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Scaling model for prediction of radionuclide activity in cooling water using a regression triplet technique

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Abstract The decommissioning of the nuclear power plant (NPP) A1 Jaslovské Bohunice (Slovakia) is a complicated set of problems that is highly demanding both technically and financially. The basic goal of the decommissioning process is the total elimination of radioactive materials from the nuclear power plant area, and radwaste treatment to a form suitable for its safe disposal. The initial conditions of decommissioning also include elimination of the operational events, preparation and transport of the fuel from the plant territory, radiochemical and physical–chemical characterization of the radioactive wastes. One of the problems was and still is the processing of the liquid radioactive wastes. Such media is also the cooling water of the long-term storage of spent fuel. A suitable scaling model for predicting the activity of hard-to-detect radionuclides ^{239,240}Pu, ^{90}Sr and summary beta in cooling water using a regression triplet technique has been built using the regression triplet analysis and regression diagnostics.

Keywords Spent fuel storage · A linear regression model · Scaling model · Plutonium · Americium · Strontium

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Introduction

Spent fuel storage (SFS) A1 Jaslovské Bohunice unit spent fuel storage—it is a water basin construction, longitude 12 m, cross size 7 × 7 m, full capacity 910 of fuel assemblies. Spent fuel (SF) in SFS was stored from 1973.

SF assemblies were stored in special caskets with one spent fuel assembly inside (casket). Caskets are made of carbon steel. There were gradually stored:

- SF assemblies with chrompik and fuel.
- Caskets with chrompik.
- Caskets with chrompik and dowtherm.

Chrompik (water solution of potassium dichromate compound with a concentration in the range 3–5%) and dowtherm (organic liquid with a high boiling point used for fuel storage) are used as an inner cooling media inside caskets. The role of these two media (chrompik or dowtherm) was

- to cool the assembly, and conduct the heat through the casket's pipe wall to the SFS cooling water
- a corrosion inhibitor.

During the A1 operation it determined, that this mode of SF storing causes

- corrosion of the SF followed by a release of fissile products into the SFS cooling media
- fuel geometry deformation.

Ten-year monitoring of basic radiometric parameters of SFS cooling water showed high importance of the methodology of taking samples and mainly of the existence of dowtherm and sludge on the bottom pool of SFS. Spent fuel is a long-term producer of residual heat. It was always said that SFS contains 560 m^3 of cooling water; its role is to cool off the caskets with spent fuel inside, and perform the role of radiation shielding. After SFS start-up (1973), the filtered river water was used as the cooling media. Later, after loading the caskets, the radiation contamination by radioisotopes isotopes gradually increased. Consequently, de-mineralized water was refilled to the pool.

The cooling water contamination consists of: fissile products, activated corrosion products and transuranium elements. We suppose that the cooling water contamination process can have the following modes:

- Chrompik leakage from the caskets due to overpressure inside the casket and wrong sealing ring.
- Inner cooling media (chrompik or dowtherm) leakage to the SFS during transport handling–unloading of SF out of caskets.
- Refilling of the SFS in order to obtain design level of cooling water.
- SFS decontamination.

In order to avoid the corrosion of pool coating and corrosion of SFC, cooling water pH was maintained in the alkaline area (pH 8.5–9) by refilling the KOH and NaOH. On the bottom of SFS there were discovered sediments—approximately 25 m^3 of non-homogenous radioactive sludge.

From 1983 to 1994, on Comenius University, Department of Nuclear Chemistry there was conducted once a month SFS cooling water analysis in order to observe the chemical and radionuclide regime. Radionuclide magnitude was observed by means of summary alfa activity, summary beta activity, activity of the radio nuclides ^{137}Cs, $^{239,240}Pu$, ^{90}Sr, and by plutonium and uranium concentration. In 1993 there was conducted an enlarged analysis with the participation of ^{238}Pu, ^{241}Am. Safe radioactive waste processing is one of the most important tasks that needs to be solved during NPP decommissioning; radioactive waste commutation and production of the new radwaste—result of decommissioning—create a potential threat to the environment.

Theoretical

A *linear* regression model is a model which is formed by a linear combination of explanatory variables **x** or their functions, $\boldsymbol{y} = \boldsymbol{X}\,\boldsymbol{\beta} + \boldsymbol{\varepsilon}$, and a procedure of the regression model building and testing with the use of the regression triplet was previously described, *cf.* Ref. [1, 2].

Experimental

Separation of strontium

Strontium-90 was determined by beta-counting the daughter activity yttrium-90. Yttrium was separated from the fraction, which also contains Am, Sr and another component, by liquid–liquid extraction with TBP (Tributyl phosphate) [3]. The extractant TBP was conditioned with concentrated HNO_3 in nitrate form. The organic phase contained yttrium and the aqueous phase contained the Am, Sr fraction. TBP phase was washed with concentrated HNO_3. Yttrium was eluted from TBP using 15 mL deionised water and 2 M HNO_3. 30 mL of saturated ammonium oxalate solution was added to the beakers with ^{90}Y formed precipitation of yttrium oxalate $Y_2(C_2O_4)_3{\cdot}9H_2O$. Continue to heat the mixture on the hot plate (70 °C) with occasional stirring, for 15 min. Cool the beakers to room temperature and filter precipitate (Whatman No. 42 filter paper), wash the yttrium oxalate precipitate with 25 mL of water, followed by 25 mL of 95% ethyl alcohol.

Yttrium oxalate and summary beta activity were measured using a plastic scintillation detector connected to NV 3101 spectrometric assembly (TESLA). The activity measurement of samples was performed with a standard error less than 1%.

Notice: The yttrium yield was determined from the ratio of the weight of the sample yttrium oxalate to the expected weight of yttrium oxalate as determined from the yttrium carrier standardisation.

Pu separation and analysis of aqueous samples

An aliquot of each sample was subjected to a thenoyltrifluoroacetone (TTA) separation [4–6]. An aliquot of each sample was initially spiked with a ^{238}Pu tracer. All of the plutonium in the samples was reduced once using hydroxylamine. An anion complexing reagent (aluminium nitrate) was then added, and the solutions were oxidized with 4 M sodium nitrite. The plutonium was then extracted from the matrix using a TTA solution. The TTA layer was mounted on a counting dish, the mount was then analyzed by alpha spectroscopy. A blank sample was run with the sample set. The analysis results for the ^{239}Pu were yielded using the ^{238}Pu recoveries from the sample separation. The alpha spectra of plutonium were measured with the silicon surface barrier detector connected with a 4096-channel analyser (Intertechniques, France).

A well-type NaI (Tl) scintillation detector (R31-2; R410-4) in connection with a single-channel amplitude analyzer AI-1024, NP 420 (MEV, Hungary) was used for measuring gamma activity.

Results and discussion

Proposal of a scaling model for original data for spent fuel storage

Using the original set of data, the ordinary least-squares method OLS finds the regression model

$$a\left[^{239,240}\mathrm{Pu}\right] = 541.9(498.3, A) + 21.7(22.1, A)\, a\left[^{137}\mathrm{Cs}\right]$$

where standard deviations of the parameters estimated are in brackets and the letter A means that $H_0 : \beta_i = 0$ is accepted and β_i is not statistically significant. The critical quantile $t_{0.975}(72 - 2) = 1.994$ of a Student t-test at 5% significance level was used to examine the statistical significance of the individual regression parameters and the estimates of $\hat{\beta}_0$ and $\hat{\beta}_1$ are found to be significant. The scaling model was built with the correlation coefficient $R = 0.1165$ and the determination coefficient $D = 1.36\%$ which also expresses a percentage of points which fulfil the model proposed. The mean error of prediction MEP = 9376041.2, the Akaike information criterion AIC = 1156.3 and the residual standard deviation $s(e) = 3029.9$ were also calculated to prove the scaling model proposed. All these statistics form the resolution criteria for the selection of the best model among several plausible ones.

Detection of influential points

While there are many suspicious points in data in Fig. 1 (2, 27, 30) which are located outside the Working-Hotteling confidence bands of the scaling model straight line. It applies that outliers are identified by an examination of the residuals.

The scatter plot of regression straight line (Fig. 1a), the index plot of squared residuals (Fig. 1b) indicate influential points which may be considered to be suspicious and some testing diagnostics for influential points should be applied. Even though the common practice of many programs for the statistical analysis of classical residuals is to examine by use of statistical measures of location and spread, such as the residual mean $\bar{e}$, the residual variance $s^2(e)$, the residual skewness $g_1(e)$and the residual kurtosis $g_2(e)$, these residual statistics do not give a correct indication of influential points, namely outliers. Diagnostic plots constructed from residuals and hat matrix elements represent a combination of various types of residuals with the diagonal elements of the projection hat matrix H_{ii} and lead to four diagnostic graphs of influential points (the analysed data set $\{x, y\} = \{^{137}\mathrm{Cs}, {}^{239,240}\mathrm{Pu}\}$ of size $n = 72$, $m = 2$):

The *graph of predicted residuals* (Fig. 1c), one of the simplest graphs indicates outliers (2, 27, 30) located far from its central pattern on the line $y = x$.

Gray = s L–R graph (Fig. 1d) indicates strongly influential points (2, 27, 30) and separates them into outlier (27, 30) points which lie high in the y-axis, and high-leverages (2) which lie in the direction of the x-axis.

The *Williams graph* (Fig. 1e) has two testing boundary lines, the first line for outliers $y = t_{0.95}(n - m - 1)$ detecting four outliers (2, 27, 30), and the second for high-leverage points $x = 2\ m/n = 0.5$ detecting two high-leverages.

The index graph of the Atkinson distance (Fig. 1f) indicates three outliers (2, 27, 30).

Examination of assumptions for the least-squares application

There are some which must be met if the least-squares method is to be applied and to give the best unbiased linear estimates of parameters, the intercept β_0 and the slope β_1:

The Fisher–Snedecor F-test [7] leads to the statistical criterion $F = 0.9634$ while the quantile $F(1 - \alpha, m - 1, n - m) = 4.121$ is higher and therefore the scaling regression model proposed is not statistically significant.

The Cook–Weisberg test of heteroscedasticity [7] has the statistical criterion SC = 3.57 while the quantile $\chi^2_{1\text{-}\alpha,1} = 3.841$ and residuals exhibit homoscedasticity.

The Jarque–Berra test for normality [7] has the statistical criterion $C = 2070.0$ while the quantile $\chi^2_{1-\alpha,2} = 5.991$ and normality of residuals is rejected.

The Wald test for autocorrelation [7] has the statistical criterion $W = 0.291$ while the quantile $\chi^2_{1-\alpha,2} = 3.841$ and autocorrelation is not significant.

Construction of a more accurate scaling regression model

The revised scaling model will then be regarded with the intercept term β_0. Since outliers may influence the regression results, they should be treated with care. There are two possible approaches to the data: either to exclude outliers from data or to use the robust regression method. One of the greatest disadvantages of robust method application is a preference for the regression model proposed, here $y = \beta_0 + \beta_1 x$. On the basis of previous graphical and numerical diagnostics of influential points it may be concluded that the seven outliers 2, 27, 30 should be excluded from the original data set, and new parameter estimates should be recalculated:

$$a\left[^{239,240}\mathrm{Pu}\right] = 187.6(72.2, R) + 6.56(3.25, R)\, a\left[^{137}\mathrm{Cs}\right]$$

the estimated standard deviations are in brackets). The new better scaling model is proven as it has been described with the higher correlation coefficient $R = 0.2395$ and also higher determination coefficient $D = 5.74\%$, thus expressing a percentage of points which fulfil the model proposed; the lower value of the mean error of prediction MEP = 199552.1 and lower value of the Akaike information criterion AIC = 840.3 prove a more accurate scaling model.

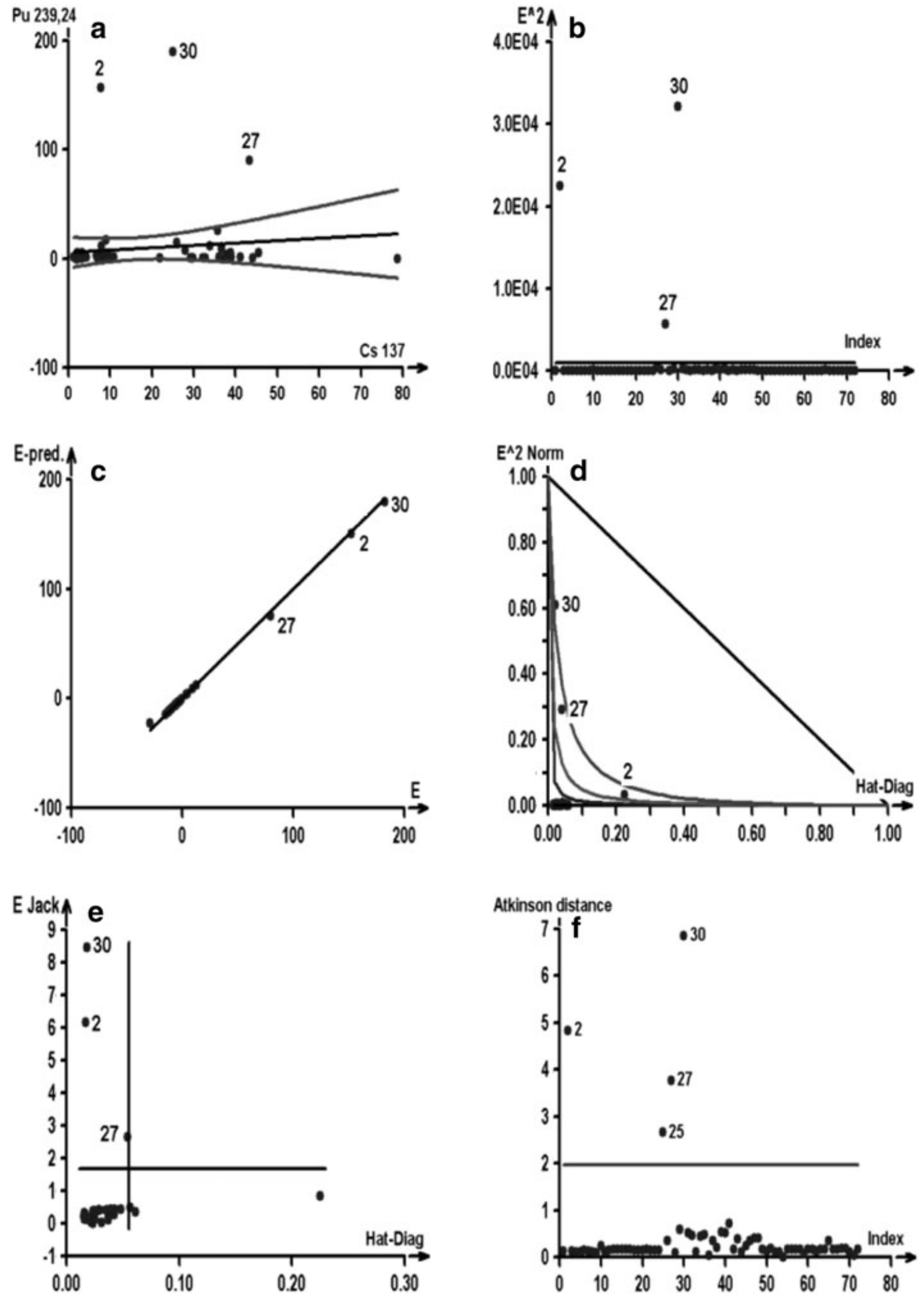

Fig. 1 **a** The scatter plot of the data set $a(^{239,240}Pu)$ [Bq kg^{-1}] vs. $a(^{137}Cs)$ [Bq kg^{-1}] presents the regression straight line of radioactivity tested and is constructed with the use of the regression triplet. Influential points which are suspicious here are tested if they are outliers. **b** Index graph of the squared ordinary residuals. **c** Graph of predicted residuals. **d** Gray = s $L-R$ graph. **e** Williams graph. **f** Index graph of the Atkinson distance

Examination of assumptions for the least-squares application

There are some which must be met if the least-squares method is to be applied and to give the best unbiased linear estimates of parameters, the intercept β_0 and the slope β_1:

The Fisher–Snedecor F-test [7] leads to the statistical criterion $F = 4.079$ while the quantile 3.984 is lower and therefore the scaling regression model proposed is statistically significant.

The Cook–Weisberg test of heteroscedasticity [7] has the statistical criterion $SC = 19.58$ while the quantile $\chi^2_{1\text{-}\alpha,1} = 3.841$ and residuals exhibit heteroscedasticity.

The Jarque–Berra test for normality [7] has the statistical criterion $C = 325.5$ while the quantile $\chi^2_{1-\alpha,2} = 5.991$ and normality of residuals is rejected.

The Wald test for autocorrelation [7] has the statistical criterion $W = 0.999$ while the quantile $\chi^2_{1-\alpha,2} = 3.841$ and autocorrelation is not significant.

Nuclides such as alpha emitting nuclides, beta emitting nuclides, and characteristic X-ray emitting nuclides whose radioactivity is difficult to measure directly from outside the waste, using a Ge semiconductor detector or the like. The list of hard-to-detect radionuclides usually includes radionuclides, which emit only beta or alpha particles; their selective detection required severe radiochemical analysis. The scaling factor method is a method for evaluating the radioactivity of difficult-to-measure nuclides (DTM) from the radioactivity of a key nuclide, based on the correlations between DTM nuclides and key nuclides [8]. Determination of the activity of the radionuclides ^{239,240}Pu, ^{90}Sr and summary beta activity in cooling water of the long-term storage of spent fuel may be determined by indirect methods such as use of the scaling model, which relate the inferred activity concentration of one radionuclide to another that is measured. ^{137}Cs was selected as a suitable key nuclide for the determination of a parameter linear scaling model for monitoring radionuclides. Gamma emitting nuclides such as ^{60}Co and ^{137}Cs that have a production mechanism and transport behaviour similar to those of hard-to-detect radionuclides. The ^{239,240}Pu fraction is the most prominent representative of the alpha-emitters to check their scalability to easily measurable [8] key nuclides ^{137}Cs. ^{239,240}Pu and ^{90}Sr are difficult to measure in waste because they are non-gamma emitting radionuclides.

Estimates of β_0 and β_1 parameters have been found by the classical least-square method. The pair correlation coefficient R suggests the statistical significance of the $a(^{137}\mathrm{Cs}) = b_0 + b_1\, a(x_i)$ regression model in which x_i is the activity of examined radionuclides ^{239,240}Pu, ^{90}Sr and summary beta activity. High values of the determination coefficient for spent fuel storage ($D = 36.05\%$ for scaling model ^{239,240}Pu vs. ^{137}Cs, $D = 55.49\ \%$ for model ^{90}Sr vs. ^{137}Cs, $D = 81.99\%$ for model summary beta vs. ^{137}Cs) and average values of the determination coefficient for chrompik in cooling water ($D = 32.26\%$ for model ^{90}Sr vs. ^{137}Cs, $D = 5.74\%$ for scaling model ^{239,240}Pu vs. ^{137}Cs) suggest that experimental points correspond to the scaling straight line model in contaminated cooling water and can be used and recommended. The statistical significance of the scaling regression models has been confirmed with the Fisher–Snedecor test and also with high values of pair-correlation coefficients R and D for chrompik and spent fuel storage. The results of regression diagnostics for chrompik and spent fuel storage are in Tables 1 and 2. The regular designed scaling model opens the possibilities of long-time activity monitoring of these radionuclides and, last but not least, decrease the number of necessary radiochemical analyses of contaminated cooling water of the long-term storage of spent fuel.

Table 1 Regression model building and testing leading to the straight line $[^{239,240}\mathrm{Pu}] = b_0 + b_1\, a[^{137}\mathrm{Cs}]$, $a[^{90}\mathrm{Sr}] = b_0 + b_1\, a[^{137}\mathrm{Cs}]$, $a[\text{sum beta}] = b_0 + b_1\, a[^{137}\mathrm{Cs}]$ for chrompik, where in statistical testing A means that $H_0{:}\boldsymbol{\beta} = 0$ is accepted while R that $H_0{:}\boldsymbol{\beta} = 0$ is rejected

	Data with outliers	Data without outliers	Data with outliers	Data without outliers
Independent variable x	^{137}Cs		^{137}Cs	
Dependent variable y	^{239,240} Pu		^{90}Sr	
Estimates of two unknown parameters				
Intercept b_0	541.9, A	187.6, R	4.84, A	3.64
Standard deviation $s(b_0)$	498.3	72.2	2.79	1.77
Slope b_1	21.7, A	6.56, R	0.62, A	0.54
Standard deviation $s(b_1)$	22.1	3.25	0.12	0.10
Goodness-of-fit statistics for a regression model building				
Correlation coefficient R	0.1165	0.2395	0.5131	0.5680
Determination coefficient D [%]	1.36	5.74	26.33	32.26
MEP criterion for the best model	9376041.2	199552.1	318.9	112.7
AIC criterion for the best model	1156.3	840.3	409.9	294.4
$s(e)$ for a fitness test	3029.9	434.6	17.0	10.2
F criterion, $F_{crit} = 3.984$, H_0: correlation is significant	0.9634, R	4.079	25.0, A	29.0
Cook–Weisberg test, $\chi^2_{crit} = 3.841$, H_0: homoscedasticity is significant	3.57, R	19.58	60.9, R	42.7
Jarque–Berra test, $\chi^2_{crit} = 5.991$, H_0: normality is significant	2070, R	325.5	23.4, R	13.0
Wald's test, $\chi^2_{crit} = 3.841$, H_0: autocorrelation is significant	0.291, A	0.999	16.54, A	9.82
Number of outliers found	30, 2, 27	–	25, 26, 29, 39, 40, 41, 45, 46, 65	–

Table 2 Regression model building and testing leading to the straight line model $a[^{239,240}Pu] = b_0 + b_1 a[^{137}Cs]$, $a[^{90}Sr] = b_0 + b_1 a[^{137}Cs]$, $a[\text{sum beta}] = b_0 + b_1\ a[^{137}Cs]$ for Spent fuel storage, where in statistical testing *A* means that $H_0{:}\boldsymbol{\beta} = 0$ is accepted while *R* that $H_0{:}\boldsymbol{\beta} = 0$ is rejected

	Data with outliers	Data without outliers	Data with outliers	Data without outliers	Data with outliers	Data without outliers
Independent variable x	^{137}Cs		^{137}Cs		^{137}Cs	
Dependent variable y	^{90}Sr		$^{239,240}Pu$		Sum beta	
Estimates of two unknown parameters						
Intercept b_0	7.01, R	3.28	0.13	0.15	−0.71	−3.18
Standard deviation $s(b_0)$	4.23	1.98	11.23	2.38	9.64	7.91
Slope b_1	1.12, A	0.95	1.37	0.67	7.35	7.73
Standard deviation $s(b_1)$	0.30	0.14	0.50	0.11	0.68	0.57
Goodness-of-fit statistics for a regression model building						
Correlation coefficient R	0.4987	0.7449	0.3134	0.6004	0.8566	0.9055
Determination coefficient D [%]	24.88	55.49	9.82	36.05	73.37	81.99
MEP criterion for the best model	327.6	69.03	4886.6	237.9	1731.0	1168.4
AIC criterion for the best model	255.6	165.8	610.2	376.0	327.9	296.4
$s(e)$ for a fitness test	17.9	8.17	68.27	14.5	40.62	33.28
F criterion, $F_{crit} = 4.121$, H_0: correlation is significant	13.9, A	46.1	7.63	38.3	115.7	182.0
Cook–Weisberg test, $\chi^2_{crit} = 3.841$, H_0: homoscedasticity is significant	1.55, A	0.54	37.48	62.66	8.73	3.92
Jarque–Berra test, $\chi^2_{crit} = 5.992$, H_0: normality is significant	34.3, A	41.8	3059.3	28.45	12.53	4.60
Wald's test, $\chi^2_{crit} = 3.841$, H_0: autocorrelation is significant	2.08, A	3.66	16.55	15.75	23.59	27.15
Number of outliers found	27, 28, 32, 33, 37	–	33, 34	–	12, 40	–

Conclusion

Declaration and verification of hard-to-detect radionuclides, based on the direct testing, imply seriously high expenses. Suitable scaling models for ^{90}Sr, $^{239,240}Pu$ and summary beta activity monitoring in cooling water of long-term spent fuel storage have been proven by a regression triplet analysis. The radioactivity of key nuclide ^{137}Cs is correlated with hard-to-detect radionuclides $^{239,240}Pu$, ^{90}Sr and summary beta activity and can be non-destructively measured beyond the detection limit. The scaling models were calculated with ^{137}Cs as the indicator variable for estimated radionuclides $^{239,240}Pu$, ^{90}Sr and summary beta activity. Regular designed scaling model opens the possibilities of long-time activity monitoring of these hard-to-detect radionuclides in cooling water. Based on this, a costly and lengthy radiochemical analysis of one of the investigated alpha radionuclides can be consequently replaced by a statistical factor connecting its content with other hard-to-detect radionuclides using a mathematical model.

Supporting information available

Complete computational procedures, input data specimens and corresponding output in numerical and graphical form for the program, QC-EXPERT or ADSTAT (Trilobyte, Pardubice, Czech, republic) are available online at http://meloun.upce.cz in the block *DATA*.

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References

1. Meloun M, Militký J, Hill M, Brereton RG (2002) The Analyst 127:433–450
2. Meloun M, Militký J (2001) Anal Chim Acta 439:169–191
3. Mikulaj V, Švec V (1993) J Radioanal Nucl Chem 175:317
4. Moore FL, Hudgens JE (1957) Anal Chem 29(12):1767–1770
5. King EL, Reas WH (1951) J Am Chem Soc 73(4):1804–1805

6. Hölgye Z (1990) J Radioanal Nucl Chem 141:101–106
7. Meloun M, Militký J, Forina M (1994) Chemometrics for analytical chemistry, vol 2. PC-Aided regression and related methods. Horwood, Chichester
8. ISO 21238:2007 Nuclear energy—nuclear waste—standard guide for the scaling factor method to determine the radioactivity of low and intermediate level radioactive waste packages generated at nuclear power plant (LWR), International Standard