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Self-attenuation corrections for Pb-210 in gamma-ray spectrometry using well and coaxial HPGe detectors

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Well and coaxial HPGe Detectors. Focus on Pb-210 self-attenuation corrections in gamma-ray spectrometry

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Abstract

Semi-empirical methodologies for self-attenuation corrections of ^{210}Pb were applied to NORM sediments in vial and cylindrical geometries and the results critically compared with Monte Carlo approaches (as regards their standard values and associated uncertainties) to establish accurate and practical procedures to be followed by environmental laboratories determining ^{210}Pb geochronology. It was showed that the transmission approach can be successfully employed in combination with Monte Carlo modelling (GESPECOR) for the determination of mass attenuation coefficients and efficiency transfer factors. Differences in apparent density (ratio sample density/standard density in a range between 0.34 – 0.54) and chemical composition between an efficiency calibration standard of soil matrix and environmental sediment samples, highlighted the necessity of self-attenuation corrections regardless of the matrix of the standard employed for the efficiency calibration of the detector.

Keywords: *^{210}Pb, well type detector, self-attenuation, gamma-ray spectrometry, GESPECOR, geochronology.*

1. Introduction

Pb-210 ($T_{1/2}$ = 22.23 years) (DDEP, 2015) is a naturally-occurring radionuclide, used as a tracer for environmental applications for example in geochronology, tracing of continental air mass movement, sediment source attribution and delivery in hydrological science and soil erosion investigations. Three approaches are available for the measurement of ^{210}Pb activity concentrations in various sample matrices: (i) direct measurement by liquid scintillation counting (LSC) and by gamma-ray spectrometry, and (ii) indirect counting by alpha-particle spectrometry, through the measurement of its daughter ^{210}Po, assuming radioactive equilibrium conditions. Iurian et al. (2016) have emphasised that 'fit-for-purpose' considerations are necessary when selecting a radioanalytical technique for the measurement of ^{210}Pb in various food and/or environmental matrices, as the measurement results uncertainties strongly depend on the specific measurement technique. High resolution gamma-ray spectrometry is commonly employed for ^{210}Pb determination in environmental samples because it is a relatively rapid and non-destructive method and a wide range of radiation detector systems are currently available. However, in case of geochronological applications, or in hydrological studies, it is often the case that only small amount of sediment sample is available and a well type detector is typically employed for ^{210}Pb measurements (either uniquely or in combination with another detector, such as a coaxial type).

The 46.5 keV gamma-emission (I_γ = 4.252%) (DDEP, 2015) is analysed for ^{210}Pb determination by gamma-ray spectrometry. As it is well known, within the low gamma energy range, any difference in chemical composition and/or density between the sample to be analysed and the standard employed for the efficiency calibration of the detector will result in a varying attenuation of the gamma-rays passing through the sample matrix itself, before reaching the detector. This difference must be accounted for by the user by applying a self-attenuation correction to the full-energy-peak-efficiency (FEPE) at 46.5 keV. There has been a tendency to use a variety of approaches to account for this effect. For convenience, environmental laboratories attempt to correct for the different degrees of sample self-attenuation by

calibrating the detector with a spiked (McMahon et al., 2004) or natural matrix material with a 'close composition' to the sample types to be analysed. However, it may be difficult to find suitable matrices for different sample types and ranges of geometry. Implementation of these approaches is time-consuming, costly and it may be difficult to acquire samples of similar density and/or chemical composition of the 'in-house calibrant' to that of the sample to be analysed. Other approaches focus on determining a self-attenuation correction factor by: (1) semi-empirical methods (Cutshall et al., 1983; Bolivar et al., 1996; San Miguel et al., 2002; Appleby and Piliposian, 2004; and others) or (2) Monte Carlo methods (Sima et al., 2001; Jurado Vargas et al., 2002; Vidmar, 2005; Furci et al., 2013). The semi-empirical approach is commonly based on the transmission model of Cutshall et al. (1983), being only applicable to measurements of cylindrical geometries directly placed on the detector window. However, there is less information in the literature regarding the self-attenuation corrections in case of well type detectors, for which the transmission method cannot be employed since these detectors have a different geometry and, therefore, a different distribution of the gamma-ray path lengths through the sample. Well type detectors are essential for small sample quantities as commonly found in sediment dating investigations, as they tend to generate a high geometrical efficiency. A simplified formula for the determination of self-absorption correction factor for well type detectors was given by Appleby et al. (1992) and Appleby and Piliposian (2004), while the successful use of the Monte Carlo computation has been achieved by Sima and Arnold (1996) and others (e.g. Furci et al., 2013).

This paper aims (i) to discuss the effect of employing well versus coaxial type detectors for self-attenuation corrections in Pb-210 activity determinations; (ii) to evaluate the accuracy of semi-empirical approaches for the determination of self-attenuation correction for both well and coaxial detectors. The study focuses on the importance of accurate and precise measurements of ^{210}Pb by gamma-ray spectrometry for environmental applications.

2. Samples description and chemical characterization

A monolith saltmarsh core was sampled from Port Elliot Marsh (Cornwall, UK) in 2015 and sectioned in layers of 1 cm thickness. The 19 sediment samples were freeze-dried, finely ground, sieved (< 1 mm) and homogenised for 24 hours using a rotating mixing system. Furthermore, each sample was prepared for the gamma-ray measurement by hand compression in two different containers (i) a cylindrical aluminium container (inner diameter 47.50 mm, filling height 15.00 mm, side wall thickness 0.12 mm, bottom wall thickness 0.12 mm), and (ii) a polyethylene-terephtalate (PETP) container of vial geometry (inner diameter 12.25 mm, filling height 41.30 mm, side wall thickness 0.94 mm, bottom wall thickness 0.72 mm). A maximal deviation of 0.5 mm was assumed for the sample filling height, for both geometries. Use of aluminium and PETP containers, tightly bound with polytetrafluoroethylene (PTFE) tape wrapped inside the screw cap, coupled with high density tape on the exterior of the cap was intended to achieve radon-tight containers, a necessary condition for the evaluation of ^{226}Ra from its short-lived daughter ^{214}Pb. The volume of the aluminium container, 26.57 cm^3, was entirely filled with sample material and compressed. The vial type containers were filled up to the edge of the screw (filling volume 4.87 cm^3) because of the restrictions given by the well detector hole diameter (21.0 mm) which did not allow an insert of the container cap. The remaining space inside the top of the vial was filled with expandable Styrofoam flakes in order to retain the sample geometry inside the vial, and to avoid the accumulation of radon which exhales from the sediment material.

Two Proficiency Test materials (PTM) which had been characterised for ^{210}Pb by the International Atomic Energy Agency (IAEA) were initially homogenized in their original bottles and prepared for measurements in cylindrical and vial containers, following the protocol described above. These materials were received by the laboratory due to participation in an IAEA Proficiency Test (PT), and are: (1) IAEA moss-soil (PTM IAEA-CU-2009-03; currently certified as IAEA-447 moss-soil) (IAEA, 2012; Shakhashiro et al., 2012), and (2) IAEA soil (PTM IAEA-TEL-2012-03; not yet certified based on

authors' knowledge). The two PTM materials were used for the quality control of the ^{210}Pb measurements.

A soil material of known chemical (Table 1) and radiometric composition was dried, sieved, milled, homogenised and spiked with a gravimetrically-determined quantity of a multi-gamma standard solution supplied by Eckert & Ziegler (QCYA17840; traceable to the National Institute of Standards and Technology-NIST). The standard liquid solution contained ^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{137}Cs, ^{88}Y and ^{60}Co with a relative uncertainty (1σ confidence) < 2% for each constituent. The material was homogenised and portions of the spiked sample transferred in the cylindrical and vial containers and prepared as secondary calibration standards (namely CSS5), with similar geometry and matrix characteristics (except a significantly higher density) to the sediment samples. The moisture content of the CSS5 standards and of each sediment sample and PTM sample was determined by oven drying about 1 g of material at exactly 105ºC. The water content ranged between 1.8% and 3.5% for the 19 sediment samples.

Sub-samples were mechanically milled (for about 20 minutes) and employed in the determination of the chemical composition of the matrices by Wavelength Dispersive X-Ray Fluorescence (WD-XRF). Major element concentrations of each sediment sample and the PTM were determined in pressed pellets, using the state-of-art PANalytical XRF Spectrometer and the dedicated software for the data interpretation. The accuracies of the XRF results were checked by three replicates of a certified reference material (CRM) of similar matrix, namely SdAR-M2 metal-rich sediment (US Geological Survey). The relative difference between the certified values and the mean measurement results of the three CRMs was 4.1% for Na_2O, 5.5% for Al_2O_3, 8.0% for SiO_2, 4.3% for K_2O, 2.3% for CaO, 2.5% for Fe_2O_3, and 7.5% for Ti. Eight major elements, having mass percentage values > 0.2%, were considered for the characterisation of the sample chemical composition in the present study. Standard uncertainty (1σ confidence) for each elemental concentration had values < 2% (e.g. for Al, Si, Fe, K) or between 2% and

5% (e.g., for Mg, Ca, Na, Ti, C). For each of the investigated materials, the difference between the sum of fractions by weight and 100 % was assumed to be oxygen. The analytical results are given in Table 1, together with the known composition of the IAEA moss-soil (Iurian et al., 2016), for which only the total carbon content was determined independently for this study.

The total carbon content was determined combustiometrically using a calibrated TOC-V Analyser (Shimadzu). The quantitative accuracy (QC) for the analysis of total carbon was within required control limits. Instrument calibration was performed with L-Cystine (30% carbon content), while the CRM PACS-1 (issued by the National Research Council of Canada) was utilized as QC Material. Average of three replicate measurements of PACS-1 gave a relative difference of 2.9% by comparison with the certified value (Table 1).

3. Gamma-ray spectrometry

All gamma-ray spectrometric measurements were performed within the CORiF accredited laboratory (ISO9001:2008) from Plymouth University, United Kingdom. Measurements were started after an incubation time of 4 weeks after the samples were sealed, to achieve equilibrium between ^{226}Ra and ^{222}Rn and its progenies used for the evaluation of ^{226}Ra. Two Ortec gamma spectrometers were used for each sample type, namely: (1) an n-type coaxial HPGe detector, model GMX5083 (65 x 70 mm), with 50% relative efficiency, and (2) a well HPGe detector, model GWL170 (65 x 67 mm); both detectors cooled with liquid N_2. Each sample was positioned directly on the detector window, using a thin cellophane foil to avoid contamination of the detector head. Live time counting of each sample was carried out for about 48 h to achieve a statistically significant number of counts and a measurement uncertainty of about 10% or less for the 46.5 keV peak. Special care was taken to keep the counting conditions and set-up arrangement constant for all samples during analysis. The commercially available software from Ortec, GammaVision, was used for data acquisition, while the data analysis was performed

in EXCEL, in combination with Monte Carlo simulation with GESPECOR (Sima et al., 2001) and EFFTRAN (Vidmar, 2005). Both detectors were experimentally calibrated in efficiency using the 'in-house' secondary standard soil material (CSS5) in cylindrical and vial geometries (see Section 2). Massic activity results were corrected for background fluctuations, moisture content and for decay within the sampling time (for sediment samples) or the reference date (for the IAEA PTM samples). Variations in the background counts were determined by statistical interpretation of blank measurements obtained separately. Massic activity results are reported with their combined standard uncertainties at a 1σ confidence level, the latter being determined according to the Guide to the Expression of Uncertainty in Measurement JCGM 100:2008 (JCGM, 2008).

3.1. Self-attenuation corrections

Typically, environmental samples (including various soil and sediment matrices) are characterized by different densities and compositions, making it difficult to identify a particular elemental composition for a certain soil or sediment type (Kaminski et al., 2014). Therefore, depending on the content of higher atomic weight elements, there is a high probability of diverse values for ^{210}Pb self-attenuation between different samples. The same reasoning follows in the case of a sample and a calibration source having different photon-attenuation properties, and a correction should be applied through an efficiency transfer (ET) approach. In the case of a direct computation of sample counting efficiency using commercial Monte Carlo codes, the correction is no longer necessary.

The ET approach uses experimentally determined efficiency calibrations, corrected for differences in geometry, matrix composition and density between the calibration source and sample to be measured. This correction is performed through an efficiency transfer factor (ETF), defined as the ratio between the sample efficiency and the efficiency of the calibration source. Use of ET is recommended instead of direct computation of the efficiency for the sample of interest because most of the uncertainties (e.g. due

to unknown detector dimensions) inherent in the computed values of the efficiencies almost cancel out in the ratio, whereas the use of experimental values of the efficiency for the calibration source removes the necessity of accurate detector data. As for the actual study, the PTMs and the sediment samples were prepared in the same geometry as the calibration source (see Section 2), the calculated correction factors only accounted for differences in the sample matrix and its density.

Two methodologies were applied in the current work to assess the efficiency transfer factors and their derived uncertainties for the sediment and PTM samples:

(1) a semi-empirical determination of the ETF values based on: (a) the transmission method of Cutshall et al., (1983) for coaxial HPGe detectors in collimated conditions, and (b) following the simplified mathematical formula of Appleby et al. (1992) for well type HPGe detectors, using theoretical photon attenuation coefficients based on sample composition; and

(2) a Monte Carlo approach, using both GESPECOR (for both detector types) and EFFTRAN (only for coaxial detectors) dedicated codes.

Routinely, environmental laboratories may prefer to use semi-empirical approaches because of the simpler methodology involved for the ETF determination, which does not require any computing knowledge or, in most cases, information on the sample chemical composition.

3.1.1. Semi-empirical determination of the self-attenuation correction

For cylindrical geometries measured on the coaxial detector, the ETFs were determined following the transmission procedure proposed by Cutshall et al., (1983). A 'home-made' liquid ^{210}Pb source was prepared from a multi-nuclide standard solution in PETP vial geometry that was covered by a thin lead foil to reduce the angular distribution of the photon beam. The ^{210}Pb source was centred on the top of a cylindrical sample container placed on the detector. The same measurement arrangement and conditions (e.g. live time) were carried out for: (1) the ^{210}Pb source above an empty cylindrical container and (2) the

source above a low-activity soil sample in a cylindrical container with the same geometric and matrix characteristics as the calibration source (before spiking). For each ^{210}Pb source – sample arrangement, the measurements were repeated three times at three different live times, and the corresponding mean count rates, having a statistical uncertainty <1.5%, and their standard deviations were analysed. Measurements were performed for a minimum live time of 2,000 s. The uncertainties of the semi-empirical ET factors for the coaxial detector were propagated from the statistics of the net peak area of ^{210}Pb in the sample spectrum and the standard deviation of the mean count rates of the ^{210}Pb source – sample arrangements. The transmission factors were calculated using the formula given by Cutshall et al., (1983). For vial geometries measured on the well detector, the ET factors were calculated using the exponential function proposed by Appleby et al. (1992).

The mass attenuation coefficients, μ, were determined with XCOM: Photon Cross Section Data Base application (NIST, 2017) for all samples, using their XRF chemical composition given in Table 1. The combined standard uncertainty of the semi-empirical ET factors for the well detector was evaluated using the standard uncertainties of the XRF data for samples and calibration source, the assumed maximal deviation of the container filling height of ± 0.5 mm, and an uncertainty of 1% due to the model.

3.1.2. Monte Carlo computation of the self-attenuation correction

The self-attenuation of a gamma-ray passing through the sample matrix and its container, before reaching the crystal detector, can be theoretically calculated based on the physical models of interaction between gamma-rays and matter, and further on computed using Monte Carlo codes. Monte Carlo dedicated codes e.g. GESPECOR (Sima et al., 2001) and EFFTRAN (Vidmar, 2005) were used in the present work for checking the consistency of the semi-empirical approach. Two datasets of ETFs were obtained through GESPECOR computations, for both coaxial and well type detectors. EFFTRAN could

only be employed for the coaxial HPGe detector, based on the author's established knowledge, since the code had not been extended to allow computations for the well type detector.

ETF determinations were performed for PTM and sediment samples using the same input data for the both codes: (1) the chemical composition of each material, as determined by WD-XRF analyses, (2) sample density, (3) detector geometry and characteristics (provided by the manufacturer on request), (4) geometrical characteristics of each sample, and (5) the matrix composition, density and geometry characteristics of the CSS5 secondary standard. The combined uncertainties of computed ET factors were determined according to the Guide to the Expression of Uncertainty in Measurement (GUM) (JCGM, 2008) and following Sima and Lépy (2016), and included the uncertainties in chemical composition of both sample and calibrant, and an assumed maximal uncertainty for the container filling height of ± 0.5 mm for sample and calibrant. An additional uncertainty component of 1% was included to account for the intrinsic uncertainty of the model computation. It has been also checked that the presence of H or N in the matrix, up to 5% (resulting in a changing of the O contribution), and at the same sample density, will not have a significant influence on the derived ETFs (< 0.3%).In both geometries, two sets of ETF values were computed by GESPECOR: one set based on μ values derived from sample composition and density and another set using experimental values of μ obtained by a full simulation of the transmission measurements (Section 4.2).

3.2. Quality assurance

Quality control procedures are in place for both detectors used for this study, while external quality control is assured by regular participation in external proficiency tests: e.g. IAEA; National Physical Laboratory (United Kingdom), Max Rübner Institute Karlsruhe (Germany). Two PTM with similar matrix characteristics with the sediment samples (e.g. IAEA moss-soil and IAEA soil) have been used for the validation of ^{210}Pb massic activity determinations. Three measurements were performed on the

IAEA moss soil for each geometry (cylindrical and vial) and for each detector, and one measurement for the IAEA soil sample (Table 2). Student's *t*-test gave an agreement at 95% confidence level between the ^{210}Pb measured values and the reference values for both sample types and both detectors. The semi-empirical approach, described in Section 3.1.1 above, was employed for the evaluation of ETFs for both coaxial and well type detectors, and validated using the GESPECOR dedicated code for the well geometry, and both GESPECOR and EFFTRAN codes for the coaxial detector (Table 3).

4. Results and discussion

4.1. Self-attenuation corrections for well and coaxial type detectors

Massic activities of ^{210}Pb in sediment samples originated from a salt marsh monolith sequence had typical values for environmental sample materials, ranging from 76-139 Bq kg^{-1}. Student's *t*-test showed agreement (95% confidence level) between sediment massic activity results of ^{210}Pb, evaluated with the coaxial and well type detectors (see Figure 1). Relative differences between the values for the same material measured with the two gamma spectrometers were in a range from 0.3-22%, with most of the relative values <10%.

However, differences were observed in results originated from the two different detector types, with regards to their combined standard uncertainties. Uncertainty budget estimation was developed for each sample following Iurian et al. (2016), and using the semi-empirical determination of ETFs. Combined standard uncertainties of gamma-ray spectrometry results (1σ confidence) for sediment samples ranged from 6 – 13% for the cylindrical geometry, and from 7 - 18% for the vial geometry. Systematically higher uncertainties (due mainly to counting stantistics) were obtained for samples in the vial geometry measured with the well type detector, compared with the same sample material analysed in cylindrical geometries using coaxial detector, and for the same live time. The uncertainty component due to self-attenuation correction by the semi-empirical approach had a higher contribution to the total uncertainty

budget for the cylindrical geometry (4.5-11.7%) compared to the vial geometry (1.3%). Moreover, higher variability was observed between the relative uncertainty values of the ET factors derived using the transmission approach for the cylindrical geometry, while they appear to be relatively constant for the vial geometry.

The semi-empirical ET factor values estimated for the cylindrical geometry, using the transmission method, ranged between 1.23 and 1.34, while the values of the ET factors for the vial geometry measured with the well detector were in a range between 1.14 and 1.19. The higher values of the ETF factors calculated for the 46.5 keV energy of ^{210}Pb for, both cylindrical and vial geometries, might be surprising considering that a secondary soil standard prepared 'in-house' was used for the efficiency calibration of the gamma spectrometers (instead of the standard liquid solution), to minimize the self-absorption corrections for samples with identical geometrical characteristics to the calibrant. This erroneous approach is currently practiced in many environmental laboratories, thus avoiding consideration of the self-attenuation corrections for gamma-ray spectrometry measurements. We showed that this approach does not give the predicted results when using a saltmarsh sediment matrix, with very low apparent densities (sample densities ranged from 0.38-0.56 g cm^{-3} in both geometries). The density of the two secondary standards was 1.1312 g cm^{-3} (cylindrical geometry), and 1.0414 g cm^{-3} (vial geometry), respectively, significantly different than the density of the saltmarsh sediment samples. Differences in the matrix chemical composition between the soil secondary standard and the sediment samples are also evident for most of the analysed major heavy elements (excepting Al). For many of these samples, the differences in the content of certain elements exceeded 100% (e.g. Na, Mg, Ca, C), when compared with the soil standard chemical composition. The authors therefore emphasize the recommendation that particular attention should be paid to self-attenuation corrections for gamma-ray spectrometry measurements when low gamma energies are involved, even when 'in-house' standard materials (e.g. soil, sediment, epoxy) are being used.

When applying computational approaches (e.g. GESPECOR, EFFTRAN) for the ETF determinations, the contribution of the uncertainty component due to the self-attenuation correction to the total uncertainty budget seemed to be relatively low (1.5%) compared to the semi-empirical ET factor approach for cylindrical geometry. No significant difference was observed in the case of the vial geometry when using GESPECOR for the efficiency transfer computation. The relative uncertainty of the GESPECOR ETFs was approximately 1.1% for all samples, similar with the relative uncertainty of the semi-empirical ETF. This outcome was expected since, in both cases, the true chemical composition is needed for the estimation of the ETFs and thus the same uncertainty components are considered for the estimation of the ETF combined standard uncertainty (see Section 3.1).

Good agreement was found between the semi-empirical ETFs and those determined with the GESPECOR dedicated code, for sediment samples in both cylindrical and vial geometries (Figure 3). The maximum difference between the semi-empirical EFTs and the computed ETF values were about 3.7%, using GESPECOR, and 2.7% using EFFTRAN, for a cylindrical aluminium geometry of 15 mm height. The results agree well with the findings of Jodłowski et al. (2014) who compared the correction factors determined by the transmission method with those determined by the Monte Carlo simulations (MCNP4C code) for cylindrical containers and identical results were found for samples of 10 mm thickness, and about 5% difference for samples filled to a height of 30 mm. Vidmar et al. (2010) also showed that the differences between the results of the different computation codes used for efficiency transfer in the case of a soil sample did not exceed 3.1% when using a p-type detector, and 1.3% for n-type detector, at 45 keV.

There are fewer reports in the literature of correction factors for the vial geometry compared with the cylindrical geometry, since the latter is commonly used by most environmental laboratories. The maximum difference between semi-empirical and computed ETF values (GESPECOR) for the vial

geometry was found 1.9%. However, it is important to note that both approaches used WD-XRF analysis of the chemical composition for estimations of the ETF.

4.2. The determination of mass attenuation coefficients (μ) and ETFs based on transmission method and Monte Carlo simulation

The Cutshall method assumes that all gamma rays emitted by the sample matrix have a parallel trajectory for both cases of sample and transmission measurements, and thus involving the use of the 'attenuation' formula for parallel beams. In reality, the photons escaping the sample matrix follow a range of trajectories at different angles in both cases, and thus the true gamma-rays attenuation does not agree the Cutshall formula for parallel beams. However, the attenuation approximations are made by Cushall for both the sample measurement and for the transmission measurement and thus they partly compensate each other giving a better result than using the formula separately (Sima and Arnold, 2002). In case the gamma beam follows a parallel direction (condition obtained through the use of a collimated transmission arrangement), the attenuation approximations discussed above do not compensate anymore and the final ETF uncertainty is greater than the one for an uncollimated gamma beam.

In fact, in our transmission measurements, the conditions of the parallel beam were not fulfilled and the μ values determined using the experimental transmission data (further called' semi-empirical') and the parallel beam attenuation formula (1) are clearly overestimated (see Table 4).

$$I_s/I_0=\exp(-\mu*h) \quad (1)$$

where I_s/I_0 is the background-corrected peak count rate for the transmission measurement arrangements source – sample, I_s and the source - empty sample container, I_0. The maximum difference between the 'semi-empirical' μ and μ computed using the chemical composition of the 19 sediment samples (given in Table 1) was as high as 25% (see Table 4).

The experimental transmission data were used to infer experimental values of μ after a full simulation of the transmission measurement, carried out with GESPECOR. The μ values determined in this way are much closer to the μ values derived from the material chemical composition (maximum difference between the two μ values was about 5%). Moreover, the ETF values derived using the μ transmission data are within a maximum of 3% difference from the ETF values based on chemical composition for the coaxial detector (see Table 4); in the case of well detector the differences are less than 2%.

4.3. Simplified approaches for self-attenuation corrections applicable in dating of sediment core

Using the semi-empirical approach of Appleby et al. (1992), combined with the WD-XRF analysis of the matrix chemical composition and the XCOM tool for deriving the correction factors of ^{210}Pb for vial geometries, a good agreement was obtained with the computed ETF values (GESPECOR). Nevertheless, for geochronology applications this method is costly in time, particularly where many samples are generated from the high resolution sectioning of a sediment core. Furthermore, the variability in chemical composition and density (factors controlling the self-attenuation corrections and involved in the semi-empirical ETF determination for vial geometry) among the sediment samples was analysed to develop a simplified approach which can deliver similar results for the semi-empirical ETF values for cylindrical and vial geometries.

The apparent density of the sealed sediment samples, g cm^{-3}, was determined individually for each sample using the geometrical characteristics of the sample container and the sample filling height. A significant (2-tailed) negative Pearson correlation was found between the sample apparent density and the semi-empirical ETF values (n=19 samples) for both cylindrical ($r = -0.9688$, $p < 0.0001$) and vial geometries ($r = -0.9814$, $p < 0.0001$) (see Figure 4). For the cylindrical geometry this type of correlation can be successfully employed to determine ^{210}Pb self-absorption corrections for unknown samples of similar geometry, with density values within a range of apparent sample densities. However, the

generalization of this approach must be used with caution and only for samples within a limited range of compositions, to keep the correlation function linear. The method has been already used by other authors (Bolivar et al., 1996) and therefore it will not be the subject of a detailed discussion in the present work. As regards the vial geometry, this approach does not bring major simplifications, as the chemical compositions are still needed for a range of samples with different apparent densities.

To reduce the time, and cost, of the determination of ETF values for the well detectors, we analysed the possibility of replacing the sample chemical composition with average elemental values of the investigated sediment core sequence (19 cm long). The concentrations of major elements within these 19 sediment samples have relatively narrow ranges (Table 1). Higher variations between the elemental mass percentages within the chemical composition of the sediments were only observed for Ca (elemental concentration in a range of 0.46-0.23%) and Fe (elemental concentration in a range of 4.9-7.7%), while other heavy elements had a relative standard deviation with the mean value <6.5% (Figure 5). The relative total carbon content varied between sediment layers in a range between 7.1% and 14.0%.

The ETF values were recalculated for each individual sample using the average chemical composition of 19 sediment samples (see Table 1), while keeping unchanged the specific apparent density of each sample. The uncertainties of the mean elemental values were derived from the standard deviation of the mean. The differences in resulting correction factors were analysed in comparison with the individual ETF values obtained using the true sample chemical composition. For the vial geometry, the maximum deviation between the ETFs determined with the mean chemical composition and the ETFs calculated using each individual matrix composition was less than 1%, much lower than the errors introduced by neglecting the self-attenuation corrections. The results indicate that for a sediment column of 19 cm length, it is appropriate to adopt an average chemical composition as a simplified approach to correct for the self-attenuation effects in gamma-ray spectrometry, when employing vial geometries in a well type detector. However, it is important to keep in mind that analysis of the chemical composition of selected

samples within the sediment column are still necessary when deriving the ETFs, using either the semi-empirical or the Monte Carlo approach.

5. Conclusions

Semi-empirical approaches for self-attenuation corrections of the ^{210}Pb gamma line are discussed in this work for coaxial and well type detectors. Both approaches were successfully validated using IAEA PT materials containing ^{210}Pb and compared against Monte Carlo dedicated codes (e.g. GESPECOR, EFFTRAN). These were further applied to the determination of ^{210}Pb massic activities in sediment sample materials in cylindrical and vial geometries and good agreement (Student *t*-test) between the activity concentrations of ^{210}Pb was achieved. Combined standard uncertainties of gamma-ray spectrometry results (1σ confidence) were higher for samples in vial geometries, measured with well type detector, compared with the same sample matrix measured in cylindrical containers with coaxial detector, under similar measurement conditions.

The high ETFs determined for both geometries highlighted the need for self-attenuation corrections in gamma-ray spectrometry of ^{210}Pb, even when secondary soil standards are being used for detector efficiency calibrations, as these may have a different density and/or chemical composition compared to the analyzed samples. As regards the contribution of the uncertainty component due to semi-empirical self-attenuation corrections to the total uncertainty budget of the ^{210}Pb massic activity, this was higher for cylindrical geometries (4.5-11.7%) compared to the vial geometry (~1.3%).

The transmission approach gave accurate results for cylindrical containers filled to a height of 1.5 cm when compared with Monte Carlo computed methods (GESPECOR and EFFTRAN), with no need of other techniques that gamma spectrometry itself. In the case of the well detector using vial geometries, the application of a semi-empirical formula resulted in very good agreement of the ETF values with the GESPECOR derived ETF data; however, additional information on the sample matrix composition was

required for the ETF evaluation. The transmission approach was also successfully employed in combination with Monte Carlo modelling (GESPECOR) for the determination of mass attenuation coefficients and ETFs, the results of the later term being as close as 3% to the ETF values determined using the true sediment chemical composition.

It was showed that, when dealing with ~ 20 cm sediment cores, relative narrow ranges were found in the mass fractions of the major elements contained by the sediments. Therefore, an average chemical composition (mean mass attenuation coefficient) of the investigated sediment sequence can be successfully employed for the ETF determination with well type detectors, while using the apparent density of each sample contained in the sediment sequence. For cylindrical geometries, the correlation between the sample apparent density and the semi-empirical ETFs can be successfully used to determine ^{210}Pb self-absorption corrections for unknown samples of similar geometry within a range of apparent sample densities.

Special consideration should be taken into account when combining 2-3 sediment cores and/or using different types of gamma detectors to reconstruct ^{210}Pb geochronology. Neglecting ^{210}Pb self-attenuation corrections in ^{210}Pb dating can lead to various ages and/or sedimentation rates, with more prominent differences for samples affected by strong self-attenuation corrections.

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Figure caption:

Figure 1. Relative differences between massic activities of ^{210}Pb in sediment samples measured with coaxial detector (cylindrical containers) and with well type detector (vial geometries). Combined standard uncertainties are given at 1σ confidence.

Figure 2. Semi-empirical efficiency transfer factors (ETF) for sediment samples in cylindrical and vial containers. Standard uncertainties for reported values are given at 1σ confidence.

Figure 3. Semi-empirical efficiency transfer factors (ETF) for sediment samples in cylindrical (a), and vial (b) containers, plotted against the ETF determined with GESPECOR.

Figure 4. Semi-empirical efficiency transfer factors (ETF) for sediment samples in cylindrical (a), and vial (b) geometries, plotted against the sample apparent densities.

Figure 5. Depth distribution of elemental content (Ca, Fe, C) in sediment samples originated from a monolith sequence.

Table captions:

Table 1. Major chemical constituents (metals and total C) of the secondary soil standard, IAEA PT materials and saltmarsh sediment samples determined by WD-XRF and Carbon Analyser. Standard uncertainties for reported values are given at 1σ confidence.

Table 2. Comparison between the measured ^{210}Pb massic activities (Bq kg^{-1}) in IAEA moss-soil and IAEA soil PT materials, decay-corrected with the reference time, and their IAEA reference values. Semi-empirical efficiency transfer factors were used. Uncertainties are given with a coverage factor k=1.

Table 3. Semi-empirical and computed efficiency transfer factors and associated uncertainties for ^{210}Pb in IAEA moss-soil and IAEA PT materials.

Table 4. The determination of mass attenuation coefficients (μ) and ETFs based on the transmission measurements and GESPECOR Monte Carlo computation.