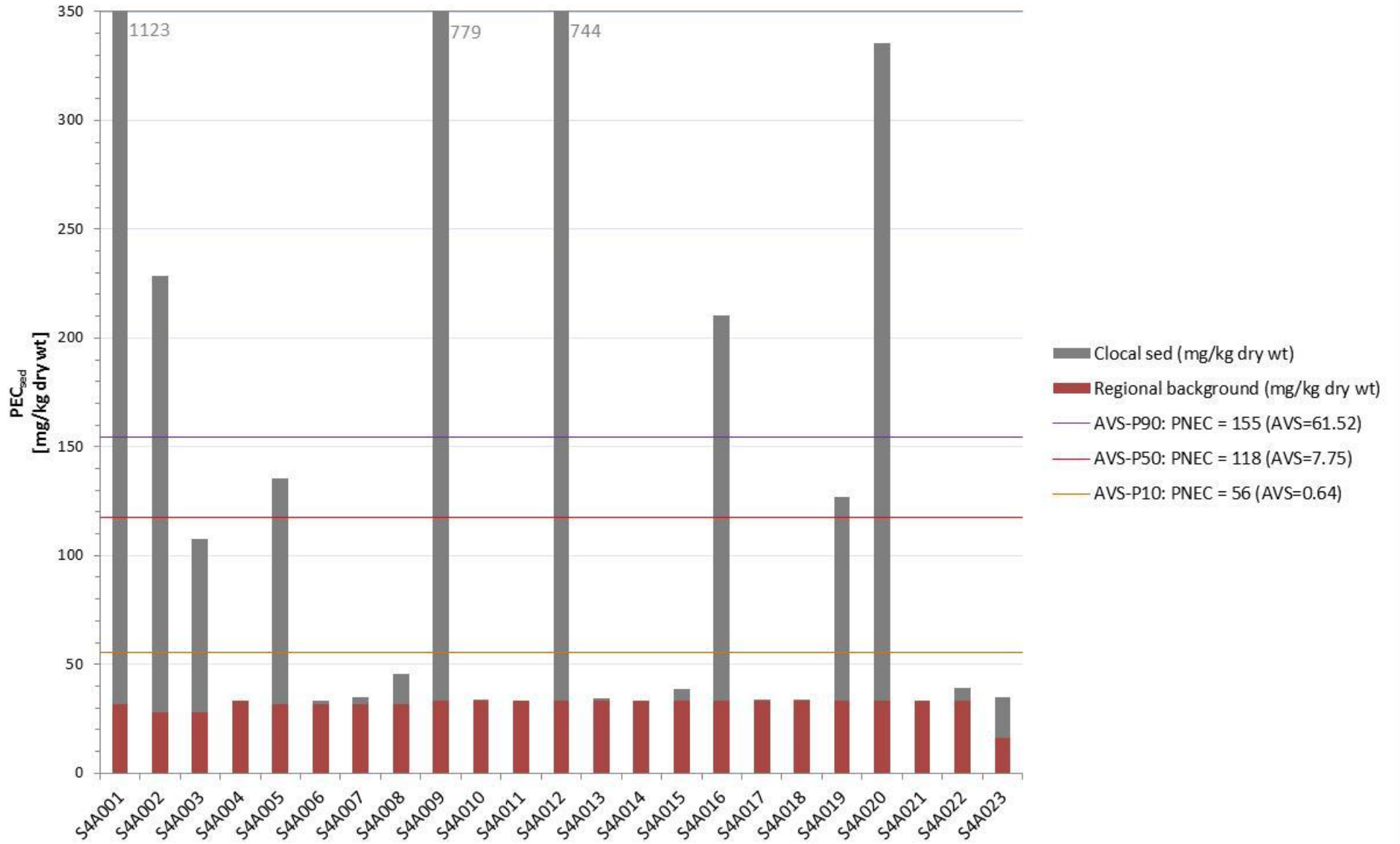
Stainless steel (AF=1)



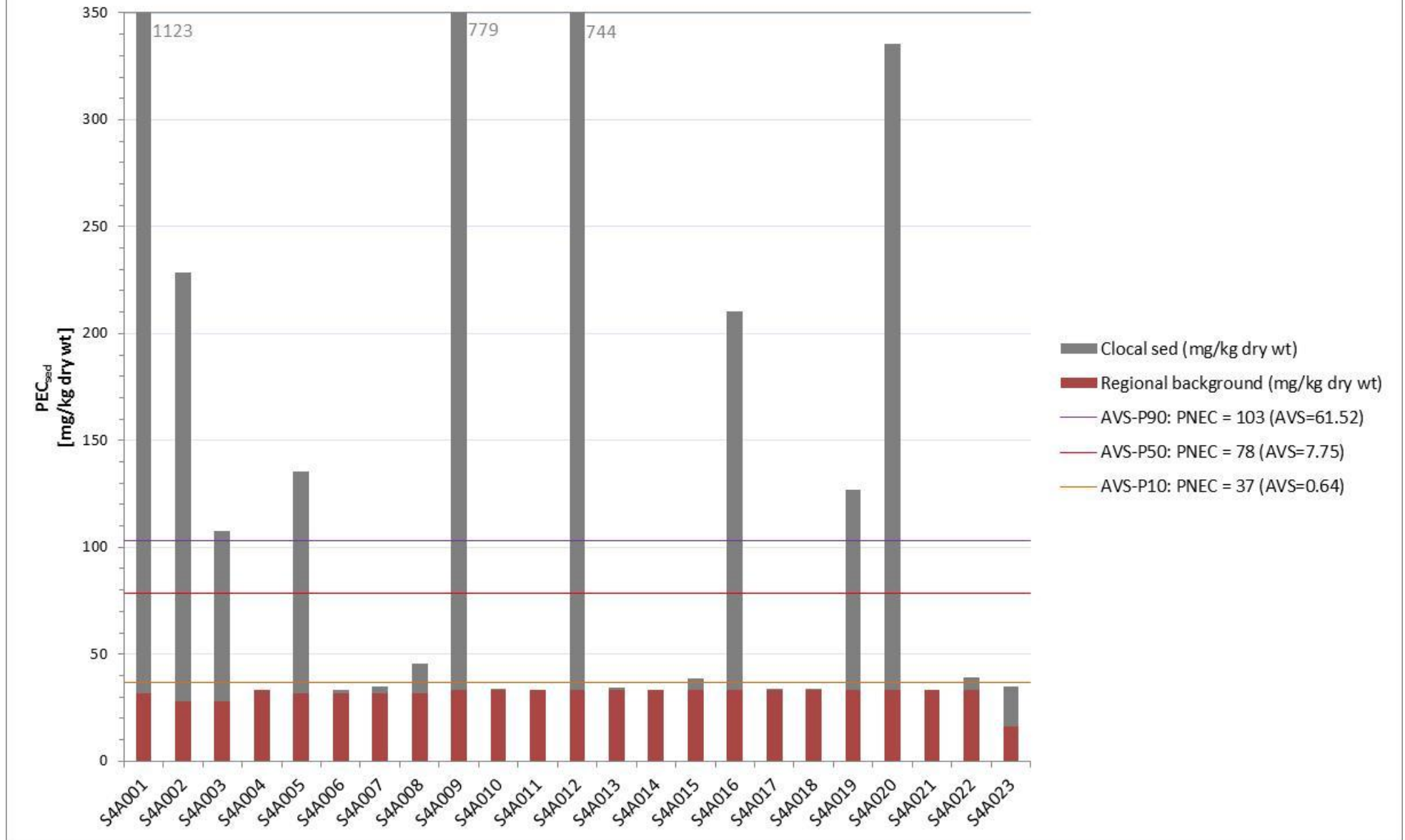
Stainless steel (AF=1.5)



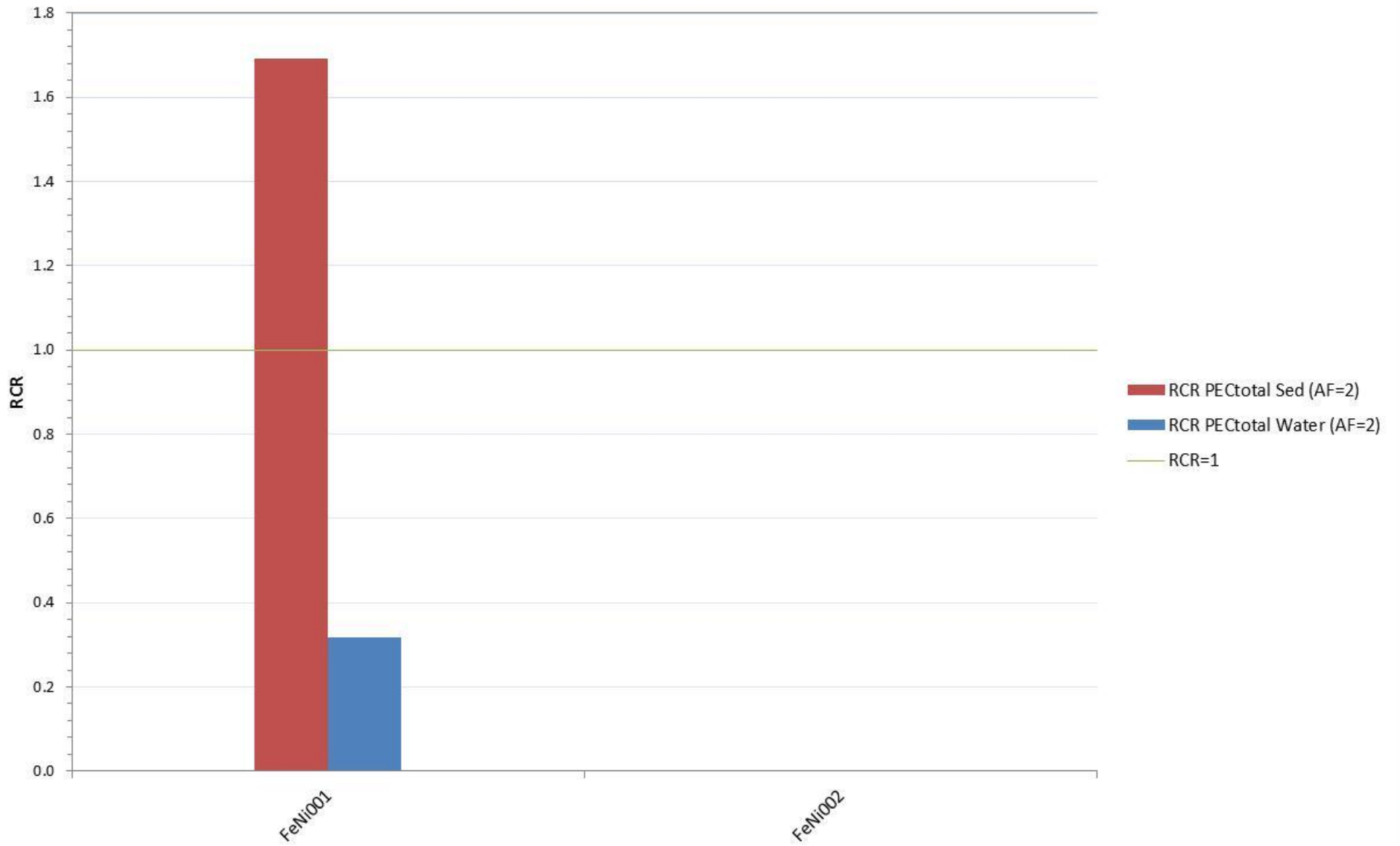
Stainless steel (AF=2)



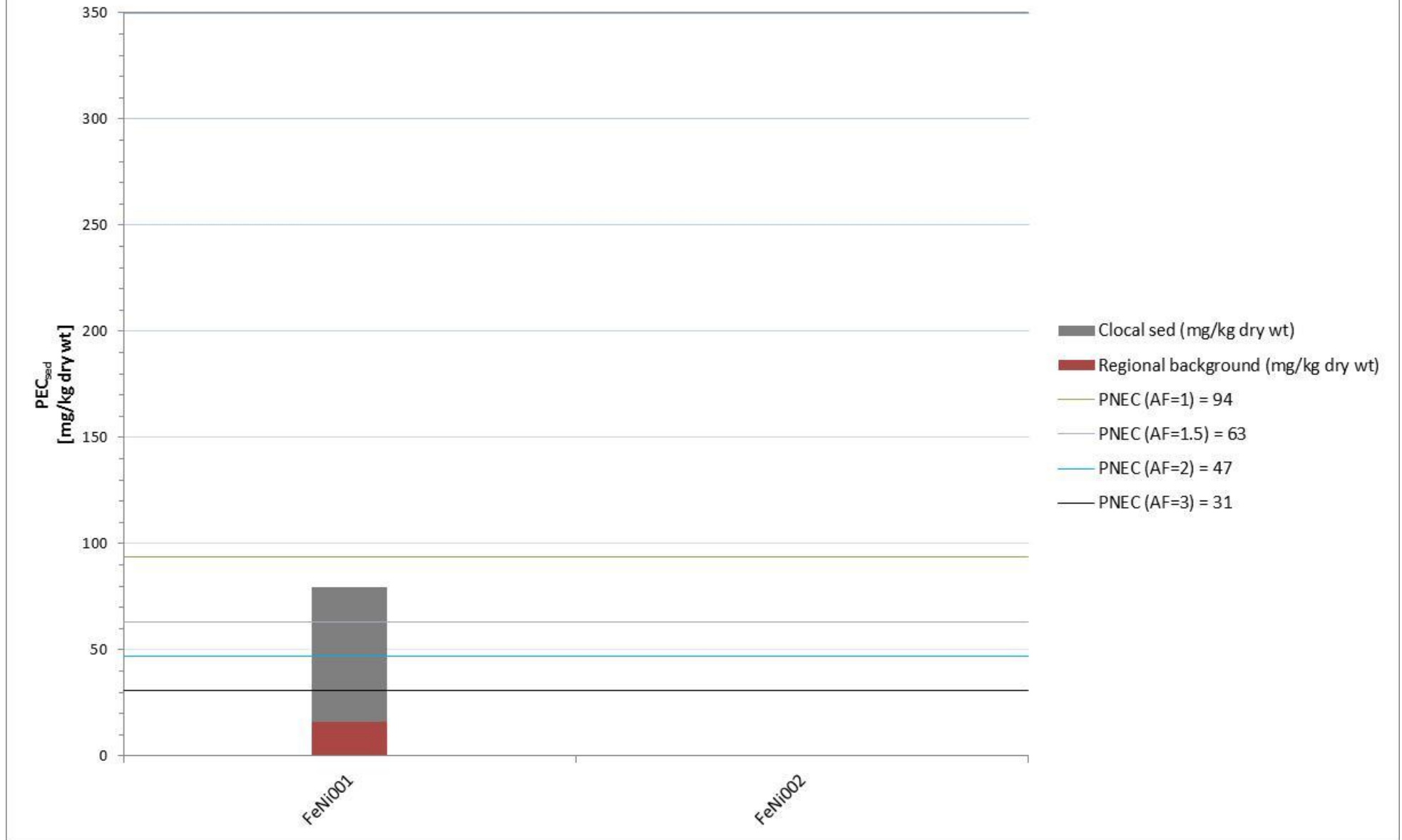
Stainless steel (AF=3)



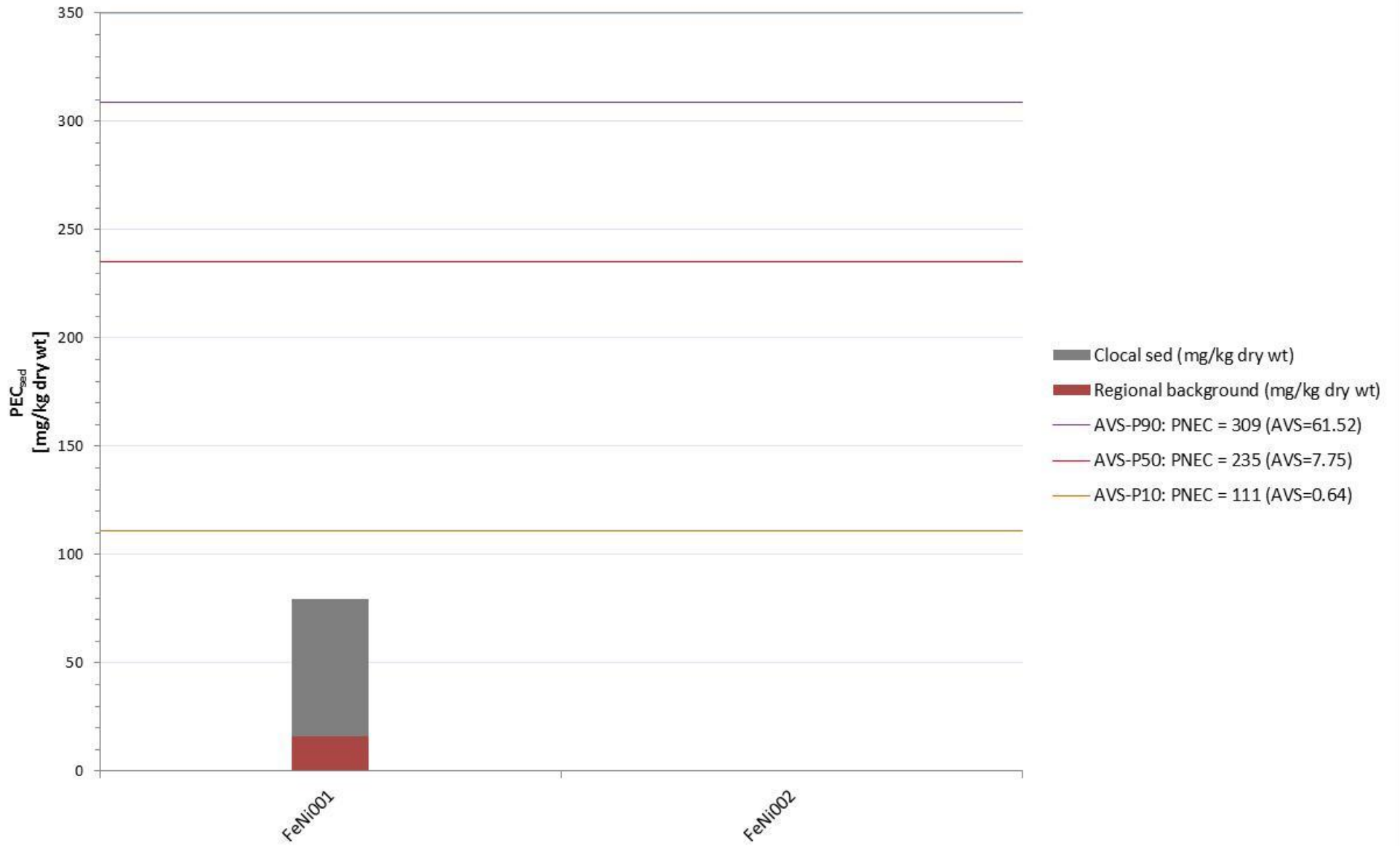
FeNi - RCR water vs. sediment



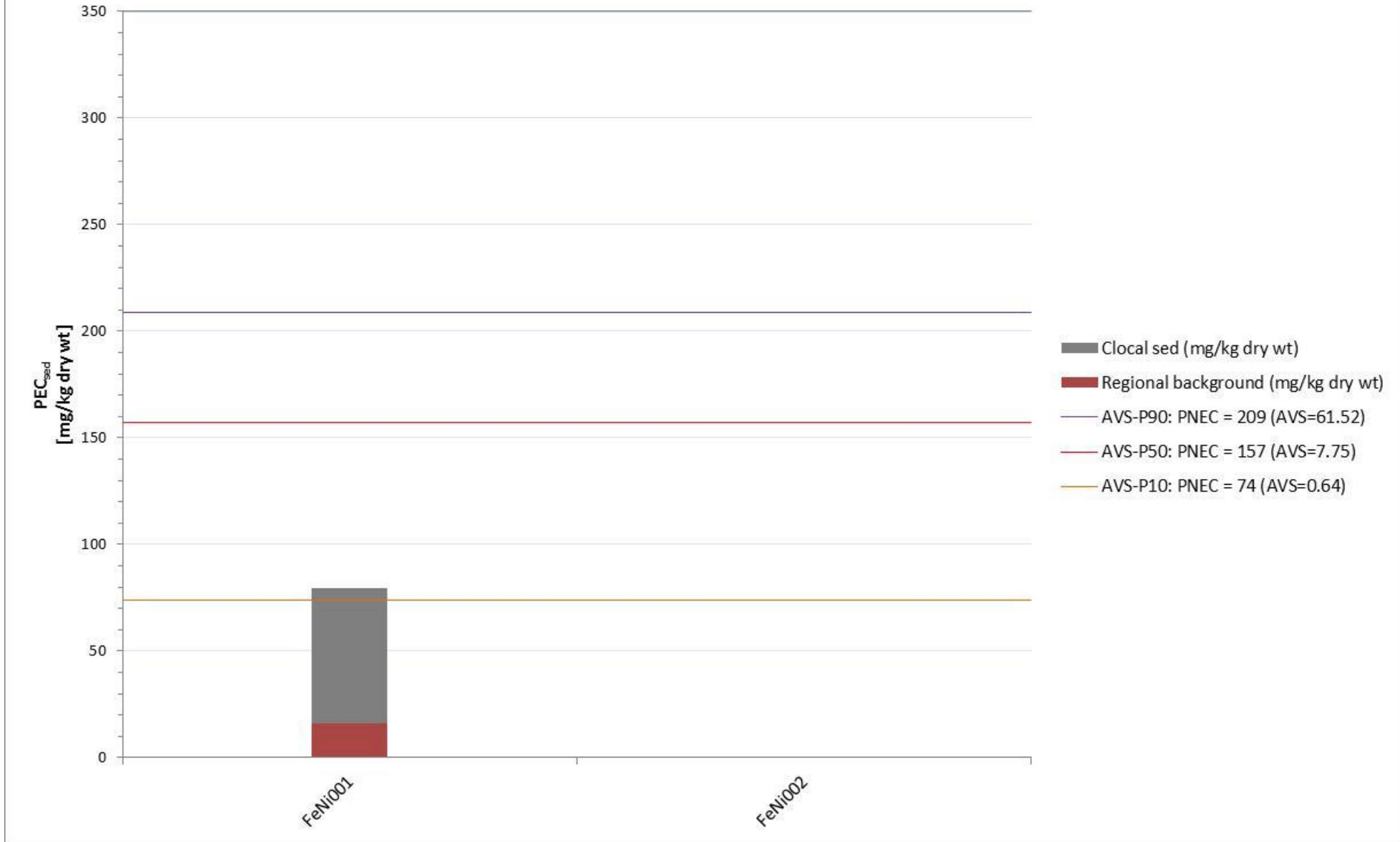
FeNi



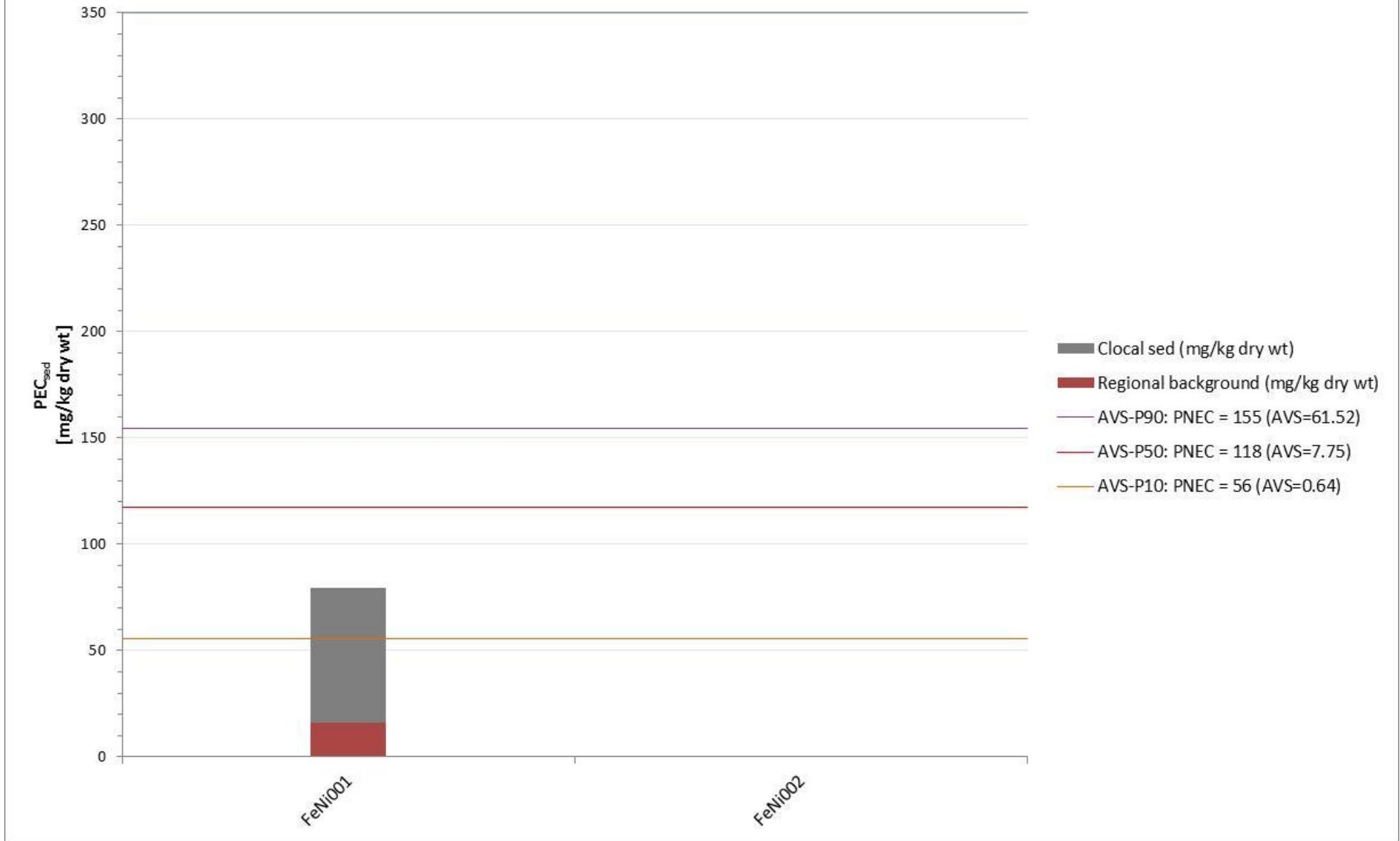
FeNi (AF=1)



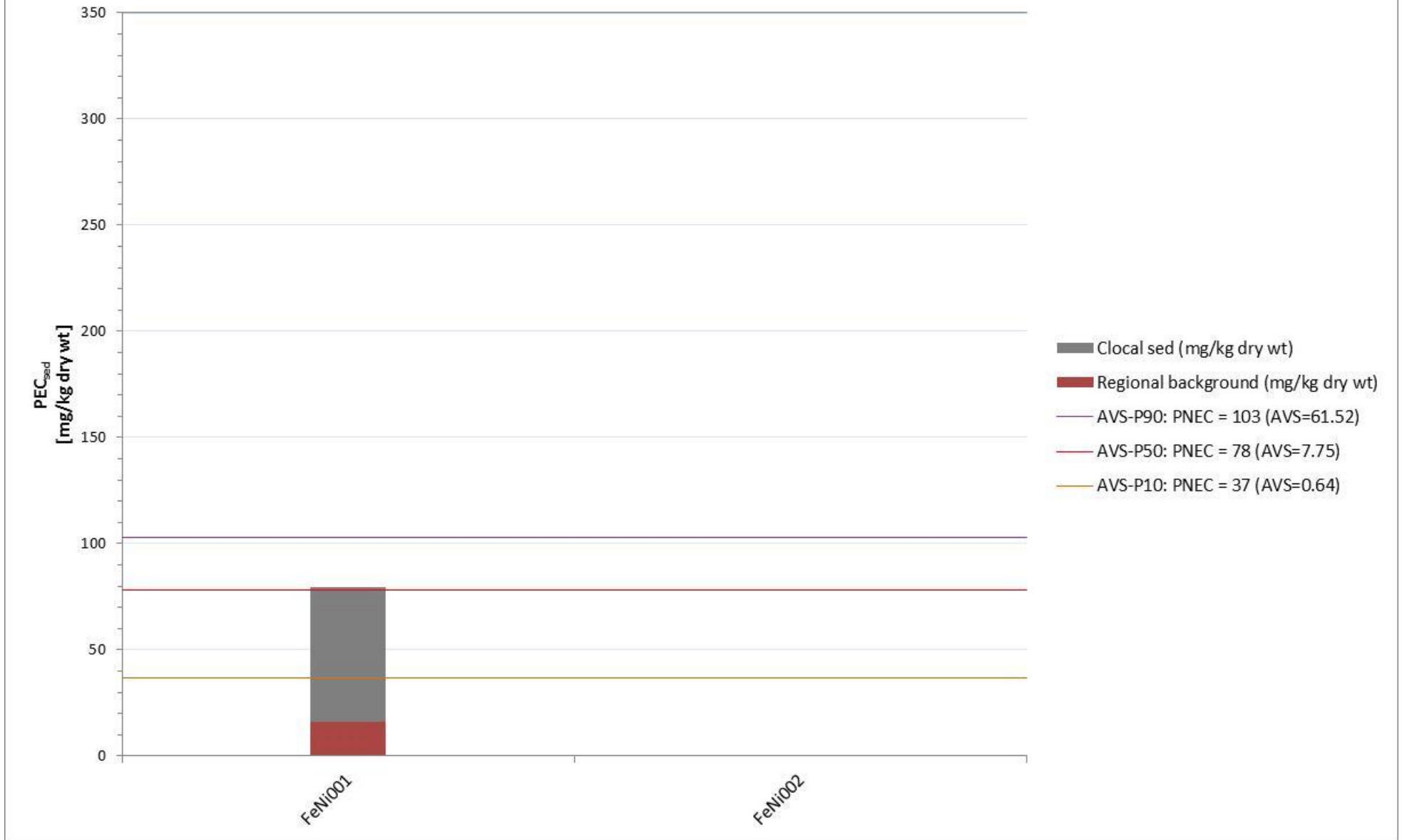
FeNi (AF=1.5)



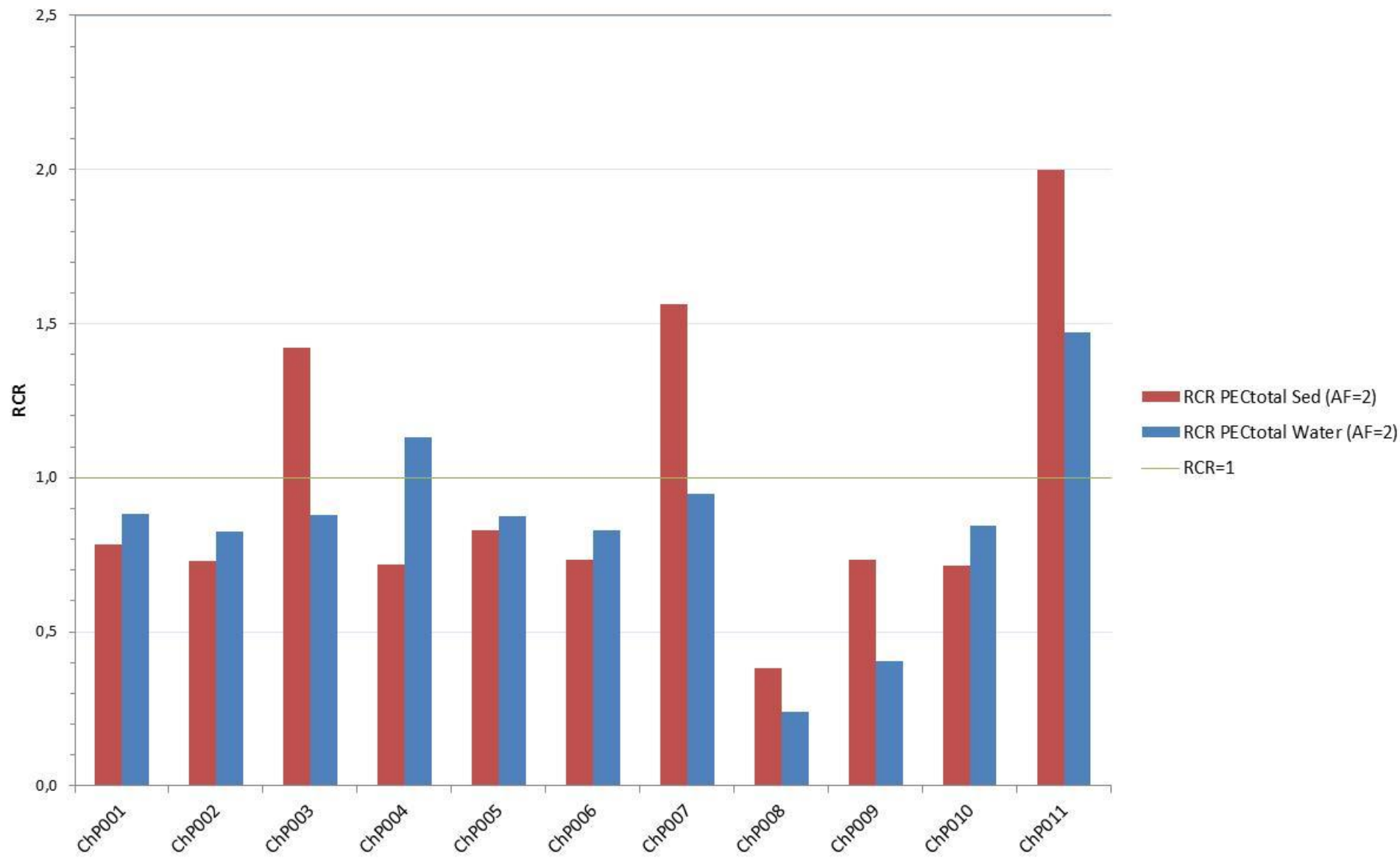
FeNi (AF=2)



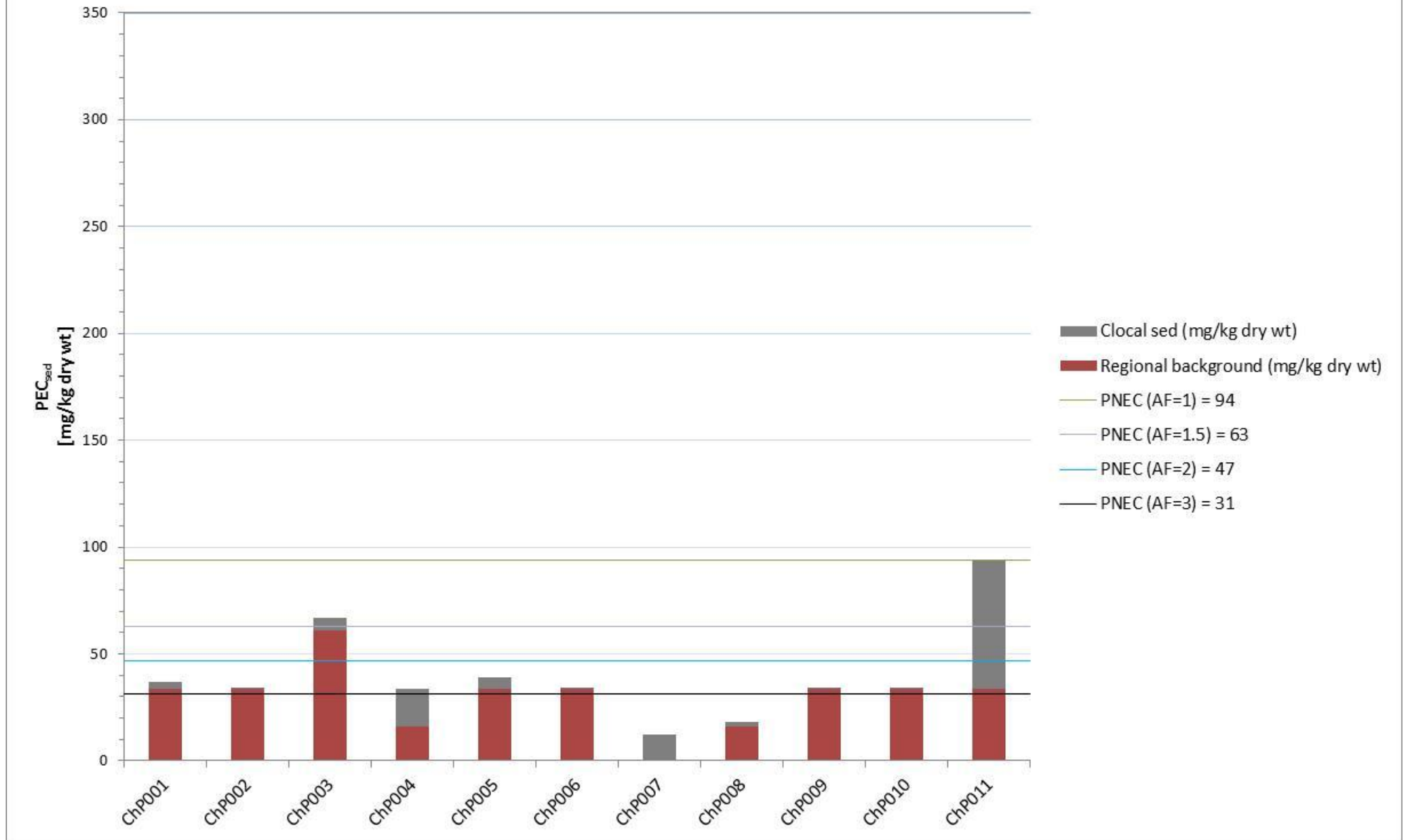
FeNi (AF=3)



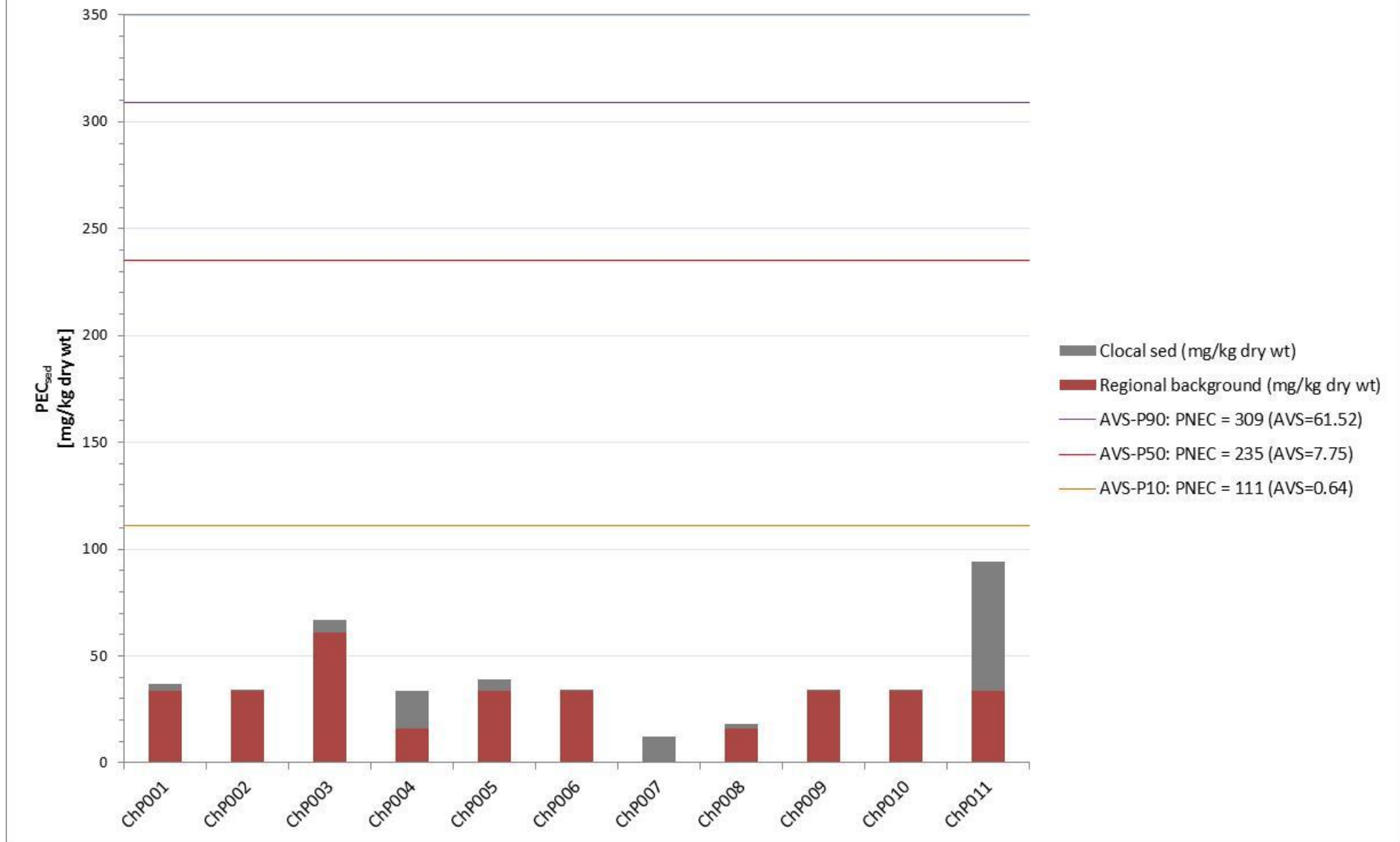
Chemical production - RCR water vs. sediment



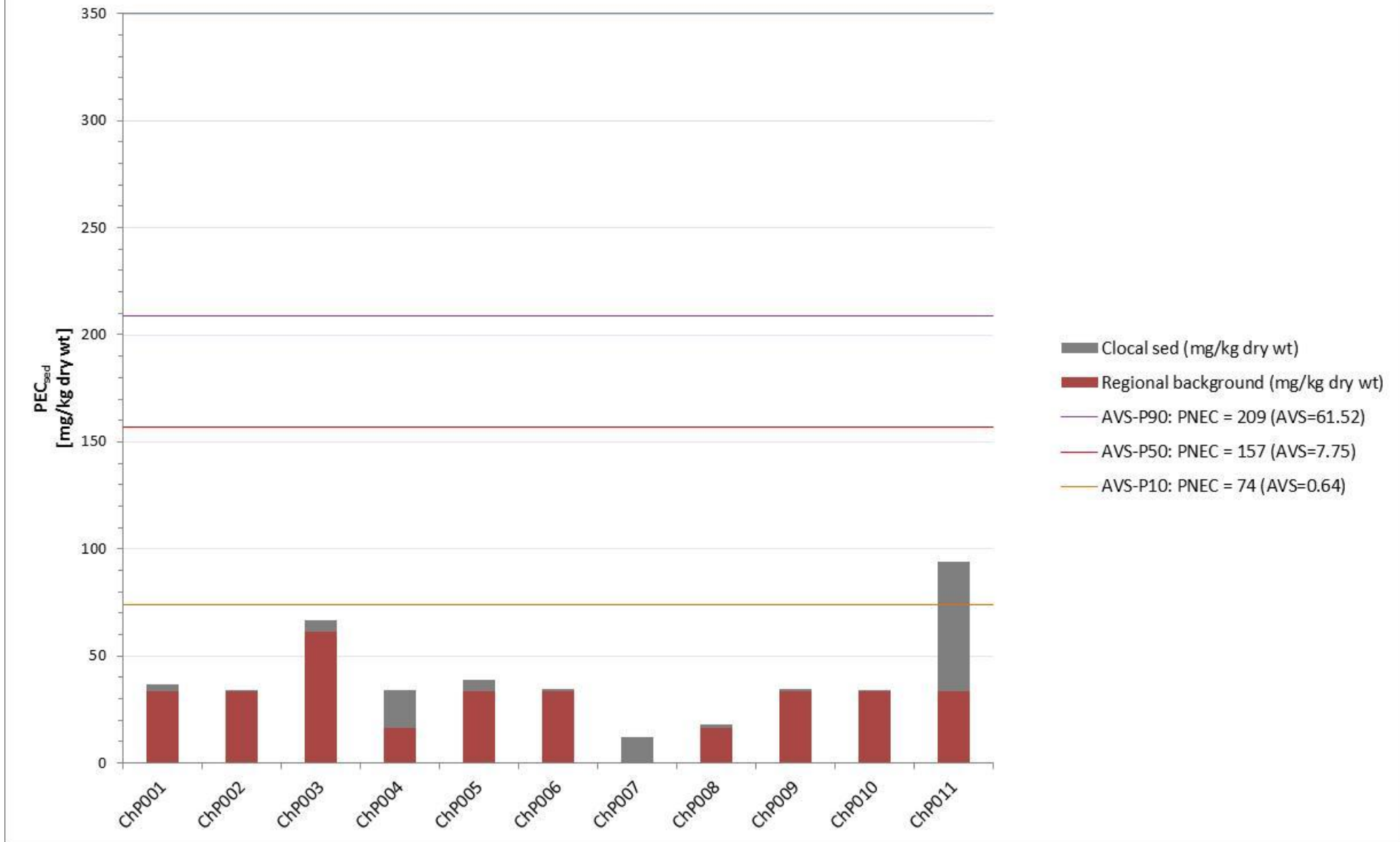
Chemical production



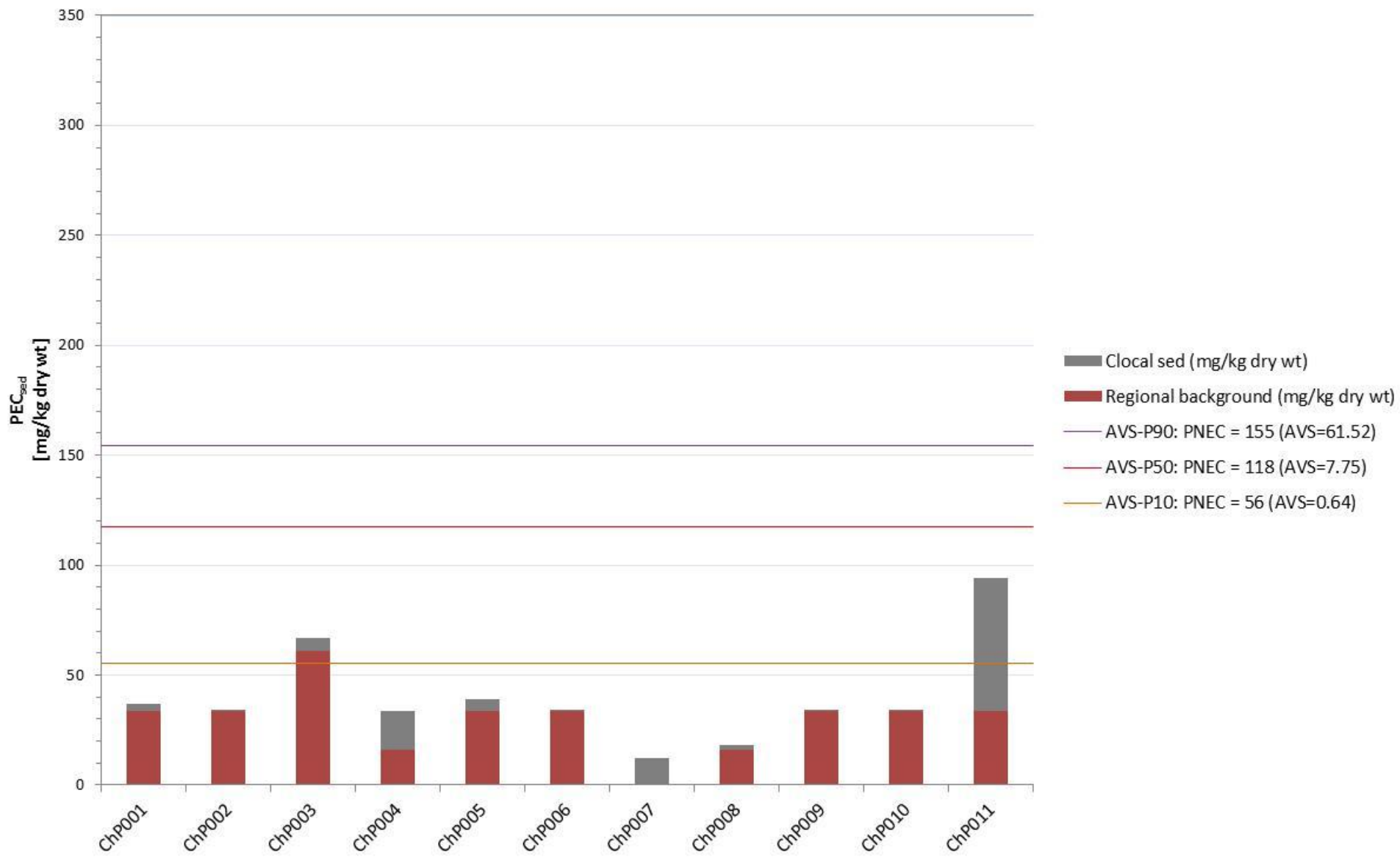
Chemical production (AF=1)



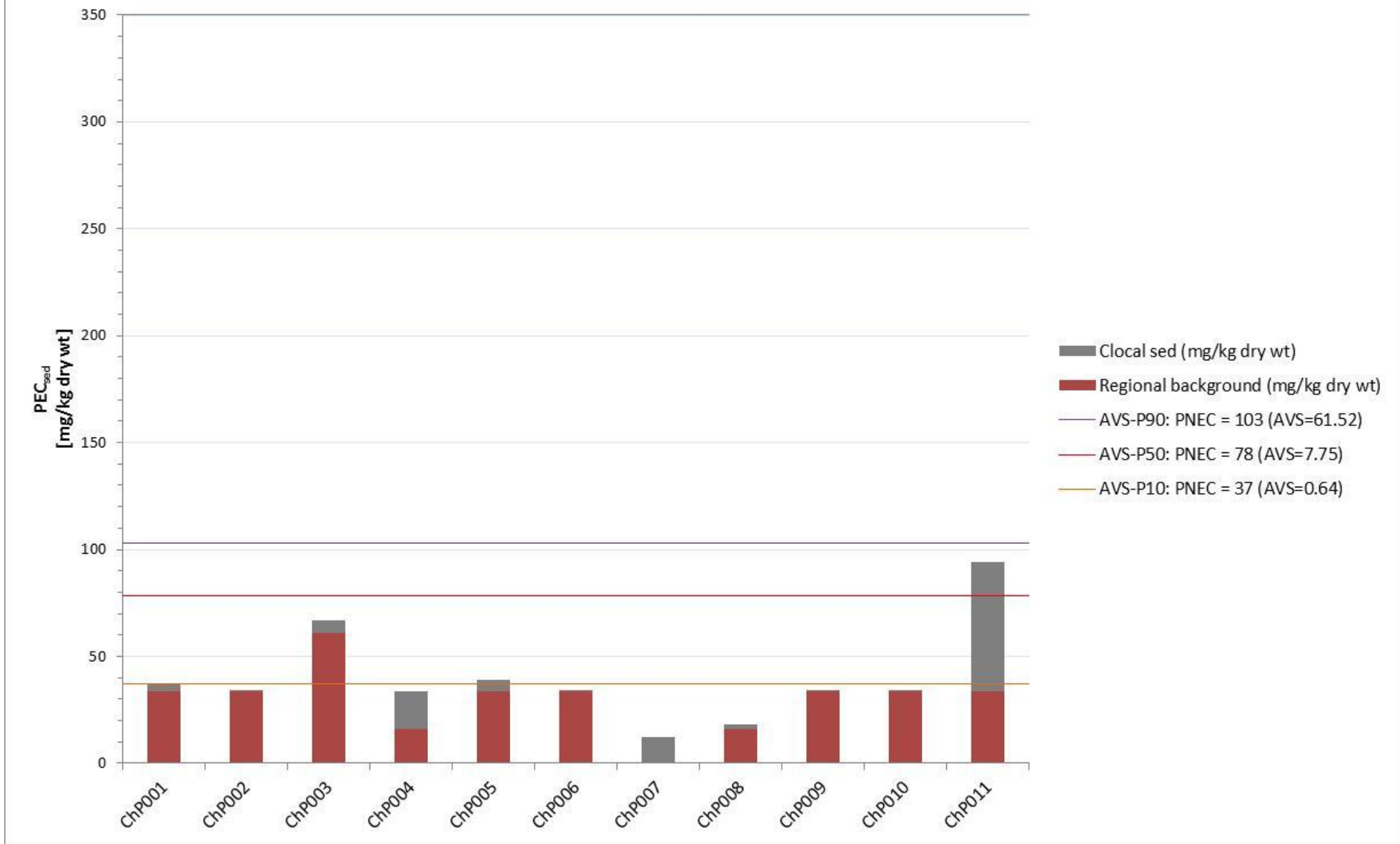
Chemical production (AF=1.5)



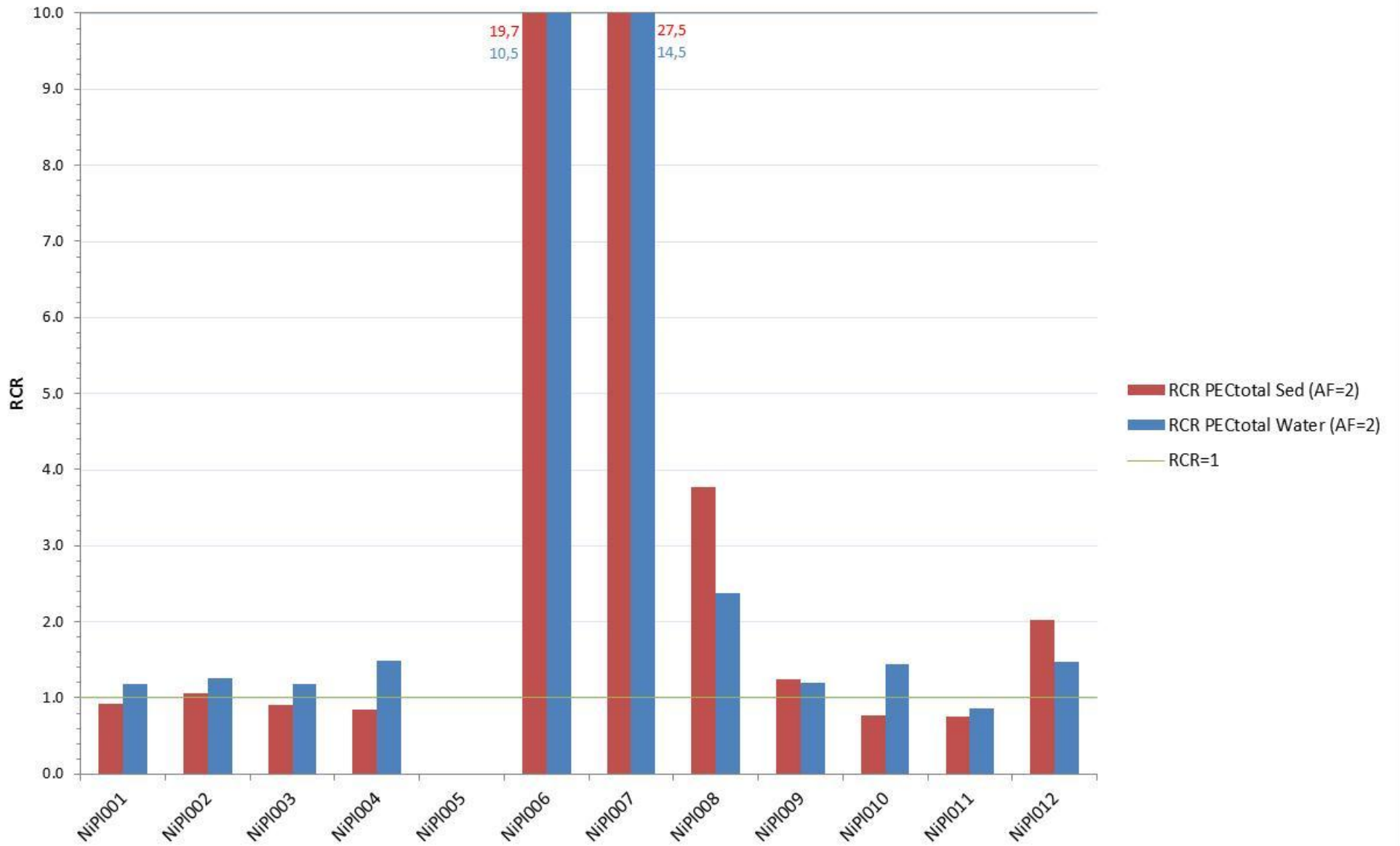
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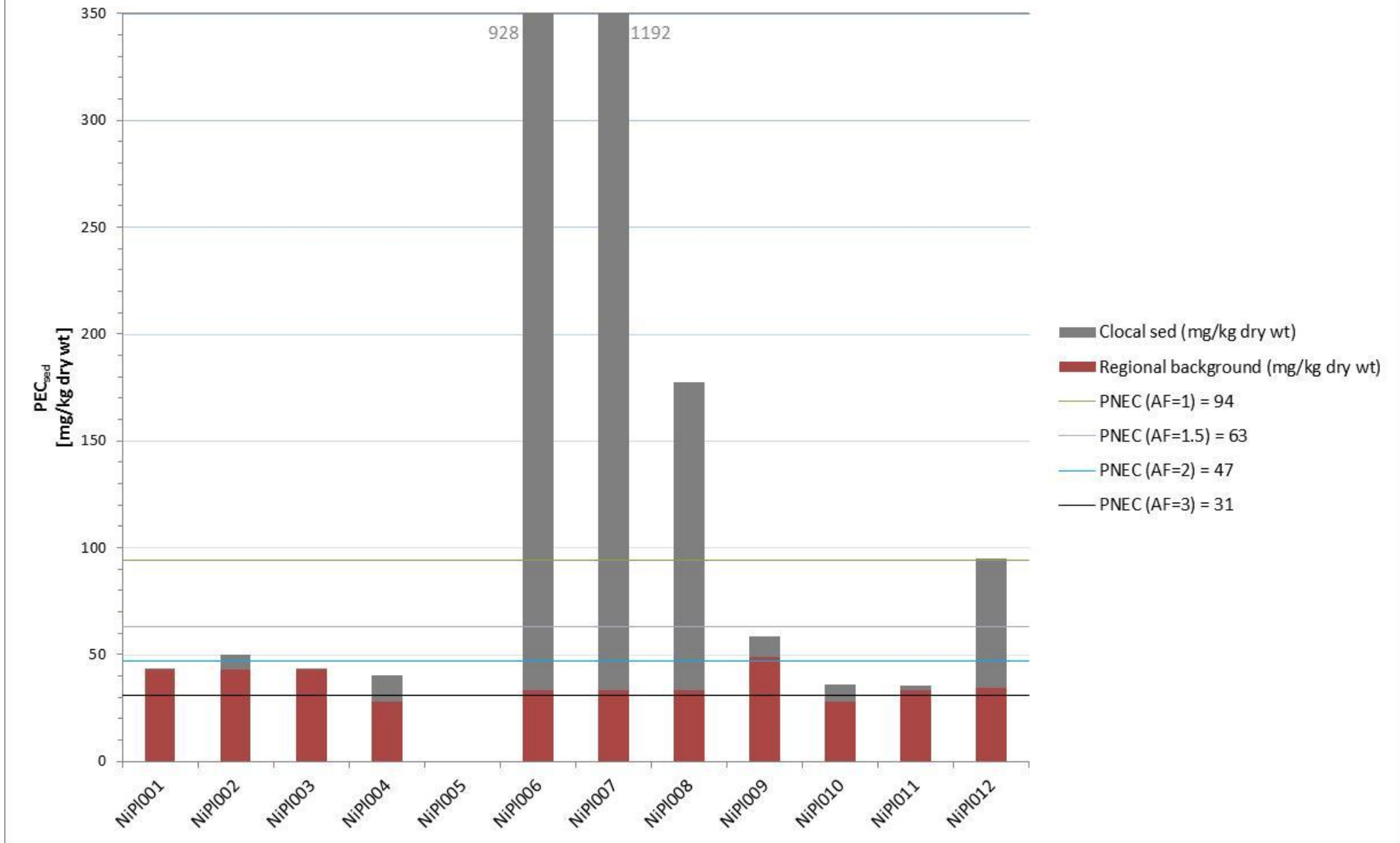
Chemical production (AF=3)



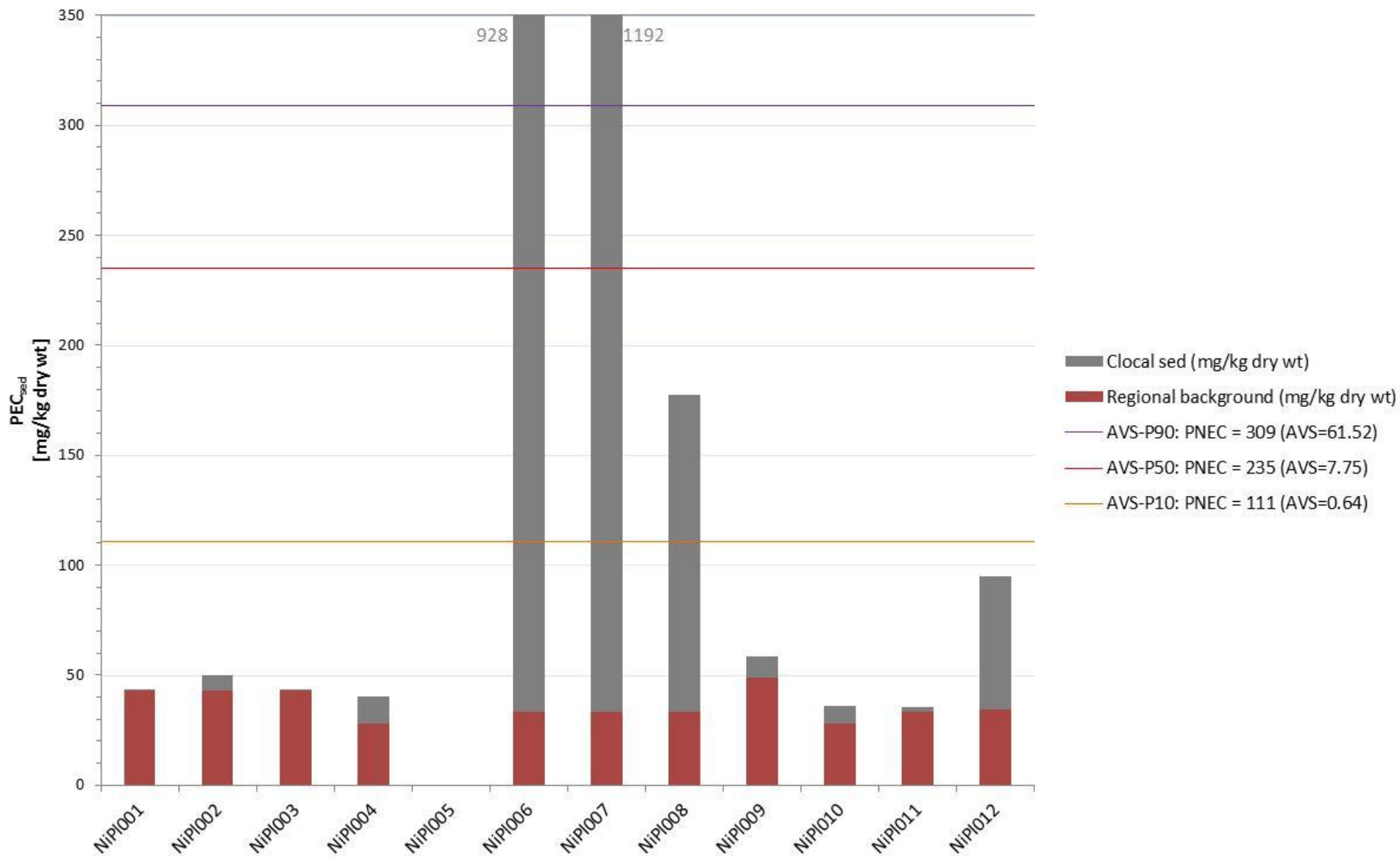
Ni plating - RCR water vs. sediment



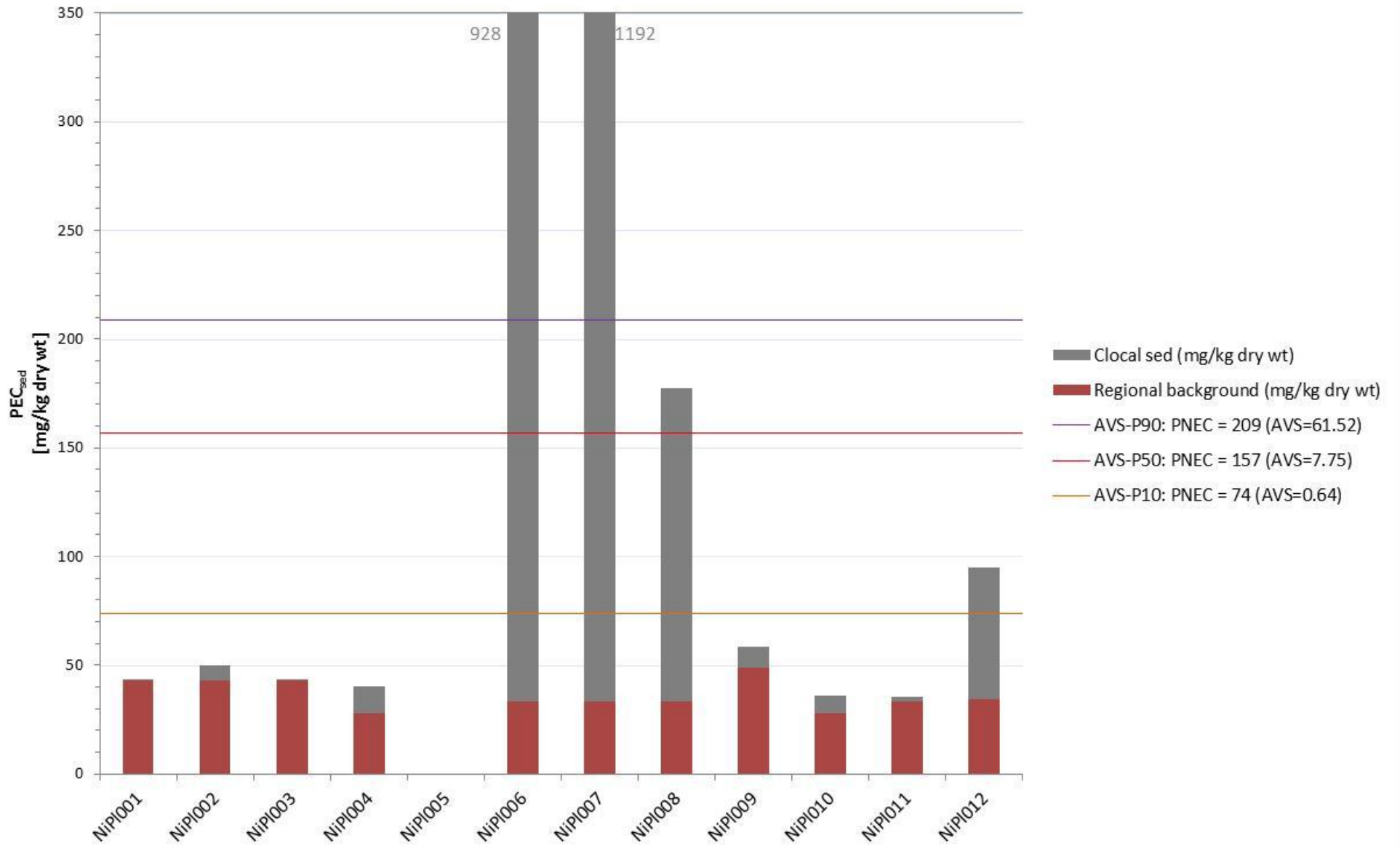
Ni plating



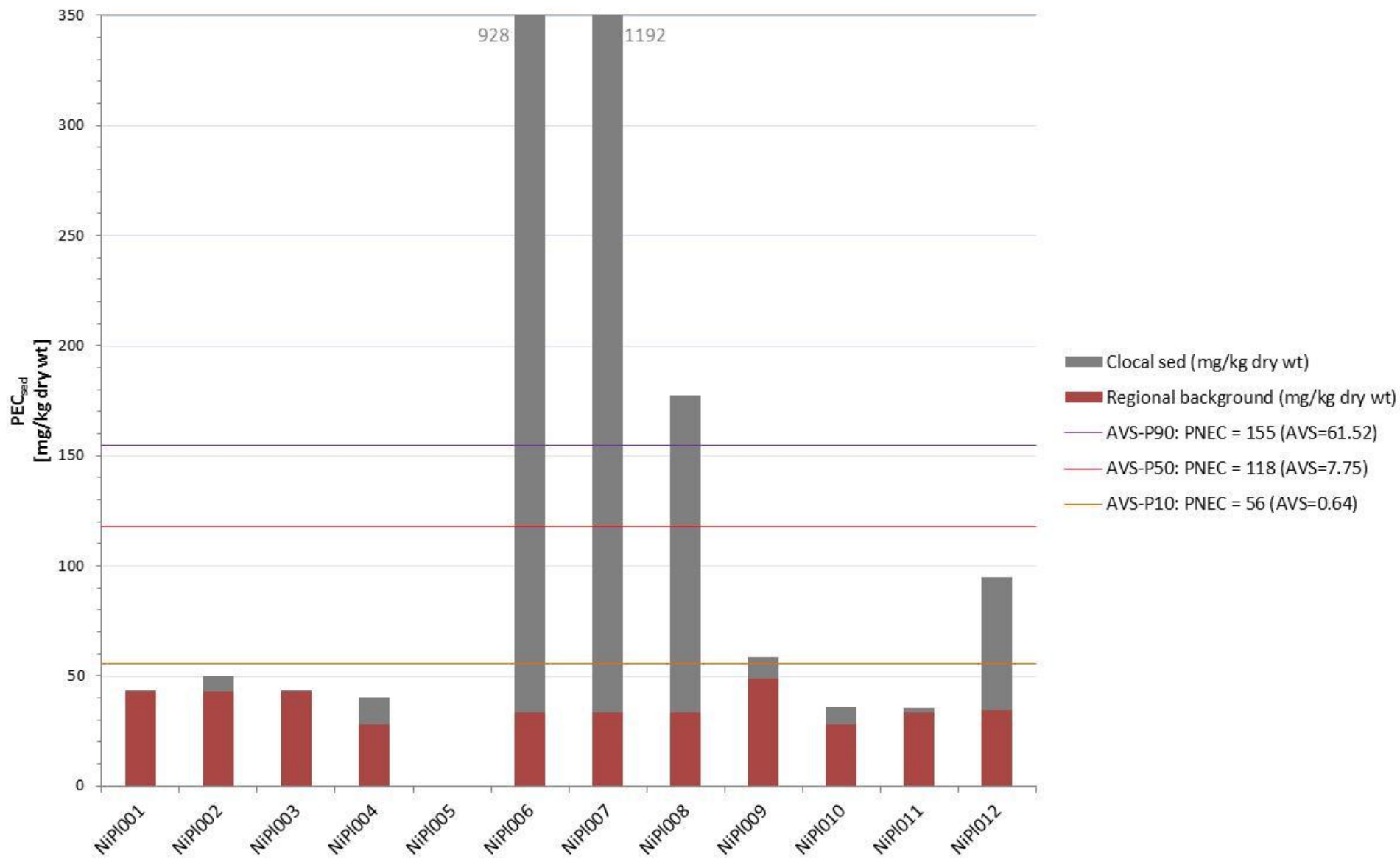
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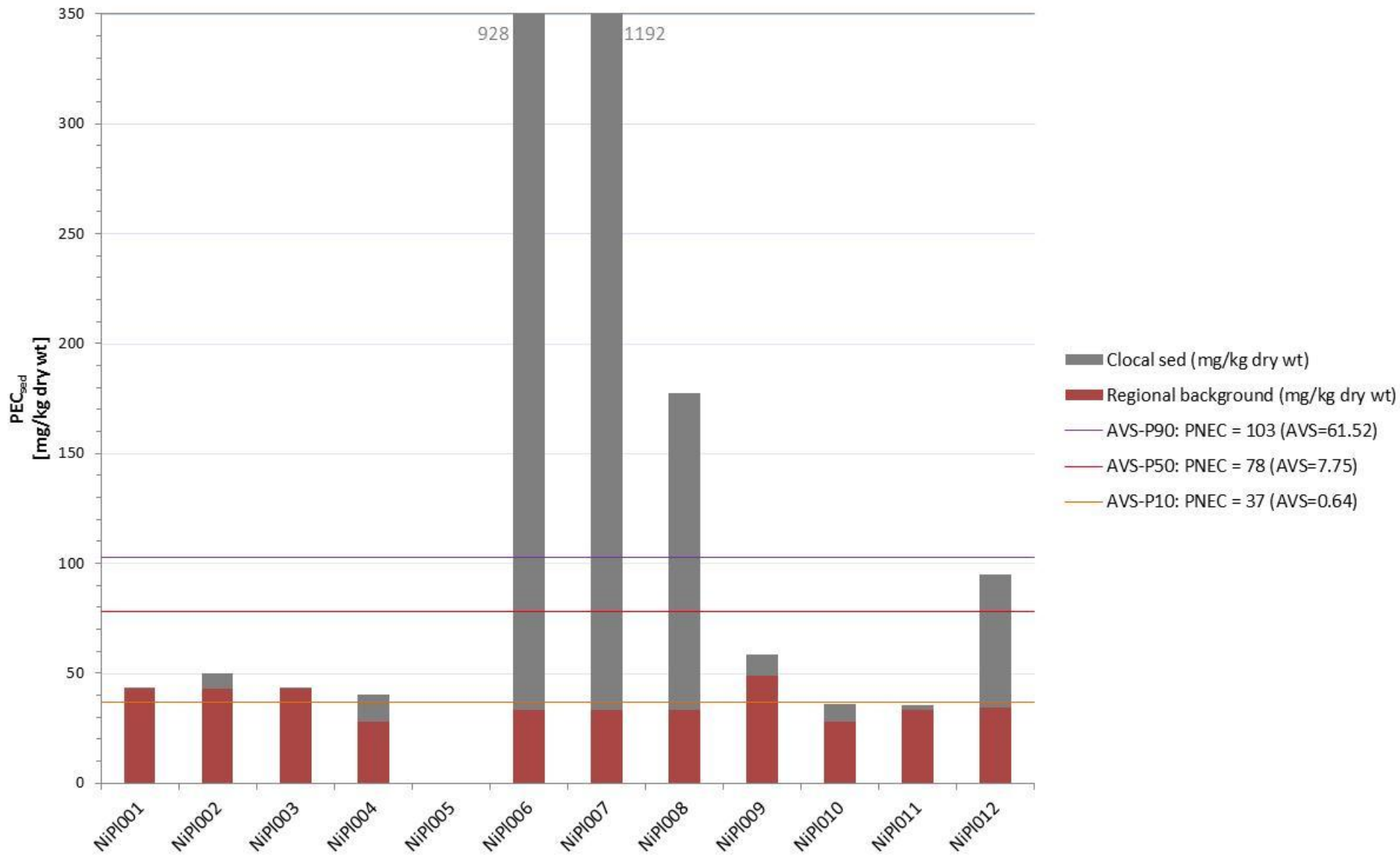
Ni plating (AF=1.5)



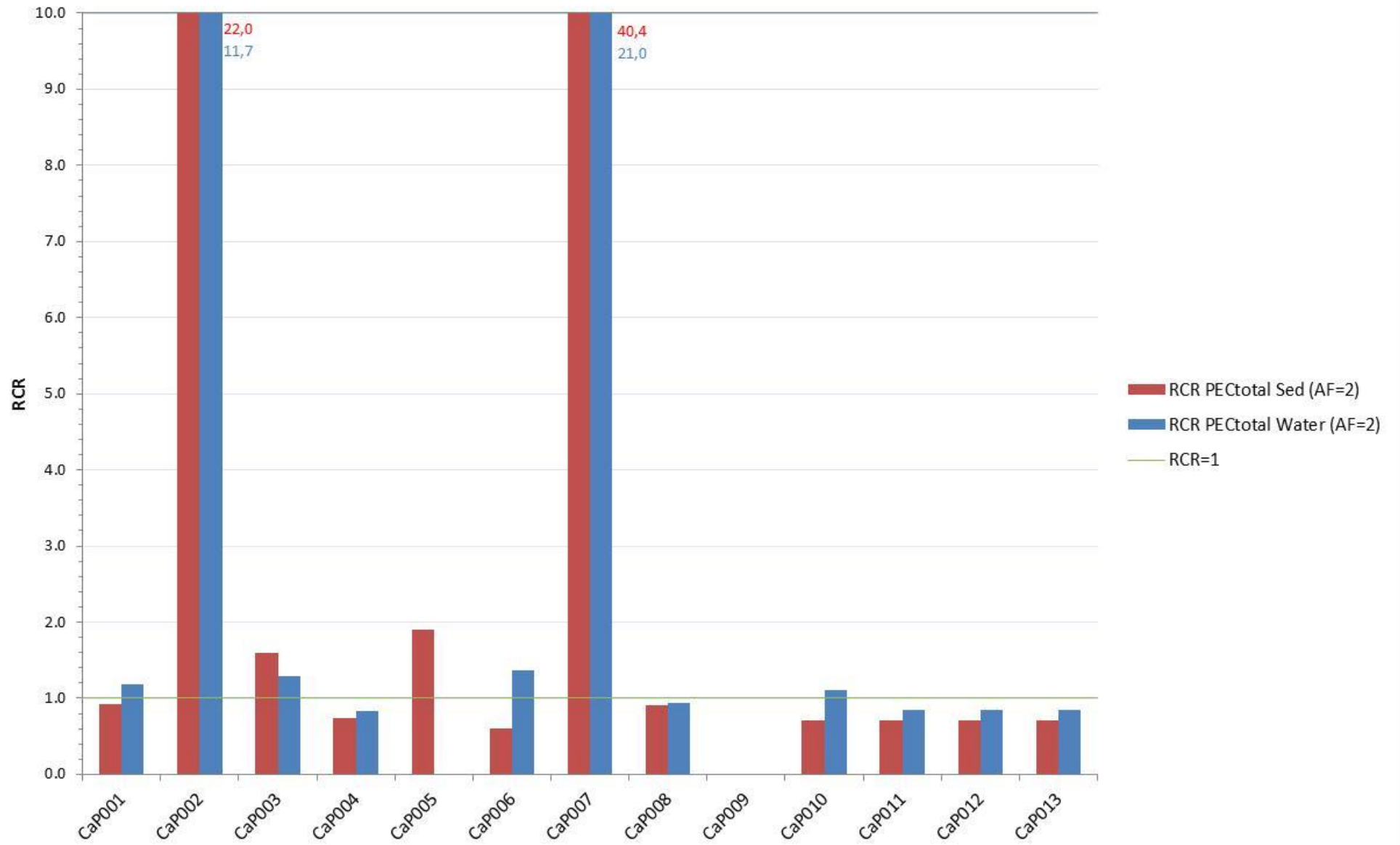
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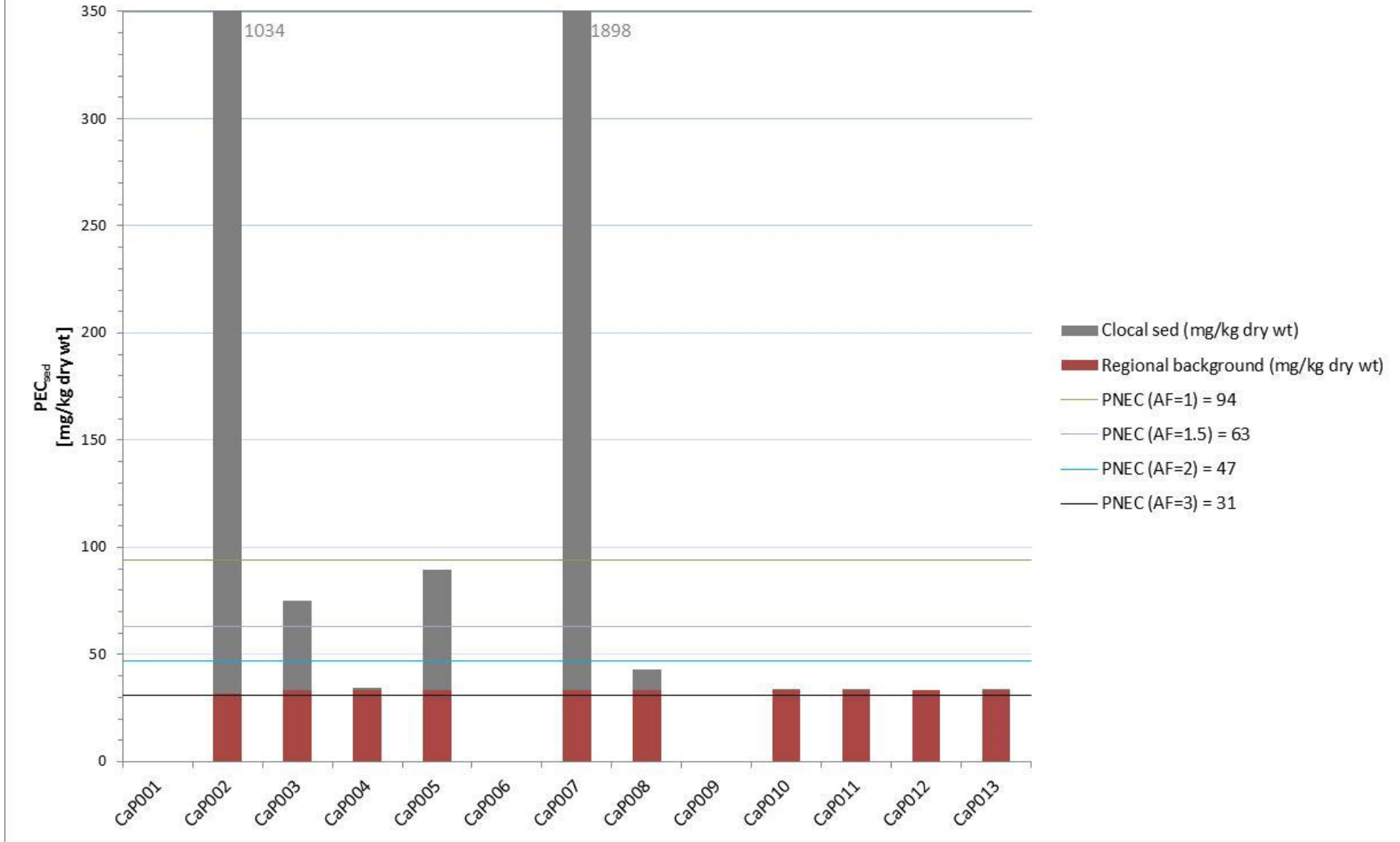
Ni plating (AF=3)



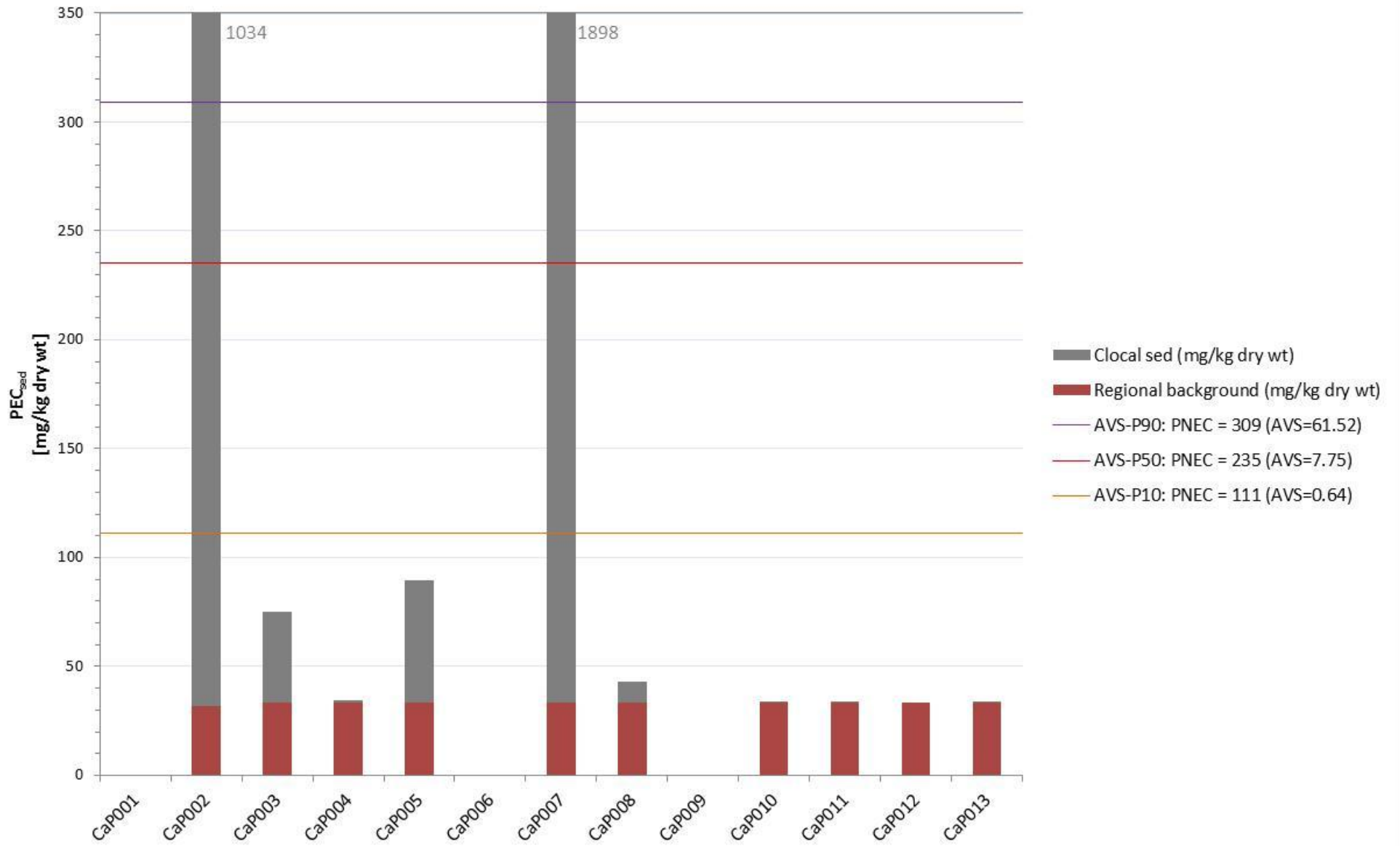
Catalyst producer - RCR water vs. sediment



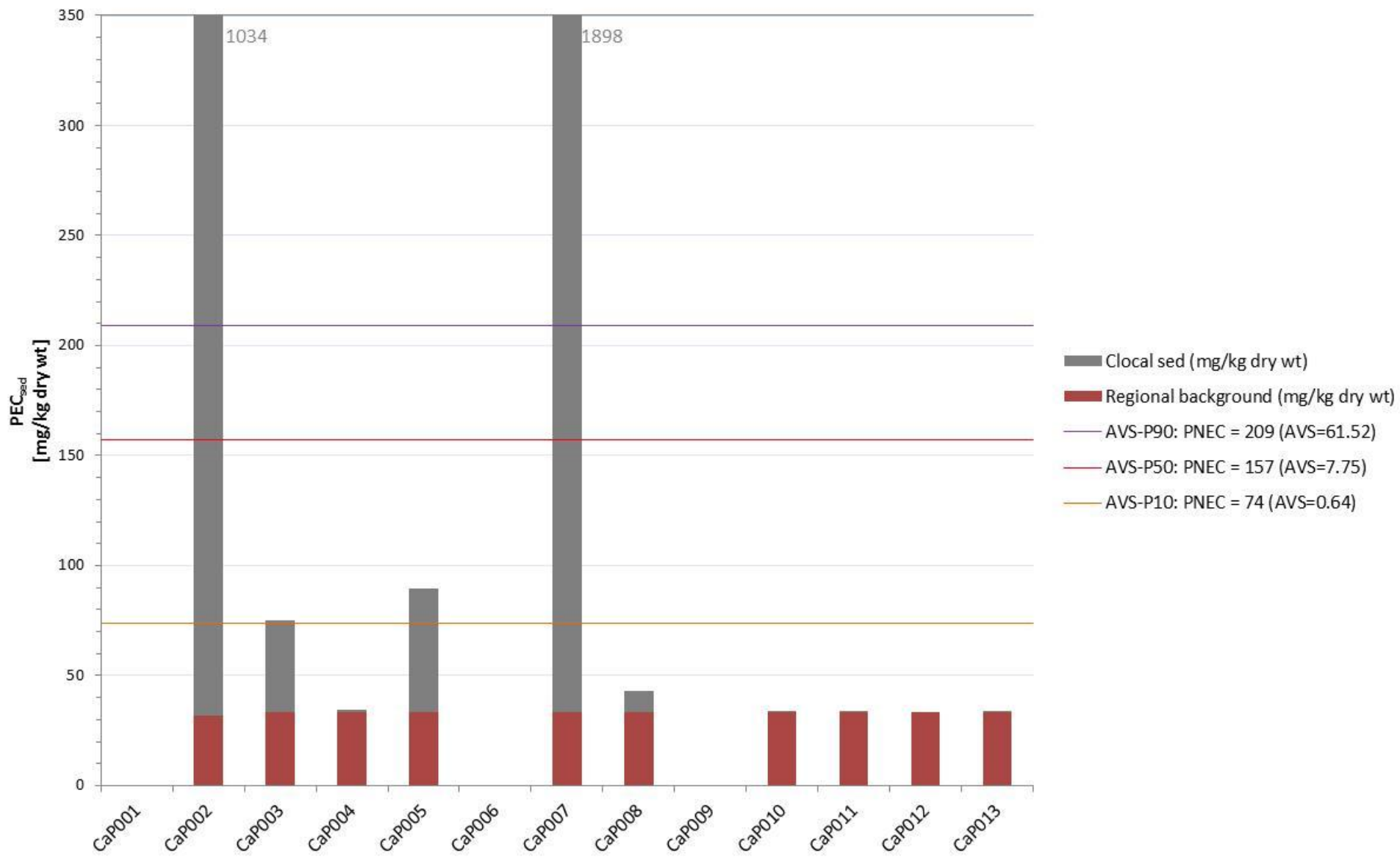
Catalyst producer



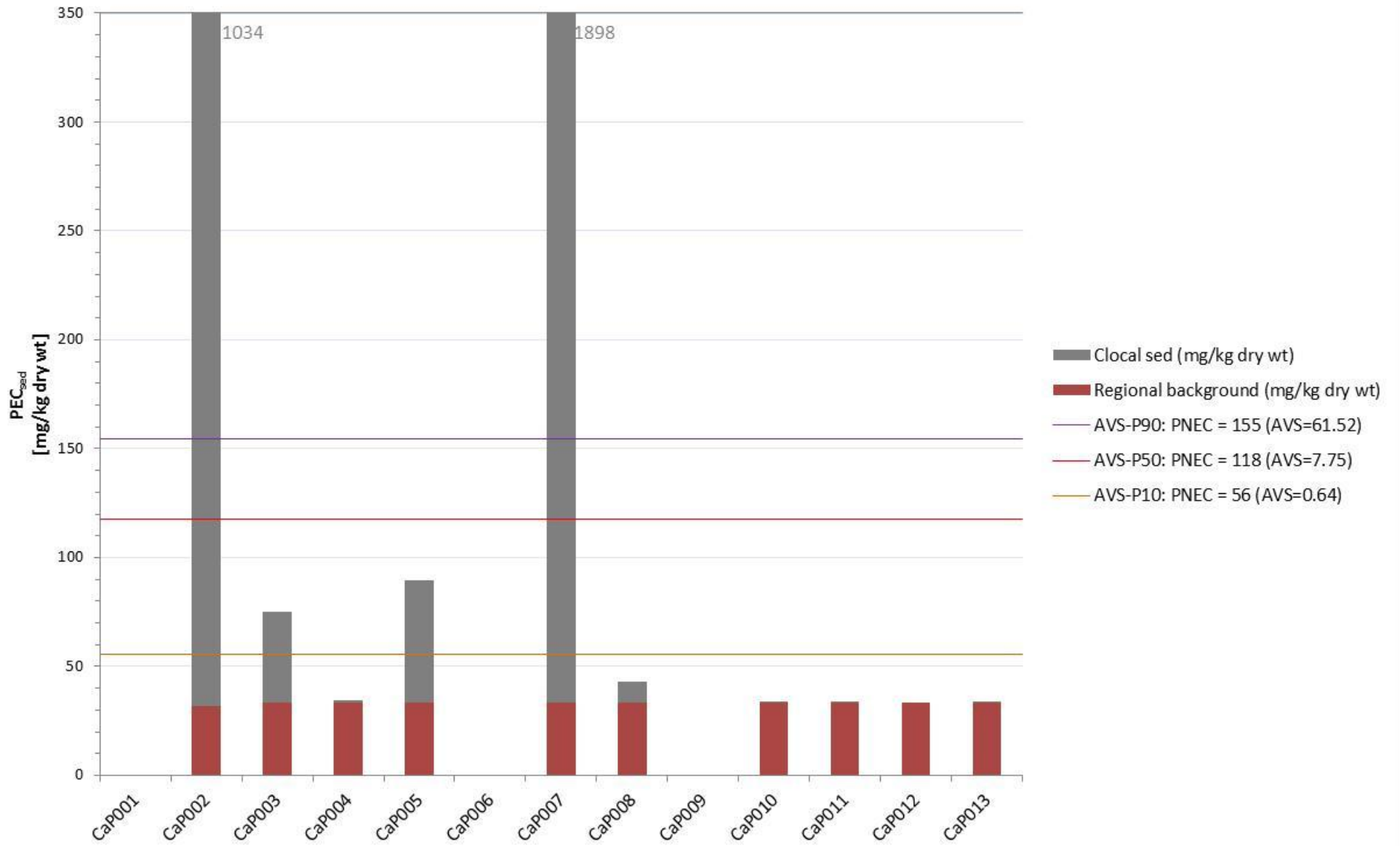
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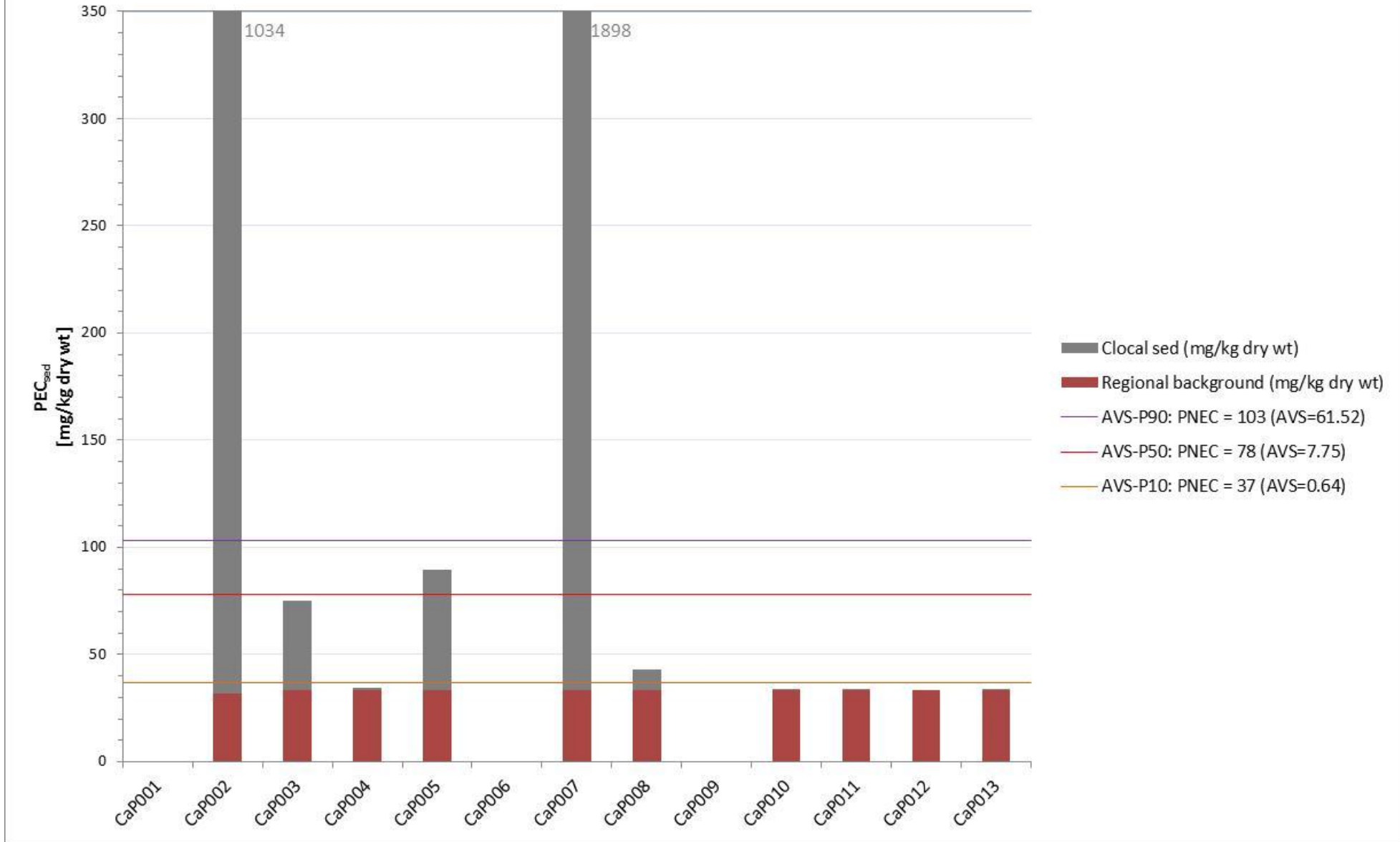
Catalyst producer (AF=1.5)



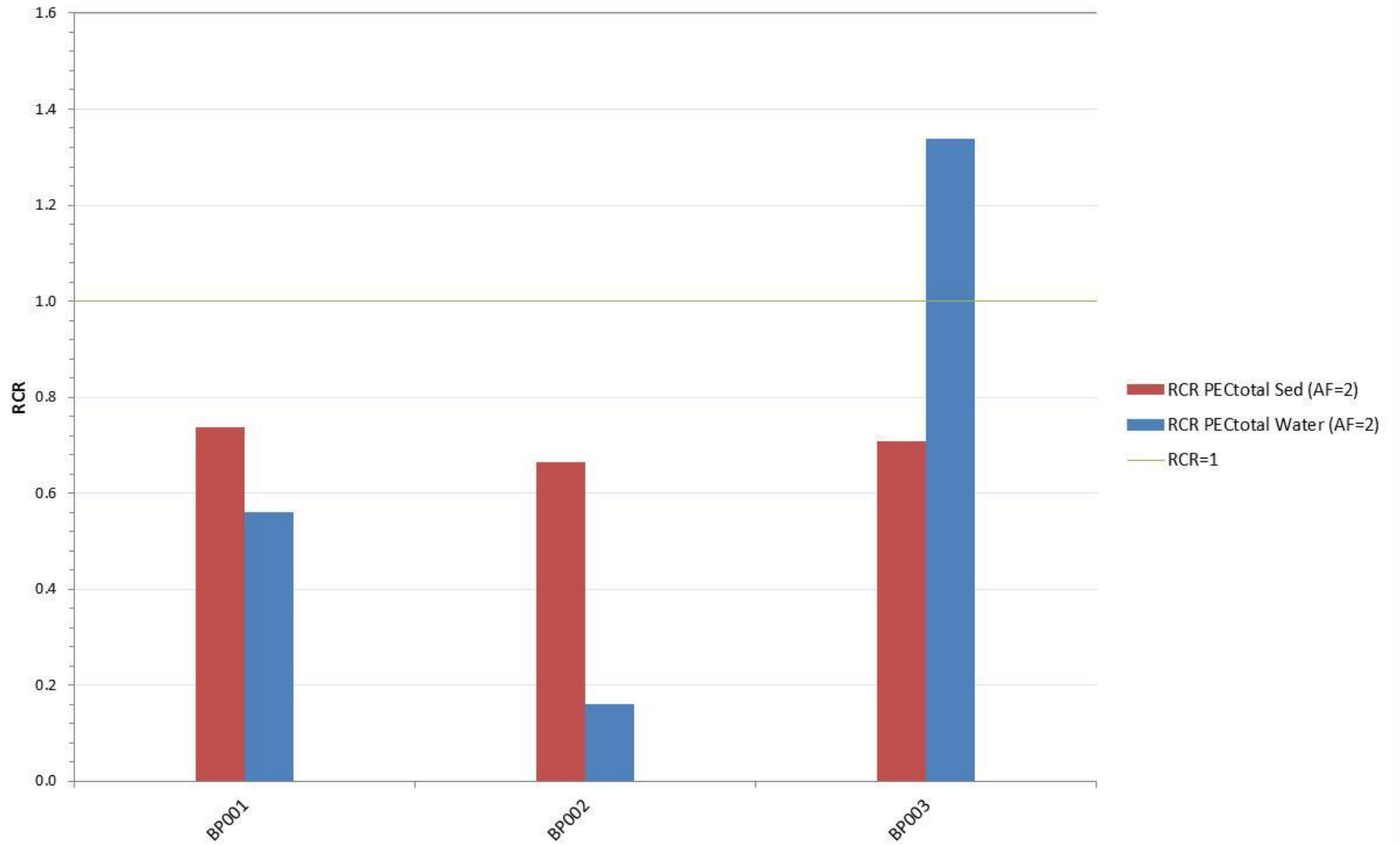
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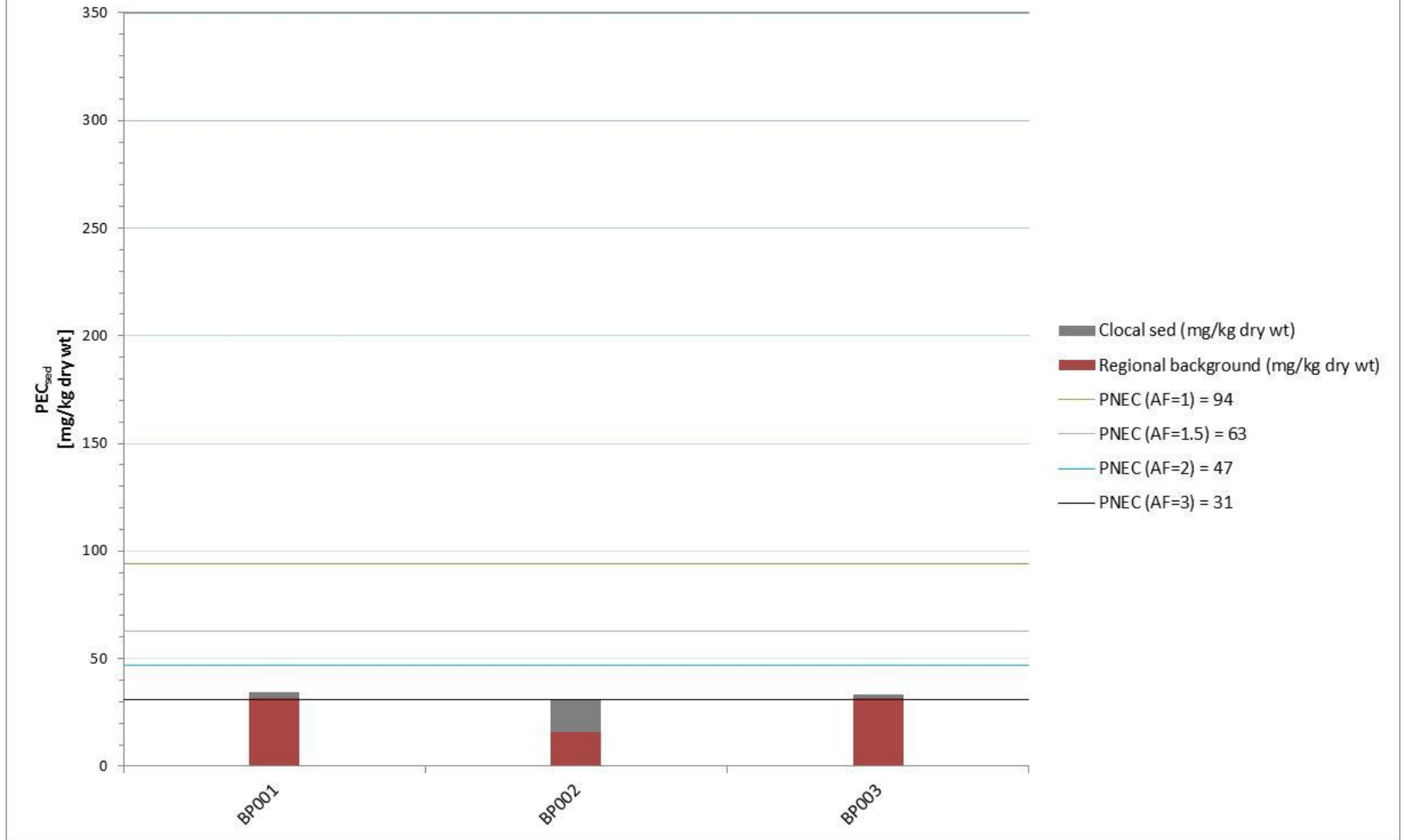
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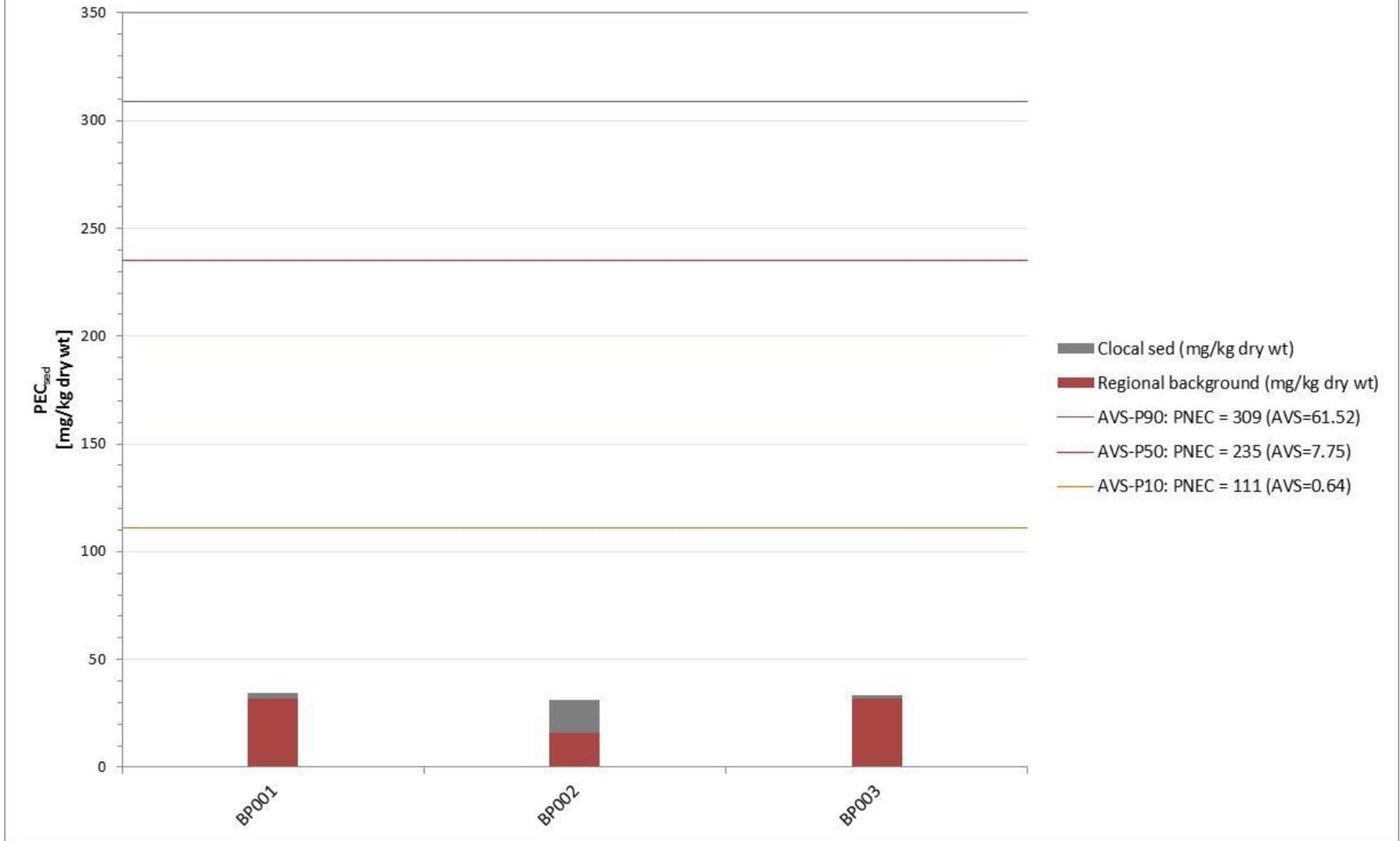
Battery - RCR water vs. sediment



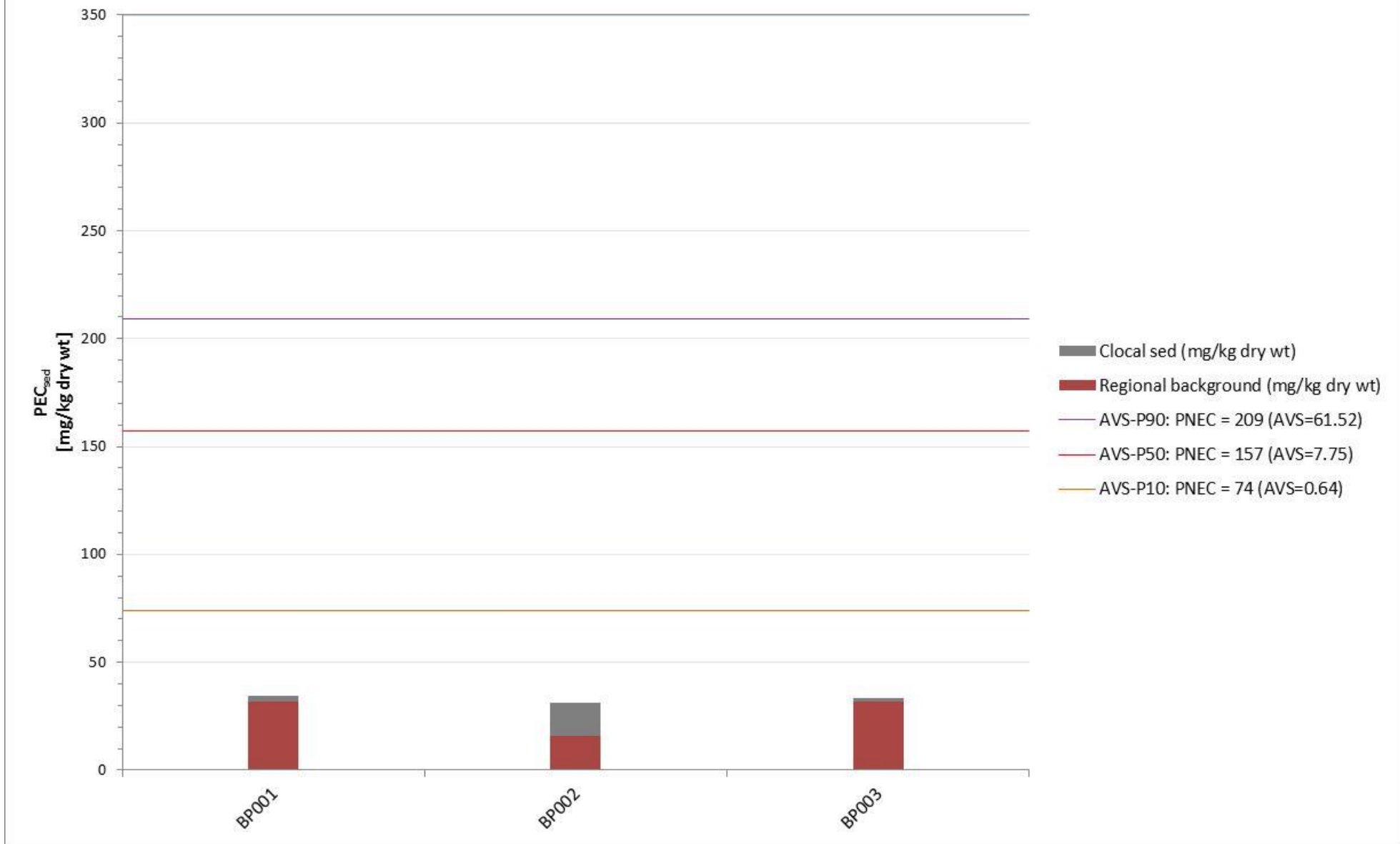
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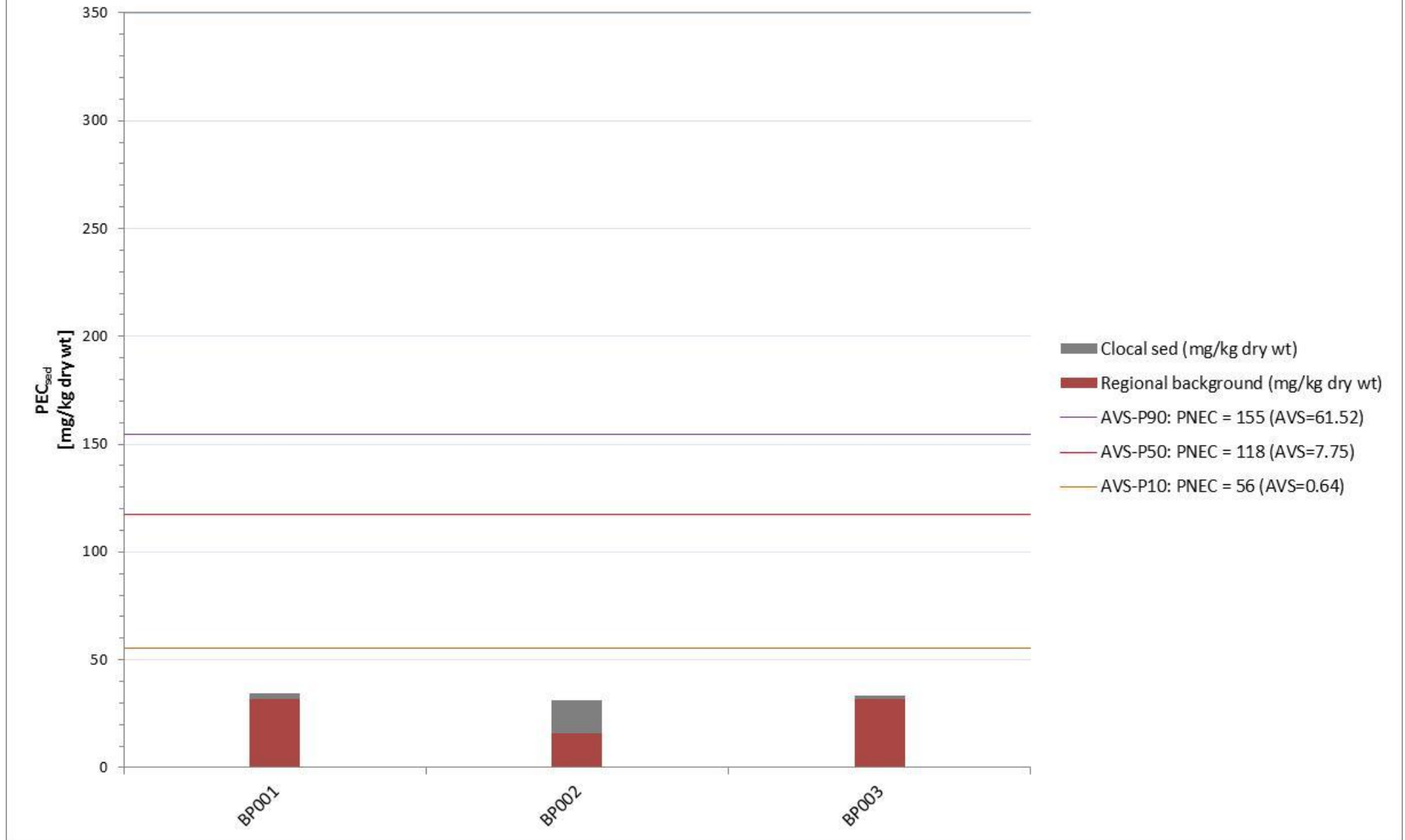
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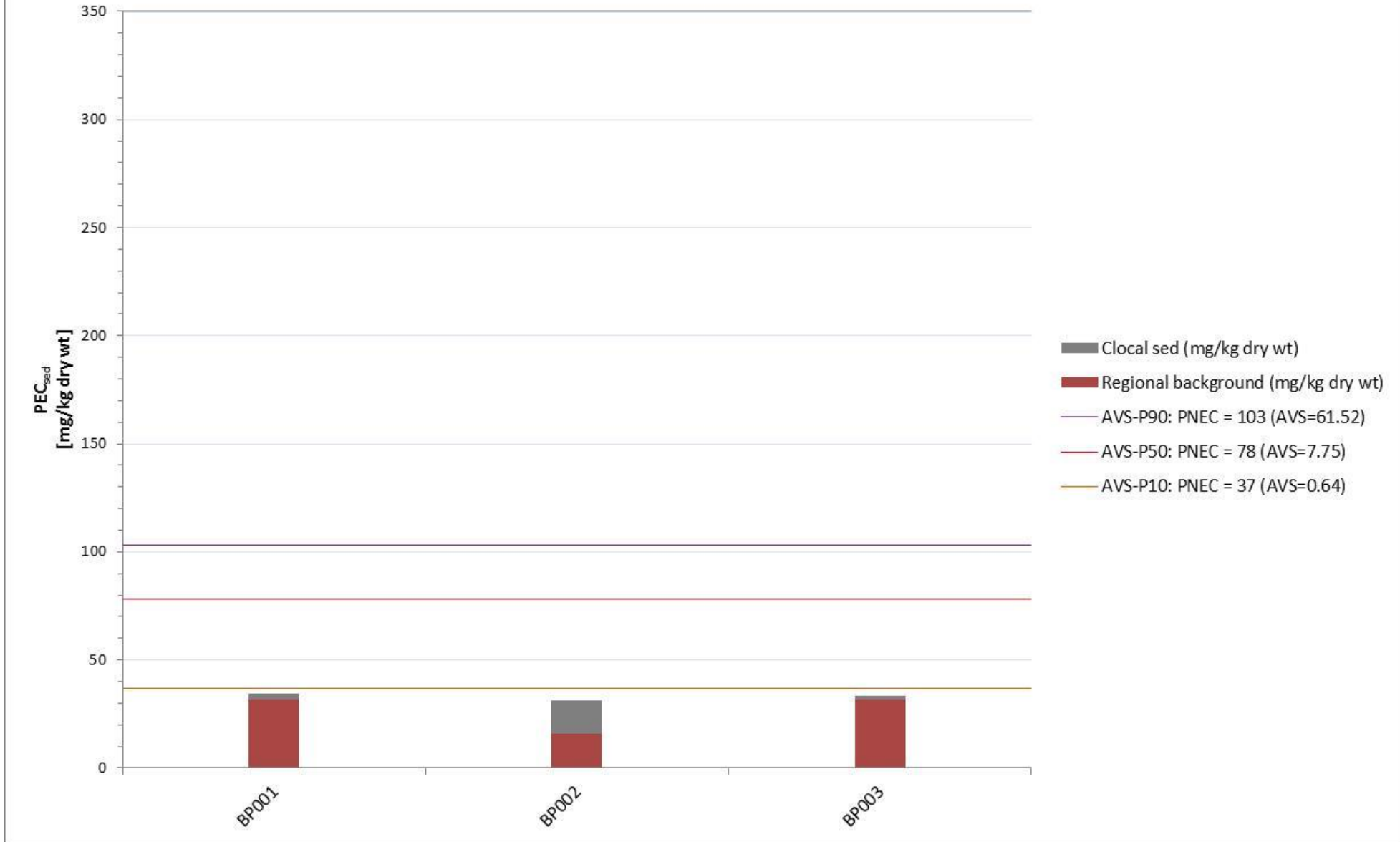
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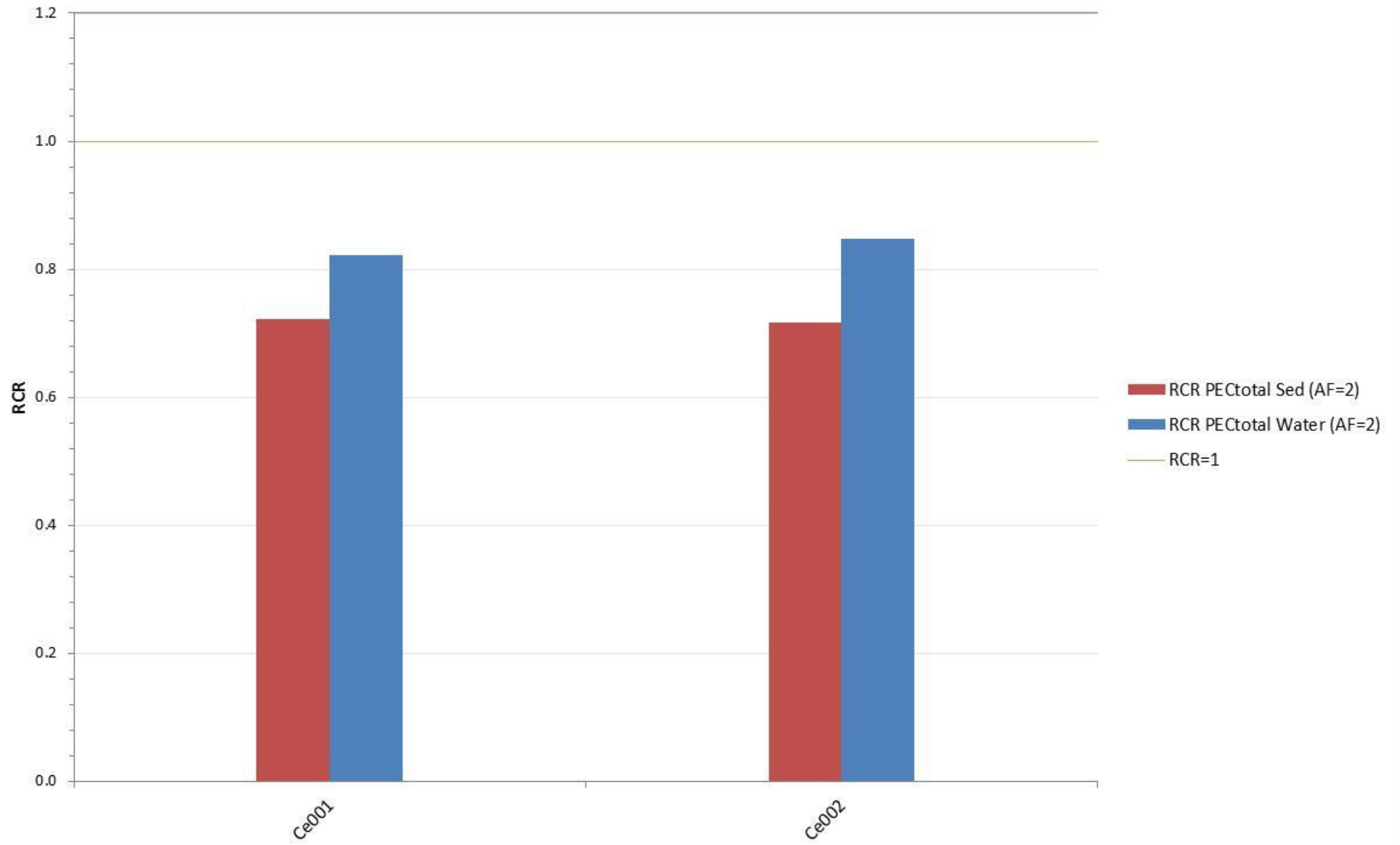
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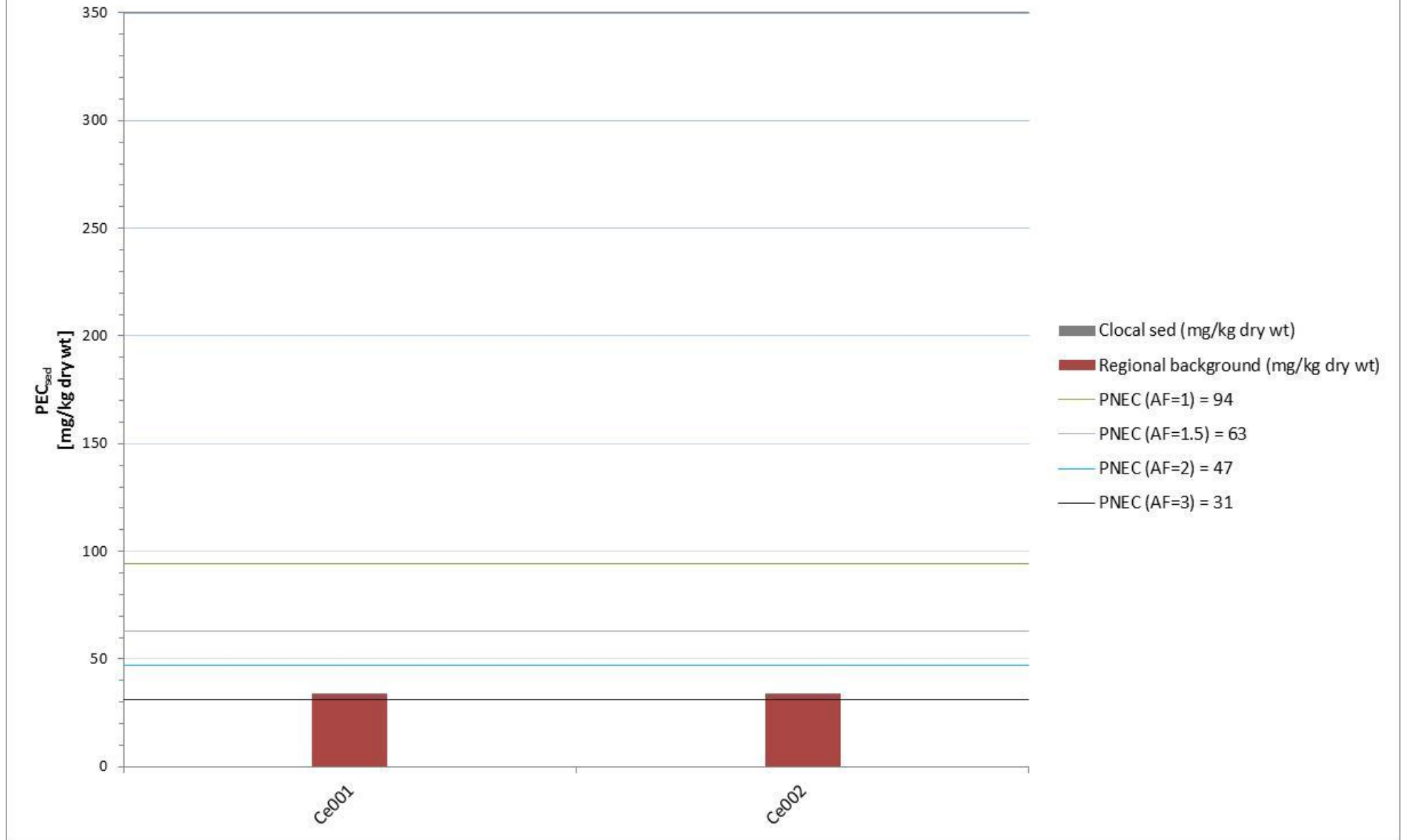
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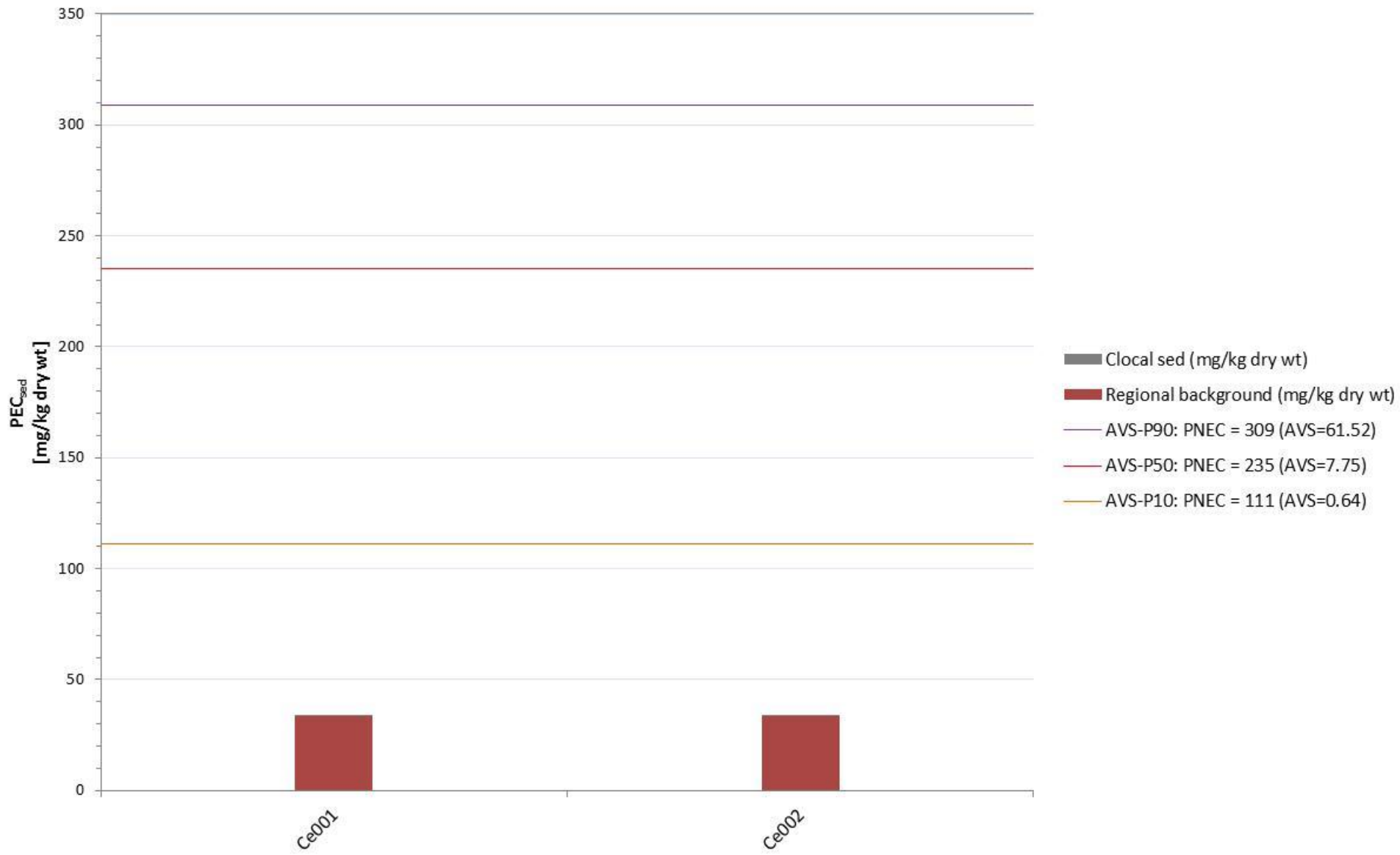
Ceramics - RCR water vs. sediment



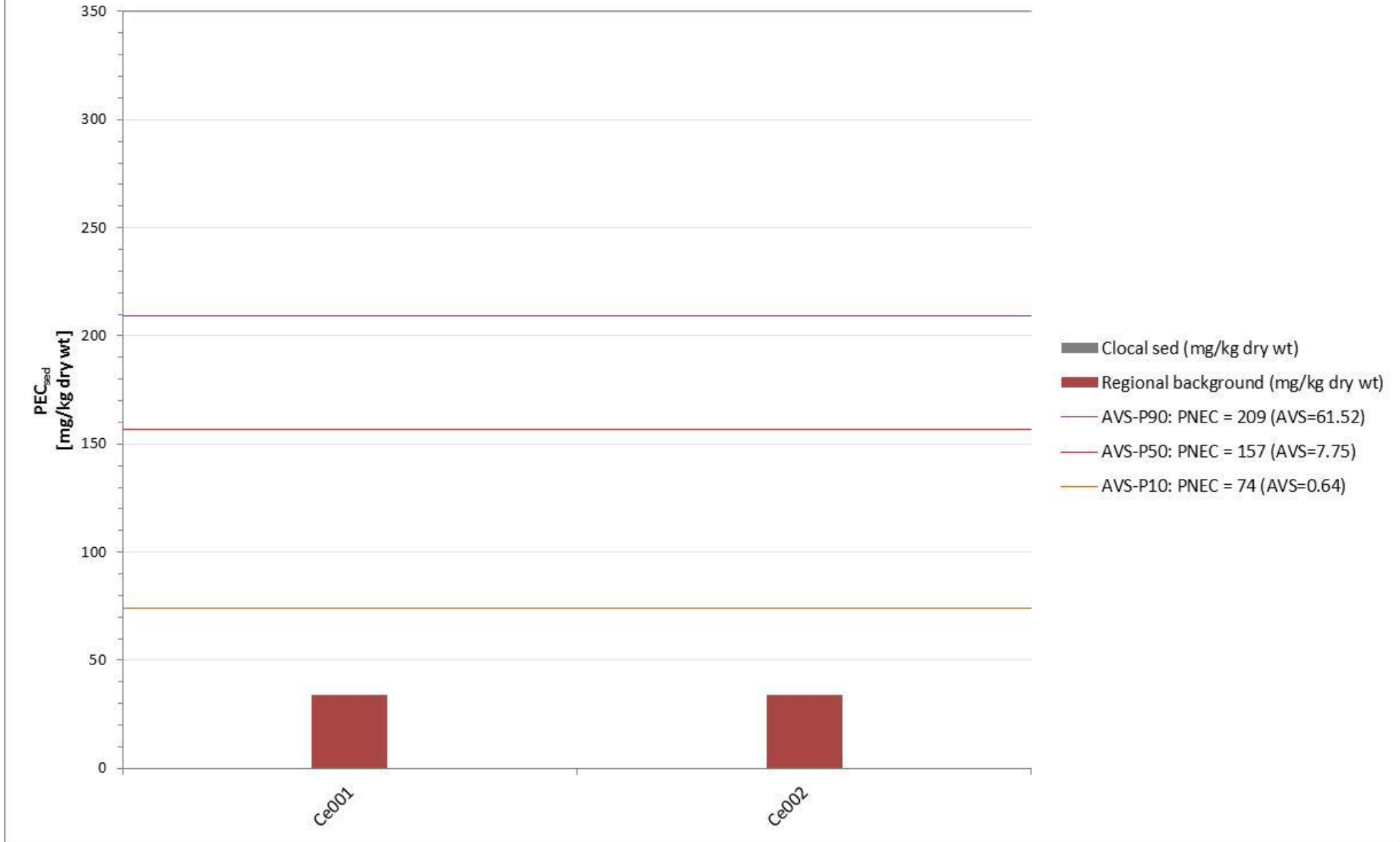
Ceramics



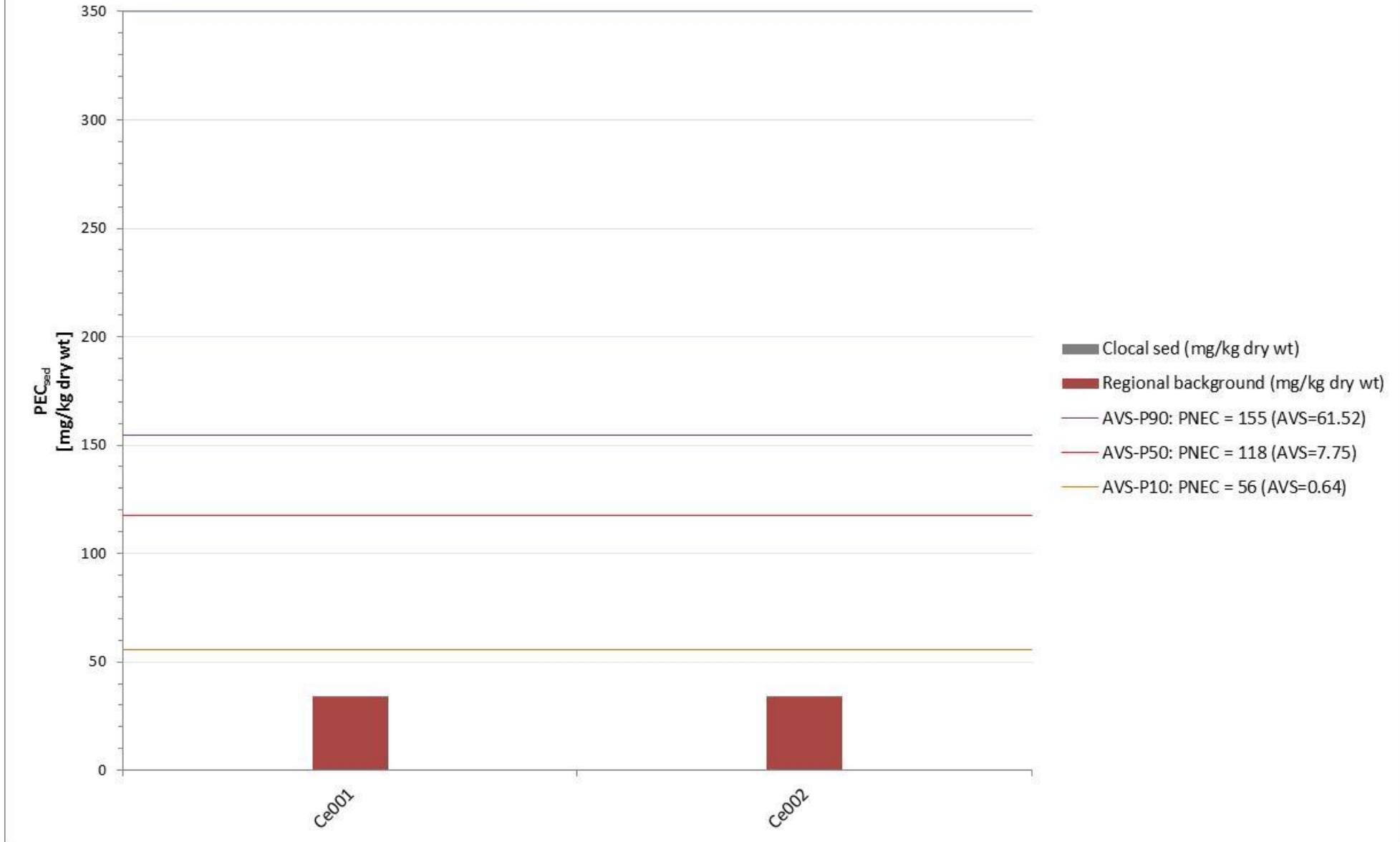
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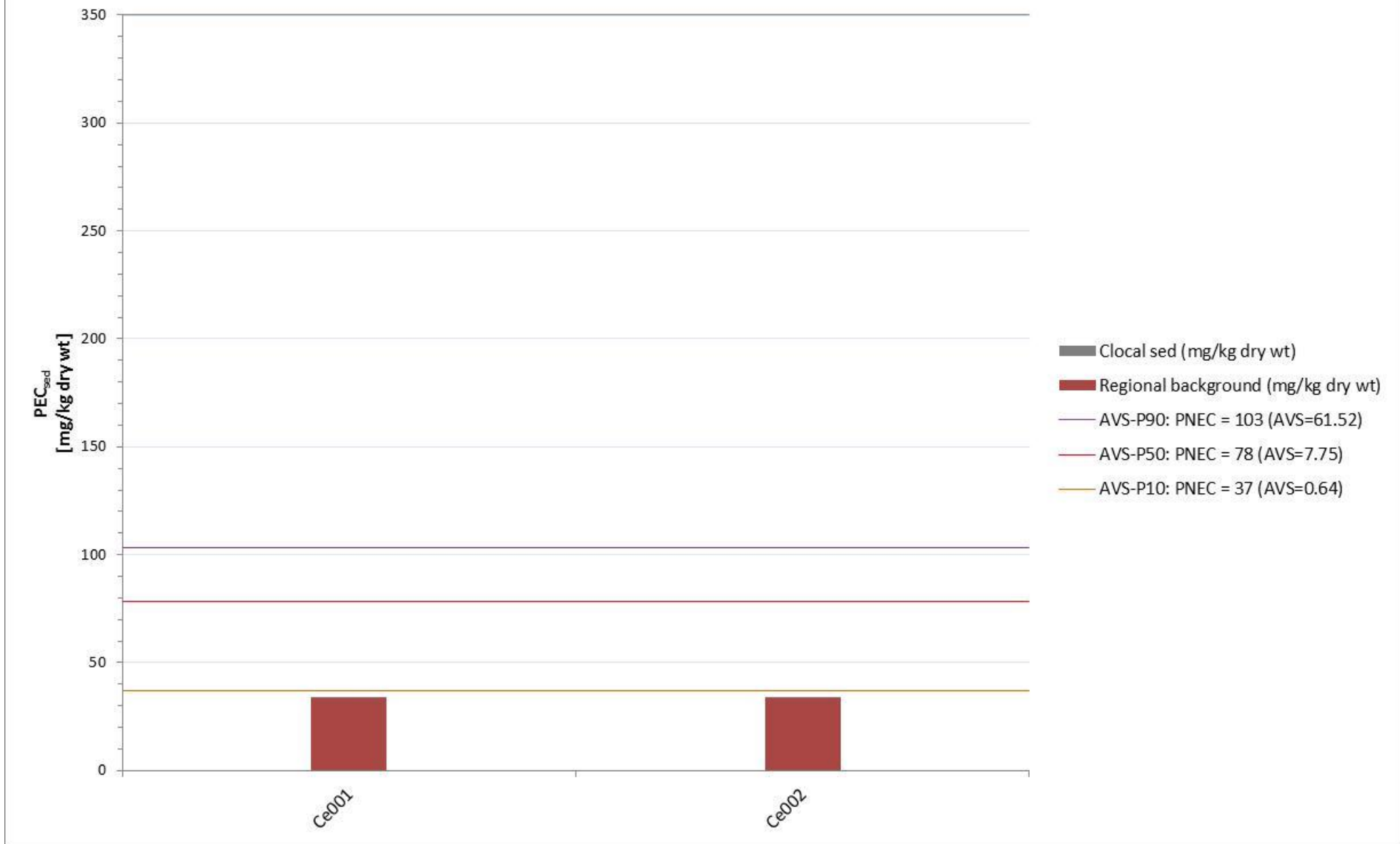
Ceramics (AF=1.5)



Ceramics (AF=2)



Ceramics (AF=3)



Number of sites within the sectors where RCR >1 compared to the total number of observation in the sector

Sector	Number of sites with RCR > 1 / total observations			
	AF = 1	AF = 1.5	AF = 2	AF = 3
Nickel metal producers	1/7	2/7	2/7	5/7
Stainless Steel production	9/23	9/23	9/23	23/23
Ferro-nickel producers	0/1	1/1	1/1	1/1
Chemicals production	1/11	2/11	2/11	9/11
Nickel plating	4/12	4/12	6/12	11/12
Catalyst producers	2/10	4/10	4/10	10/10
Battery production	0/3	0/3	0/3	3/3
Ceramics production	0/2	0/2	0/2	2/2
No. of sites RCR>1/ total no. of sites	17/69	22/69	24/69	64/69

Number of sites within the sectors where RCR >1 compared to the total number of observation in the sector. Figures are shown for different levels of AVS. All observations are based on a PNEC derived using AF = 1

	Number of sites with RCR > 1 / total observations at different AVS levels			
AVS ($\mu\text{mol/g dw}$)	0 (AF=1)	0.64 (P10)	7.75 (P50)	61.52 (P90)
Nickel metal producers	1/7	1/7	0/7	0/7
Stainless Steel production	9/23	8/23	4/23	4/23
Ferro-nickel producers	0/1	0/1	0/1	0/1
Chemicals production	1/11	0/11	0/11	0/11
Nickel plating	4/12	3/12	2/12	2/12
Catalyst producers	2/10	2/10	2/10	2/10
Battery production	0/3	0/3	0/3	0/3
Ceramics production	0/2	0/2	0/2	0/2
Number of sites where RCR>1	17/69	14/69	8/69	8/69

Number of sites within the sectors where RCR >1 compared to the total number of observation in the sector. Figures are shown for different levels of AVS. All observations are based on a PNEC derived using AF = 1,5

	Number of sites with RCR > 1 / total observations at different AVS levels			
AVS ($\mu\text{mol/g dw}$)	0 (AF=1.5)	0.64 (P10)	7.75 (P50)	61.52 (P90)
Nickel metal producers	2/7	1/7	1/7	1/7
Stainless Steel production	9/23	9/23	6/23	6/23
Ferro-nickel producers	1/1	1/1	0/1	0/1
Chemicals production	2/11	1/11	0/11	0/11
Nickel plating	4/12	4/12	3/12	2/12
Catalyst producers	4/10	4/10	2/10	2/10
Battery production	0/3	0/3	0/3	0/3
Ceramics production	0/2	0/2	0/2	0/2
Number of sites where RCR>1	22/69	20/69	12/69	11/69

Number of sites within the sectors where RCR >1 compared to the total number of observation in the sector. Figures are shown for different levels of AVS. All observations are based on a PNEC derived using AF = 2

AVS ($\mu\text{mol/g dw}$)	Number of sites with RCR > 1 / total observations at different AVS levels			
	0 (AF=2)	0.64 (P10)	7.75 (P50)	61.52 (P90)
Nickel metal producers	2/7	2/7	1/7	1/7
Stainless Steel production	9/23	9/23	8/23	6/23
Ferro-nickel producers	1/1	1/1	0/1	0/1
Chemicals production	2/11	2/11	0/11	0/11
Nickel plating	6/12	5/12	3/12	3/12
Catalyst producers	4/10	4/10	2/10	2/10
Battery production	0/3	0/3	0/3	0/3
Ceramics production	0/2	0/2	0/2	0/2
Number of sites where RCR>1	24/69	23/69	14/69	12/69

Number of sites within the sectors where RCR >1 compared to the total number of observation in the sector. Figures are shown for different levels of AVS. All observations are based on a PNEC derived using AF = 3

	Number of sites with RCR > 1 / total observations at different AVS levels			
AVS ($\mu\text{mol/g dw}$)	0 (AF=3)	0.64 (P10)	7.75 (P50)	61.52 (P90)
Nickel metal producers	5/7	3/7	1/7	1/7
Stainless Steel production	23/23	12/23	9/23	9/23
Ferro-nickel producers	1/1	1/1	1/1	0/1
Chemicals production	9/11	2/11	1/11	0/11
Nickel plating	11/12	9/12	4/12	3/12
Catalyst producers	10/10	5/10	3/10	2/10
Battery production	3/3	0/3	0/3	0/3
Ceramics production	2/2	0/2	0/2	0/2
Number of sites where RCR>1	64/69	32/69	19/69	15/69