



Radiological environmental monitoring of groundwater around NPP: A proposal for its assessment

S. Petisco-Ferrero, R. Idoeta^{*}, S. Rozas, C. Olondo, M. Herranz

Dpt. Ingeniería Energética, University of the Basque Country UPV/EHU, Escuela de Ingeniería de Bilbao, Plaza Ingeniero Torres Quevedo, 1. 48013, Bilbao, Spain

ARTICLE INFO

Keywords:

Radionuclides in groundwater
Detection limit
Radiological environmental monitoring
Nuclear power plant dismantling and decommissioning

ABSTRACT

Whether a nuclear installation has radiological impact and, in that case, its extension, are the questions behind any environmental analysis of the installation along its operational life. This analysis is based on the detailed establishment of the radiological background of the area.

Accordingly, the dismantling and decommissioning process (D&D) of a nuclear power plant starts with a radiological monitoring plan, which includes the radiological characterization of the area and of its surroundings. At the completion of the D&D, unrestricted use for the site will be permitted strictly in accordance with results of the radiological survey within the limits established by the local authorities.

Groundwater quality is typically included in any radiological analysis since, among other reasons, a significant part of it is highly likely to end up being extracted for domestic use and hence, human consumption.

While there is no regulation containing maximum activity concentration or radionuclide guidance values for water that may be destined for uses other than public consumption, if groundwater is considered a “part” of the land, dose criteria for site release can be applied. Therefore, together with the guidance levels to be established for the different radionuclides expected in the groundwater, the detection limits to be employed when performing routine radio analytical characterization procedures in the laboratory should also be provided.

In this paper, we first propose a relation of the potential radionuclides to be analyzed in groundwater, together with their detection limits to be achieved when the determinations are performed in a laboratory, and subsequently, we discuss the most suitable analytical methodologies and resources that would be necessary to undertake radiological characterization plans from a practical point of view.

1. Introduction

As part of the safety commitment to workers, the public and the environment of all nuclear power plants, a detailed site assessment is required to evaluate the interactions between the environment and the nuclear installation, not only for operational and accident conditions, but also for decommissioning [1].

As the analysis of the interactions is based on the activity concentration of some radionuclides present in the different

^{*} Corresponding author.

E-mail address: raquel.idoeta@ehu.es (R. Idoeta).

<https://doi.org/10.1016/j.heliyon.2023.e19470>

Received 30 March 2023; Received in revised form 17 August 2023; Accepted 23 August 2023

Available online 28 August 2023

2405-8440/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

environmental sectors, such as air, water, soil, biota, or foodstuffs, that might potentially be affected by the nuclear installation, the definition of which radionuclides should be considered is one of the main points of what is known as the radiological characterization of the area.

Accordingly, the aim of the radiological characterization prior to the commissioning of the nuclear plant is to establish the radiological background of the area [1–4] so that a conclusion upon the occurrence of the radiological impact associated with the operational and functioning period of the installation, and in that case, upon its extension [3], can be unambiguously reached.

Control systems for the continuous inspection of the radiological impact are implemented at all nuclear power plants under the Radiological Environmental Monitoring Plans (REMPs) of the facilities. In addition, different on-site measuring plans are developed and implemented.

There are different types of REMPs, depending on the stages of the nuclear installation, but it is always the competent Regulatory Authority who must give the guidelines for their implementation and approve them.

In general, those established in the surroundings of the installations, for which the licensees are responsible for its realization following the guidelines of the Regulatory Authority competent in the matter, depend on the type of installation and on some characteristics of the site such as demography, land and water uses, as well as habits of the population. The other type of REMPs, the national programs, are drawn up in the different countries developing specific plans depending on their needs, the characteristics of their facilities and resources. For example, in Europe they are drawn up taking into account the agreements reached in the framework of Articles 35 and 36 of the Euratom Treaty [5]; in view of the different practices followed by the Member States, the Commission of the European Union drew up a recommendation on the minimum scope of these programs, which was published in the Official Journal of the European Communities on July 27, 2000 [6].

After the shutdown, the process of dismantling and decommissioning (D&D) of the nuclear power plant is initiated, and the timing depends on the D&D approach selected by the plant owner. During the D&D process, which consists of several phases, major civil works are performed. As such, the structural demolition of the plant is executed when the high-level waste and, therefore, the most hazardous waste has already been removed from the plant. Although the D&D process is carried out in a tightly controlled manner, again a radiological monitoring plan adapted to it must be implemented to ensure that no contamination of the area or the environment occurs [7,8]. The last stage of the D&D is the final release of the site for its unrestricted use. To reach this goal, compliance within the limits established by local authorities must be demonstrated. Hence, it is necessary to perform a complete radiological survey of both the site and the environment around it, which at this stage includes the measurement of direct radiation levels as well as the determination of the concentration of potential radionuclide contaminants in the construction materials and in the soil near the nuclear site [4]. Furthermore, groundwater should also be included in this survey [3].

From the above, it follows that radiological monitoring plans should begin years before the plant is commissioned and continue through its operational time, the years following its shutdown and, finally, in the course of its decommissioning [3,4].

At this point it should be mentioned that the scope of the environmental and site monitoring plans changes as the life of the plant evolves and depends on the characteristics of the plant. Hence, the radionuclides that are determined before the plant is put into operation are not necessarily the same ones determined during routine operation, with the most rigorous plan carried out through the different stages of the D&D process. As such, before the operation of the plant, most of the expected radionuclides will be of natural origin, while during the functioning or at the decommissioning, the sought traces will be chiefly of artificial radionuclides, that is, the ones produced in the Nuclear Power Plants (NPP).

In this sense, it must be mentioned that although radionuclides that may be released from nuclear installations have an anthropic origin, some of them have also natural origin, like H-3, C-14 and some uranium isotopes.

In addition, the determination of any release that could occur is also a secondary method of analysing the correct operation of the plant. In particular, guaranteeing that a plant does not emit substances which have not been previously authorized qualitatively and quantitatively constitutes a system that allows the detection of any minor radiological incidents in the operation of the plant.

Among the environmental areas studied in the aforementioned plans, water is of paramount importance due to its great capacity to transfer substances contained therein to other environmental segments and transport them over long distances. In addition, a significant part of natural surface and groundwaters ends up being exploited for domestic use or irrigation and hence, human consumption [6,8–12].

During the routine operation of the nuclear power plants, radionuclides are released in the freshwater environment in a controlled manner, and always under authorization, both through the water exiting the cooling system and in the condensation gases from the cooling towers. A historical database on discharges of radionuclides is available to the public by the International Atomic Energy Agency (IAEA) [13]. Thus, relevant data to characterize the hydrogeological and hydrological parameters at the site and in the region need to be gathered to permit the determination of the potential movement of radionuclides through surface water and groundwater, and the subsequent assessment of the radiological impact. In particular the dilution and dispersion characteristics of water bodies, the migration, retention and transfer mechanisms for radionuclides in the hydrosphere [14–16] as well as the associated exposure pathways, constitute a safety requirement in the evaluation of the potential effects of the nuclear installation on the region, human beings and other biota [1].

Among the water bodies, the most intensive monitoring plans are usually applied to groundwater. Since an aquifer may be fed by means of surface water as well as by complex underground drainage systems and caves, the radioactive contamination in it may have different origins, ranging from direct deposition by air, to direct contamination via the water in the plant cooling circuit or through the migration of radionuclides deposited in the ground by any route. Therefore, since the renewal of the water within each aquifer is a very specific feature of each one, so is the evolution of the radiological contamination at a given point within it.

Consequently, hydrogeological investigations must include descriptions of the main characteristics of the water-bearing formations

and their interaction with surface water, as well as data on the uses of groundwater in the region [1,17]. The fate of the nuclides is influenced by the physical and chemical properties of the environment. Radionuclides speciation is also dependent on their origin, natural or anthropic. In the case of aquifer, the mobility of a nuclide strongly depends on its respective charge and the composition of mineral surfaces and dissolved species.

Some case studies that exemplify the transport phenomena from the release of radioactive materials from different sources terms up to groundwater and the ultimate drinking of transported radionuclides can be found in chapter 5, “Transport of Radionuclides in Groundwater” [18], in chapter 18 “Modeling of Radionuclide Transport in Groundwater” [19], which contain some case studies, or [20,21]. The bibliography states that the analysis and monitoring of groundwater should be performed not only during the lifetime of the NPP but also during its D&D process [1,3].

The maximum permissible concentrations of radionuclides, both in the cooling system water and in gaseous emissions, are well defined by different national and, more generally, by international regulations, as International Atomic Energy Agency ‘Convention on Nuclear Safety’ and the corresponding control systems are strictly implemented [1,22–26].

In the case of drinking water or water for public consumption, there is a fairly broad consensus [27], and considerable documentation which includes European directives [28,29], whose requirements have been transferred to most of the European national legislations. In these, the guidance values for a set of radionuclides of interest, likely to end up in drinking water, as well as the detection limits to be used in their determination are well established. There, the guidance values represent the concentration of a constituent that does not result in any significant risk to health for the public over a lifetime of water consumption, based on the dose limit of 0.1 mSv/year.

However, equivalent documentation or regulation for water that may be exploited for other uses is lacking. To name some examples, dose criteria for site release are gathered in Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) [4] and the IAEA [3], but are not specific for water. Some national and international regulations [30], which include groundwater as a “part” of the land, establish dose limits for the release of the land of an installation again with the criterion of 0.1 mSv/year. In NUREG 1757 [8, 12], in compliance with License Termination Rule (LTR), leading to unrestricted use of building structures, systems and components, as well as all other media (i.e., soils or groundwater), the total effective dose must not exceed 0.25 mSv/y. See Table 1 for a summary of the dose limits for water established by different organizations and regulators.

From the aforementioned dose criteria, the maximum activity concentration permissible for each one of the radionuclides that can potentially exist in the water can be typically established.

Most of the determinations of the radionuclide activity concentrations are performed in specific laboratories where for most of the determinations, complex processes to isolate the radionuclide must be completed to prepare the sample before its usual determination by means of radiometric equipment (gamma, beta and alpha spectrometry and counters).

It must be considered that some radionuclides, most of them of natural origin, can appear to a variable extent not only in the sample, but also in the chemicals and other materials used for the sample preparation, as well as in the radiometric equipment and in the environment. The signal coming from these radionuclides, together with spurious electronic signals, constitutes the measurement background signal, which can be variable for each sample. Often, the activity being determined in a sample exhibits values very close to the measurement background, making the discrimination between induced radiological impact and background from the signal a challenge. In such cases, the uncertainty in measurements as well as the Detection Limit (DL), sometimes referred to as the Minimum Detectable Activity (MDA), are of utmost importance.

For the sake of ease of calculations, guides to the expression of uncertainty in measurements have been developed by specifically addressed working groups. In this paper, we refer to the guide from the Joint Committee for Guides in Metrology [33].

Regarding the detection limit, it is defined as the smallest true value of the measurand that ensures a specified probability of being detectable by the measurement procedure. An alternative definition defines the smallest true value of the measurand as that for which the probability of incorrectly deciding that the true value of the measurand is zero is equal to a specified value, when, in fact, the true value of the measurand is not zero. Despite the general agreement on this definition, with respect to its numerical evaluation, different formulations and approaches have been presented over the years [34,35] all of which are based to a greater or lesser extent on the general formulation proposed by Currie [36]. However, in recent years, the formulation and evaluation mechanism presented in ISO 11929 [37] has been increasingly considered as that in common use and evermore countries are requesting for it in their regulations as a standard form for DL assessment to be used by laboratories/agencies in charge of radiological monitoring.

At this point, it should be highlighted that the detection limit depends, as will be shown in more detail below, on many factors, such

Table 1
Annual effective dose equivalent limit established by different organizations.

Organization	Scenario	Limit on annual effective dose equivalent	Reference
WHO	Drinking water	0.1 mSv	[27]
European Commission	Drinking water	0.1 mSv	[28]
IAEA	Drinking water	1 mSv	[31]
US DOE	Drinking water supplies operated by or for the DOE, not including naturally occurring radiation sources	0.04 mSv	[32]
US NRC	Criterion for license termination of nuclear facilities with unrestricted release, including the residual radioactivity from groundwater sources of drinking water	0.25 mSv	[8,12]

as the measurement background, the counting time, the volume of the sample being treated, and the performance of the process. Therefore, the detection limit is inherently variable for each type of determination, as are the background and other parameters. Consequently, in the field of radionuclide determinations, for any result to be meaningful, not only uncertainty must be stated but also the DL.

From the above, the question of the definition of the maximum DL that needs to be achieved for any particular radionuclide is raised. Although the question seems to have a straightforward answer: for each radionuclide relevant to the case or facility, the established DL, being far below the guidance levels, must be such as to meet the objective of the survey, enhancing the determination of the guidance levels as stated in the legislation. However, as explained above, in the case we are dealing with, namely, the analysis of groundwater in the area of influence of the NPP, neither the guidance levels nor their corresponding detection limits are established in specifications.

Quotation of the maximum values for the detection limits is of paramount importance for the laboratories responsible for undertaking the radiological plans, as parameters like the sample volume to be used or the measurement time depend on the DL to be achieved. Furthermore, depending on the required DLs, the capability of a laboratory to provide meaningful results can be seriously compromised; at its worst, the whole method of determination would be inappropriate to achieve the required detection limits.

In this paper, we propose a recommendation for the detection limits to be required by the corresponding regulatory authorities when performing routine radio analytical procedures for radiological monitoring of groundwater by using laboratory procedures.

For that aim, according to the type of the NPP and the stage of its operating life, we propose a list of the most likely artificial radionuclides to be eventually found in groundwater around NPP in the frame of specific radiological monitoring plans.

Next, starting from the most conservative annual effective dose (0.01 mSv to the population in the event of contaminated water ingestion), and applying the reasoning described in the Guidelines for drinking-water quality of the World Health Organization (WHO) [27], we determine a set of activity concentration levels for the listed radionuclides following the methodology used by WHO to determine the guidance levels. We make a proposal for their corresponding detection limits as 10% of the obtained activity concentration levels to be attained by the laboratories in charge of the radiological determinations. Finally, and from a practical standpoint, we suggest the most suitable analytical methodologies and resources necessary to undertake the radiological monitoring plans in the water bodies under the required conditions.

2. Methods

When referring to the impact of a nuclear power plant, we mean the radionuclides that may appear in the environment, both during its operational period and during the decommissioning activities following its shutdown.

The released radionuclides provide a radiation dose in individuals either by external irradiation or by ingestion or inhalation. When dealing with groundwater, the origin of the dose to the population will be either by direct water ingestion or by the transfer of the radionuclides contained therein to other compartments, environmental or not. In a conservative estimate of the impact, the worst-case scenario would be that where contaminated groundwater is directly drunk.

Under these circumstances, we show how to obtain the activity concentration levels or maximum desirable activity concentration for each radionuclide, and under what conditions. Then we will introduce the expressions to obtain the detection limits.

2.1. Activity concentration levels

To define the activity concentration levels, here the same method as WHO has followed to define the guidance levels for drinking water has been followed. Assuming that people could drink directly from contaminated groundwater, the calculation of the annual effective dose due to ingestion of radionuclides by drinking water consumption by people (adults) would be obtained using values for consumption of drinking-water [27] and ingestion dose coefficients for adults [38]. The equation for the annual effective committed dose is Eq. (1):

$$E(50) = \sum_j e_j(50) \bullet I_{j,ing} \quad (1)$$

Where,

$E(50)$ is the annual effective dose $\left(\frac{mSv}{year}\right)$.

$e_j(50)$ is the committed effective dose coefficient for ingestion of radionuclide j for members of the public $\left(\frac{mSv}{Bq}\right)$. These coefficients for all age groups, including children and infants, are provided by the International Commission on Radiological Protection (ICRP) [38].

$I_{j,ing}$ is the activity intake of a radionuclide j by ingestion, calculated by using Eq. (2):

$$I_{j,ing_j} = A_j \bullet C_j \quad (2)$$

Where,

$A_j \left(\frac{Bq}{litre}\right)$ is the radionuclide activity concentration in drinking-water of radionuclide j

$C_j \left(\frac{litres}{year}\right)$ is the consumption rate of drinking-water for adults; assumed to be 2 litres/day for adults [27].

According to the guidelines of WHO [27] regarding situations of prolonged radiation exposure of the public, in planned exposure situations (according to IAEA [38], exposure to radionuclides due to ingestion of drinking-water in non-emergency situations is regarded as an existing exposure situation) it is prudent to restrict the prolonged component of the individual dose to 0.1 mSv in any given year [27] (a value ten times lower than the regulatory dose limit for members of the public. In this sense, and following the WHO definition for guidance levels, activity concentration level (ACL_j) for each radionuclide is defined as that radionuclide concentration that, at an intake of 2 litres/day for 1 year, will result in an effective dose of 0.01 mSv/year [27]. Then, each ACL_j are obtained by using expression of Eq. (3)

$$ACL_j = \frac{0.01}{e_j(50) \bullet C_j} \quad (3)$$

for radionuclide j.

If several radionuclides are identified, then the sum across radionuclides needs to be considered to check that it does not exceed unity, i.e., to check if the individual effective dose of 0.01 mSv/year has not been exceeded. The equation to use is Eq. (4):

$$\sum_j \frac{A_j}{ACL_j} \leq 1 \quad (4)$$

as established in the Guidelines for drinking-water [27].

2.2. Detection limit calculation

The formulation for the detection limits strongly depends on the uncertainties and on the decision threshold parameters.

2.2.1. Uncertainty

The general expression for the uncertainty evaluation comes from the Guide to the expression of uncertainty in measurement (GUM) [33], following the law of propagation of uncertainty.

Then, if a measurand y is not directly measured, but is determined from N (other quantities: $x_1, x_2, x_3, \dots, x_N$) through its relationship function [Eq. (5)]:

$$y = f(x_1, x_2, \dots, x_N) \quad (5)$$

If these quantities are not correlated with each other, then, the combined standard uncertainty of y, $u_c(y)$, is the positive square root of the combined variance $u_c^2(y)$, which is given by Eq. (6):

$$u_c^2(y) = \sum_{i=1}^N \left[\frac{\partial}{\partial x_i} \right]^2 u^2(x_i) \quad (6)$$

This general case is the most common for the radiometric techniques used in radioactivity measurement laboratories and its application will help determine the uncertainty of the activity concentration, which, in this case, will be our y.

It must worth noting that among the different variables which may affect the measurand and which are being evaluated, in addition to the signal provided by the equipment in the measurement of the sample, all those factors related to the calibration of the equipment, the preparation of the sample and the background signal will be at play.

2.2.2. Decision threshold

The expressions for the calculation of the decision threshold come from the ISO standard 11929 [37], where,

The decision threshold, y^* , is defined by the condition that the probability of obtaining a primary measurement result, y, which is larger than the decision threshold, y^* , is equal to α if in reality the true value, \tilde{y} , is zero.

If GUM [33] is used to obtain the evaluation of the uncertainty, then [Eq. (7)]

$$y^* = k_{1-\alpha} \tilde{u}(0) \quad (7)$$

with $k_{1-\alpha}$ being the $(1-\alpha)$ quantile of the standardized normal distribution and $\tilde{u}(0)$ is the uncertainty of the measurand when its value is zero.

2.2.3. Detection limit

The expressions for the calculation of the detection limit come from the ISO standard 11929 [37] where,

The detection limit, $y^\#$, is defined by the condition that the probability of obtaining a primary measurement result, y, that is smaller than the decision threshold, y^* , is equal to β if in reality the true value, \tilde{y} , is equal to the detection limit, $y^\#$.

If GUM [33] is used to obtain the evaluation of the uncertainty, then [Eq. (8)]

$$y^\# = y^* + k_{1-\beta} \tilde{u}(y^\#) \quad (8)$$

with $k_{1-\beta}$ being the $(1-\beta)$ quantile of the standardized normal distribution and $\tilde{u}(y^\#)$ is the uncertainty of the measurand when its

value is equal to the detection limit.

Values of $\alpha, \beta = 0.05$, being in this case $k_{1-\alpha} = k_{1-\beta} = 1.65$, are often chosen by default.

As follows, the decision threshold and thus the detection limit is background dependent.

Accordingly, the detection limit established in such a way should be fit for purpose, meaning that it should be able to meet the objective of the monitoring plan so that the measured concentration values are clearly distinguished from the activity concentration levels for each radionuclide, considering the uncertainties associated to those measured values. In other words, under routine laboratory operating conditions, the achievable detection limits should be set at concentrations lower than the activity concentration levels.

In this sense, one of the recommended practices in MARSSIM [4] is to work with methods that provide detection limits that are set between 10 and 50% of the guidance levels. Furthermore, WHO [27] sets detection limits for chemicals between the guideline value and 1/100th of its value.

In this paper, we propose to achieve detection limits (derived detection limits, $Dy^{\#}$) that are 10% of the corresponding activity concentration levels in accordance to WHO [27] for radioactive concentration in drinking water.

3. Expected radionuclides in the NPP and in the environment

According to the IAEA Safety Guide 1.8 [39] one of the main objectives of any Radiological Environmental Monitoring Plan is to provide data for dose assessment purposes of radionuclides in the environment originating from nuclear practices.

Therefore, radiation-monitoring programmes entail measurements of radionuclide content in the media of release and in the environmental samples and, in very rare cases, in the human body.

These measurements largely depend on the characteristics of the release (the source, medium, rate, radionuclide composition and radionuclides physical and chemical form) and the environment of the area potentially contaminated with radionuclides. Hence, for the environmental radiological monitoring, specific programmes are applied at the different stages of a nuclear facility: pre-operational stage, operational stage, and D&D stage.

In this section, the radionuclides that are susceptible to be measured in groundwater at different NPP operation stages are summarized. In this paper, noble gases are not considered given their low capacity, due to their high diffusivity, to be transferred to groundwater, which is the subject of this paper [40]. Radionuclides with a half-life of less than 24 h are also not considered in this section. Limiting this study to radionuclides with a half-life >24 h has been considered a reasonable hypothesis taking into account that the transfer of radionuclides from the source term to the groundwater is highly variable as it will depend, in the first place, on the specific radionuclide but also on the source term and the physical structure of the nuclear power plant; once the radionuclide is outside the plant, the transfer will depend on the type of soil, its composition, structure and permeability, but also on the location of the repository, or groundwater flow, with respect to the point of entry of the radionuclide into the environment. Bearing in mind that what is being analyzed in this work is the impact on people derived from the ingestion of these radionuclides, it has been considered that the probability that radionuclides with a half-life <24 h produced in the plant will travel through the plant and the environment to reach the point of ingestion can be considered negligible.

It should also be noted that not all of the radionuclides summarized here are necessarily measured; the definition of the radionuclides to be monitored will depend on the history of the NPP, the incidents and problems at the plant or the radionuclides detected during its operation. Moreover, it must be considered that these radionuclides may vary throughout the life of the NPP, depending on the results obtained at different stages.

In addition, it must be highlighted that, activity determination of all these radionuclides is not always feasible due to their short half-life, the low activity concentration and in some cases, its difficulty in measurement, which can be caused by the physical or chemical form, solubility, difficulties in the chemical isolation or spectral issues of the radionuclides in question. In these cases, the activity of these radionuclides is determined using correlation analyses. For example, Thierfeldt and Deckert [41] define two key radionuclides, Co-60 and Cs-137, and establish correlations with many radionuclides, such as C-14, Cl-36, Ca-41, Ni-59, Ni-63, Mo-93, Tc-99, I-129, Cs-135, Np-237, Pu-241 and Am-241.

3.1. - Pre-operational stage

Pre-operational radiological environmental monitoring programmes are performed to establish the 'baseline' environmental radiation levels and activity concentrations. This information permits the subsequent determining of the NPP impacts.

Preoperational assessments are made considering expected inventories of radionuclides during operation and D&D of a nuclear facility, which are described in sections 3.2. and 3.3. The possible discharge pathways and the expected amounts that will be discharged to the environment must also be considered.

The preoperational studies should also provide basic environmental data for use in the prediction of doses to the public and discharges to the environment.

3.2. - Operational stage

Operational stage of a nuclear facility is understood as the period of time between the first fuel load into the reactor and its shutdown.

In the operational stage of the most common nuclear reactors, LWR (Light Water Reactor), NPP radionuclides are found in three

main components: the nuclear fuel, the reactor structural materials and the coolant. Among them, those appearing in the coolant are those most likely to appear in the environment.

In nuclear fuel, fissions and neutron captures of U-235, U-238, Pu-239 and Pu-241 can produce many different nuclides, which can lead to other active nuclides by radioactive decay processes. However, the accurate content of radionuclides in the nuclear fuel depends on several aspects, such as the fuel type, the reactor type, the irradiation history, and the fuel management.

The main radionuclides in the reactor structural materials – such as stainless steel and alloys – are produced by activation of trace amounts of Cr, Mn, Fe, Co, Ni, Zn, Zr, Mo and Ag producing the following radionuclides: Cr-51, Mn-54, Fe-55/59, Co-58/60, Ni-63, Zn-65, Zr-95, Mo-99 and Ag-110m [42]. These radionuclides may also be encountered in the coolant passing through the reactor core, from corrosion of the structural materials.

In the coolant, relevant radionuclides are the activation products of the structural materials and H-3, which is generated by ternary fissions and by different nuclear reactions with isotopes from the coolant additives, water, and air. These radionuclides appear summarized in the ANSI/ANS-18.1-1999 standard [43]. Those that meet the condition of having a half-life of less than 24 h and not being a noble gas are listed in Table 2.

ANSI standard also establishes typical long-term concentrations of the principal radionuclides in fluid streams of LWR NPPs, for use in estimating the expected release of radioactivity from the coolant. These concentrations, related to the radionuclides considered in this text and for a reference boiling water reactor (BWR) and pressurized water reactor (PWR) are also shown in Table 2.

The above radioactive inventories from the coolant of LWRs are in clear agreement with the real liquid discharges recorded in the IAEA Database on Discharges of Radionuclides to the Atmosphere and the Aquatic Environment (DIRATA) [13] from NPPs in normal operation. For example, as shown in DIRATA, when liquid discharges from French NPPs between 1965 and 2008 are analyzed, many of the radionuclides from Table 2 were present in the releases.

An extension of the IAEA's classic 1975 list for the radionuclides usually monitored in water in the operational radiation monitoring programmes [44], is provided in ANSI [43] where the radionuclides to be measured in water are: I-131, Cs-134, Cs-137, H-3, Mn-54, Co-58, Fe-55, Fe-59, Co-60, Ni-63, Zn-65, Sr-90, Zr-95, Nb-95, Ba-140, La-140 and Ce-144.

Discharges of radionuclides to a natural body of water during NPP normal operation come from the treatment system of radioactive liquid waste, after being collected by an active plant drainage system.

Table 2

Typical long term activity concentration of main radionuclides in fluid streams of BWR and PWR reactors. Values are in Bq g⁻¹ [43]. *Short half-life radionuclides in radioactive equilibrium.

Nuclide	BWR water	PWR coolant	PWR secondary coolant
	Bq g ⁻¹	Bq g ⁻¹	Bq g ⁻¹
I-131	8.1E+01	7.4E+01	3.0E-03
Cs-134	1.1E+00	1.4E+00	6.3E-05
Cs-136	7.4E-01	3.2E+01	1.5E-03
Cs-137	3.0E+00	2.0E+00	9.3E-05
H-3	3.7E+02	3.7E+04	3.7E+01
P-32	1.5E+00	–	–
Cr-51	1.1E+02	1.1E+02	4.8E-03
Mn-54	1.3E+00	5.9E+01	2.4E-03
Fe-55	3.7E+01	4.4E+01	1.8E-03
Fe-59	1.1E+00	1.1E+01	4.4E-04
Co-58	3.7E+00	1.7E+02	7.0E-03
Co-60	7.4E+00	2.0E+01	8.1E-04
Ni-63	3.7E-02	–	–
Zn-65	3.7E+00	1.9E+01	7.8E-04
Sr-89	3.7E+00	5.2E+00	2.1E-04
Sr-90, Y-90*	2.6E-01	4.4E-01	1.8E-05
Y-91	1.5E+00	1.9E-01	7.8E-06
Zr-95	3.0E-01	1.4E+01	5.9E-04
Nb-95	3.0E-01	1.0E+01	4.1E-04
Mo-99	7.4E+01	2.4E+02	9.3E-03
Ru-103	7.4E-01	2.8E+02	1.1E-02
Ru-106, Rh-106m*	1.1E-01	3.3E+03	1.4E-01
Ag-110m	3.7E-02	4.8E+01	2.0E-03
Te-129m	1.5E+00	7.0E+00	2.9E-04
Te-131m	3.7E+00	5.6E+01	2.0E-03
Te-132	3.7E-01	6.3E+01	2.4E-03
Ba-140	1.5E+01	4.8E+02	1.9E-02
La-140	1.5E+01	9.3E+02	3.4E-02
Ce-141	1.1E+00	5.6E+00	2.3E-04
Ce-143	–	1.0E+02	3.7E-03
Ce-144, Pr-144*	1.1E-01	1.5E+02	5.9E-03
Np-239	3.0E+02	8.1E+01	3.1E-03

3.3. - D&D stage

LWR NPPs final stage is D&D, which is commonly divided into three phases. In the first, spent fuel and components with high activity (i.e., control rods) are removed from the reactor. In the second one, decontamination, dismantling and removal of radioactive material, waste, structures, and components take place. Finally, materials originated from the second phase that exceed exception levels of activity [45] are managed following the regulatory requirements [46].

During D&D, potential radionuclides released into the environment may be different to those from the operational stage. When fissile materials are removed from the reactor, the probability of a radioactive liquid discharge decreases significantly. However, in the D&D process of LWR NPPs some occasional radioactive releases into the surrounding environment may take place, especially by the creation, suspension, and resuspension of contaminated aerosols. In any case, the principal radionuclides to be considered in the releases are those produced in the reactor components by neutron activation reactions [3], which appear in Table 3. In this table, the expected inventory of radionuclides in a nuclear power plant, at the time of shutdown and after removing fissile materials, per thermal MW is also shown.

From Table 3, the main activation products in reactor materials at shutdown are: in steels Mn-54, Fe-55, Ni-59, Co-60, Ni-63, Nb-94, Ag-108m and Sb-125; and in reinforced concretes H-3, C-14, Ca-41, Fe-55, Co-60, Ba-133, Eu-152 and Eu-154.

Together with the above, the radioactive contamination of material surfaces, especially near the fuel discharging equipment, the storage pools, and the processing and storage facilities for radioactive effluents and wastes must also be considered. The radioactive inventory of such potential contamination includes actinides (Pu-238/239/241, Am-241, Cm-242/244 and U-232/233/234/235/236/238) and fission products (Sr-90, Tc-99, Ru-106, I-129, Cs-137 and Ce-144) [3].

A recent paper published by Seo in 2021 [10] indicates interest in additionally measuring the following radionuclides: Nb-93m (fast neutron activation product); Pm-147 (fission, fast neutron activation and thermal neutron activation product), Np-237 (Am-241 decay product), Pu-240 (thermal neutron activation product), Am-243 (thermal neutron activation product) and Cm-243 (thermal neutron activation product).

All the aforementioned radionuclides may appear as aerosols during the D&D process, to a greater or lesser extent, and end up in groundwater [3,10].

However, as previously explained, depending on the historical data of the plant, radionuclides other than those considered here may be measured during the D&D processes other than those considered here. For example, in Spain, already experienced in D&D processes, the following radionuclides are measured in groundwater: H-3, C-14, Mn-54, Fe-55, Co-57, Fe-59, Co-58, Co-60, Ni-63, Zn-65, Sr-90, Nb-94, Zr-95, Nb-95, Ru-106, Ag-108m, Ag-110m, Sb-125, Sn-126 and Ba-133 [47]. As can be seen, some of these radionuclides are those previously considered as specific to the D&D processes, whilst others belong to the "history" of the plant and are those typically determined during its operation.

Thus, Table 4, which summarizes the radionuclides, with half-lives >24 h, which could be found in the groundwater around NPPs during their lifetime, according to the different information sources presented, is subject to changes arising from the above-mentioned issues. Therefore, this list should be considered as dynamic over time.

4. Results

4.1. - Dose to the population and detection limits proposed due to radionuclides

Assuming the criterion of 0.01 mSv/year [] as the maximum individual dose that could be attributed to the ingestion of any single radionuclide throughout the year at a rate of 2 litres per day, the activity concentration level, i.e., the concentration that if present in

Table 3
The principal radionuclides formed by neutron activation reactions in LWR NPPs [3] and their expected activity per MW_{th}.

Nuclide	Activity
	Bq MW _{th} ⁻¹
H-3	4.3E+09
C-14	4.1E+08
Ca-41	2.9E+06
Mn-54	1.4E+08
Fe-55	4.2E+11
Ni-59	3.7E+09
Co-60	1.1E+12
Ni-63	3.7E+11
Nb-94	1.4E+07
Ag-108m	4.8E+08
Sb-125	5.3E+08
Ba-133	4.2E+05
Eu-152	1.9E+10
Eu-154	1.9E+09

Table 4

List of potential radionuclides to be analyzed in groundwater in REMPs together with the ingestion dose coefficients for adults, the proposed activity concentration levels (ACL_j), the derived detection limits (Dy[#], 10% ACL_j) and their half-life (T_{1/2}). The corresponding phase of life of the NPP where they appear is also shown [O: Operational stage, D: D & D stage].

	$e_j(50)$	ACL _j	Dy [#]	T _{1/2}	NPP stage
	Sv Bq ⁻¹	Bq l ⁻¹	Bq l ⁻¹	s	
Ag-108m	2.30E-09	5.96E+00	5.96E-01	1.38E+10	D
Ag-110m	2.80E-09	4.89E+00	4.89E-01	2.16E+07	O
Am-241	2.00E-07	6.85E-02	6.85E-03	1.37E+10	D
Am-243	2.00E-07	6.85E-02	6.85E-03	2.33E+11	D
Ba-133	1.50E-09	9.13E+00	9.13E-01	3.33E+08	D
Ba-140	2.60E-09	5.27E+00	5.27E-01	1.10E+06	O
C-14	5.80E-10	2.36E+01	2.36E+00	1.80E+11	D
Ca-41	1.90E-10	7.21E+01	7.21E+00	3.16E+12	D
Ce-141	7.10E-10	1.93E+01	1.93E+00	2.81E+06	O
Ce-143	1.10E-09	1.25E+01	1.25E+00	1.19E+05	O
Ce-144	5.20E-09	2.63E+00	2.63E-01	2.46E+07	O
Cl-36	9.30E-10	1.47E+01	1.47E+00	9.53E+12	D
Cm-242	1.20E-08	1.14E+00	1.14E-01	1.41E+07	D
Cm-243	1.50E-07	9.13E-02	9.13E-03	9.12E+08	D
Cm-244	1.20E-07	1.14E-01	1.14E-02	5.72E+08	D
Co-57	2.10E-10	6.52E+01	6.52E+00	2.35E+07	D
Co-58	7.40E-10	1.85E+01	1.85E+00	6.12E+06	O
Co-60	3.40E-09	4.03E+00	4.03E-01	1.66E+08	O, D
Cr-51	3.80E-11	3.60E+02	3.60E+01	2.39E+06	O
Cs-134	1.90E-08	7.21E-01	7.21E-02	6.51E+07	O
Cs-135	2.00E-09	6.85E+00	6.85E-01	7.30E+13	O
Cs-136	3.00E-09	4.57E+00	4.57E-01	1.14E+06	O
Cs-137	1.30E-08	1.05E+00	1.05E-01	9.48E+08	O
Eu-152	1.40E-09	9.78E+00	9.78E-01	4.27E+08	D
Eu-154	2.00E-09	6.85E+00	6.85E-01	2.71E+08	D
Fe-55	3.30E-10	4.15E+01	4.15E+00	8.67E+07	D
Fe-59	1.80E-09	7.61E+00	7.61E-01	3.84E+06	D
H-3 b	1.80E-11	7.61E-02	7.61E+01	3.89E+08	O, D
I-129	1.10E-07	1.25E-01	1.25E-02	5.08E+14	O
I-131	2.20E-08	6.23E-01	6.23E-02	6.93E+05	O
La-140	2.00E-09	6.85E+00	6.85E-01	1.45E+05	O
Mn-54	7.10E-10	1.93E+01	1.93E+00	2.70E+07	O, D
Mo-93	3.10E-09	4.42E+00	4.42E-01	1.26E+11	D
Mo-99	6.00E-10	2.28E+01	2.28E+00	2.37E+05	O
Nb-93m	1.20E-10	1.14E+02	1.14E+01	5.09E+08	D
Nb-94	1.70E-09	8.06E+00	8.06E-01	6.31E+11	D
Nb-95	5.80E-10	2.36E+01	2.36E+00	3.02E+06	D
Ni-59	6.30E-11	2.17E+02	2.17E+01	2.40E+12	D
Ni-63	1.50E-10	9.13E+01	9.13E+00	3.11E+09	D
Np-237	1.10E-07	1.25E-01	1.25E-02	6.77E+13	D
Np-239	8.00E-10	1.71E+01	1.71E+00	2.04E+05	O
P-32	2.40E-09	5.71E+00	5.71E-01	1.23E+06	O
Pm-147	2.60E-10	5.27E+01	5.27E+00	8.28E+07	D
Pu-238	2.30E-07	5.96E-02	5.96E-03	2.77E+09	D
Pu-239	2.50E-07	5.48E-02	5.48E-03	7.61E+11	D
Pu-240	2.50E-07	5.48E-02	5.48E-03	2.07E+11	D
Pu-241	4.80E-09	2.85E+00	2.85E-01	4.52E+08	D
Sb-125	1.10E-09	1.25E+01	1.25E+00	8.71E+07	D
Sn-126	4.70E-09	2.91E+00	2.91E-01	3.15E+12	D
Sr-89	2.60E-09	5.27E+00	5.27E-01	4.37E+06	O
Sr-90	2.80E-08	4.89E-01	4.89E-02	9.09E+08	O, D
Ru-103	7.30E-10	1.88E+01	1.88E+00	3.39E+06	O
Ru-106	7.00E-09	1.96E+00	1.96E-01	3.21E+07	O
Ta-182	1.50E-09	9.13E+00	9.13E-01	9.90E+06	O
Tc-99	6.40E-10	2.14E+01	2.14E+00	6.67E+12	D
Te-131m	1.90E-09	7.21E+00	7.21E-01	1.08E+05	O
Te-132	3.80E-09	3.60E+00	3.60E-01	2.79E+05	O
U-232	3.30E-07	4.15E-02	4.15E-03	2.23E+09	D
U-233	5.10E-08	2.69E-01	2.69E-02	5.02E+12	D
U-234	4.90E-08	2.80E-01	2.80E-02	7.75E+12	D
U-235	4.70E-08	2.91E-01	2.91E-02	2.22E+16	D
U-236	4.70E-08	2.91E-01	2.91E-02	7.39E+14	D
U-238	4.50E-08	3.04E-01	3.04E-02	1.41E+17	D
Y-91	2.40E-09	5.71E+00	5.71E-01	5.06E+06	O
Zn-65	3.90E-09	3.51E+00	3.51E-01	2.11E+07	O
Zr-95	9.50E-10	1.44E+01	1.44E+00	5.53E+06	O

Table 5

List of potential radionuclides from Table 4, the proposed technique for their measurement (γ , α , β - spectrometry or proportional counter, PC), the need of isolation before measurement (RI) and suitable volume (V in ml) and counting time (CT in minutes) to achieve the detection limit ($y^\#$ in Bq/l).

	RI	γ -S	α -S	β -S	PC	V (ml)	CT (m)	$y^\#$ (Bq/l)
Ag-108m		X				500	1440	0.04
Ag-110m		X				500	1440	0.07
Am-241	X		X			100	5000	0.002
Am-243	X		X			100	5000	0.002
Ba-133		X				500	1440	0.05
Ba-140		X				500	1440	0.3
C-14	X			X		100	300	0.1
Ca-41	X			X		500	300	0.2
Ce-141		X				500	1440	0.2
Ce-143		X				500	1440	0.2
Ce-144		X				500	1440	0.5
Cl-36	X			X		60	300	0.3
Cm-242	X		X			100	5000	0.002
Cm-243 + 44	X		X			100	5000	0.002
Co-57		X				500	1440	0.06
Co-58		X				500	1440	0.08
Co-60		X				500	1440	0.05
Cr-51		X				500	1440	0.3
Cs-134		X				500	1440	0.1
Cs-135 (*)								
Cs-136		X				500	1440	0.1
Cs-137		X				500	1440	0.1
Eu-152		X				500	1440	0.5
Eu-154		X				500	1440	0.2
Fe-55	X			X		400	180	0.03
Fe-59	X	X				500	1440	0.08
H-3	X			X		25	1440	1
I-129	X				X	2000	1000	0.01
I-131		X				500	1440	0.066
La-140		X				500	1440	0.4
Mn-54		X				500	1440	0.04
Mo-93	X			X		500	300	0.2
Mo-99		X				500	1440	0.1
Nb-93m	X	X				100	1440	4
Nb-94		X				500	1440	0.09
Nb-95		X				500	1440	0.09
Ni-59	X			X		400	180	0.03
Ni-63				X		400	180	0.03
Np-237	X		X			100	5000	0.005
Np-239		X				500	1440	0.3
P-32	X			X		500	100	0.15
Pm-147 (*)								
Pu-238	X		X			100	5000	0.002
Pu-239 + 40	X		X			100	5000	0.002
Pu-241	X			X		100	3000	0.2
Sb-125		X				500	1440	0.4
Sn-126	X	X				500	1590	0.30
Sr-89	X				X	250	1000	0.03
Sr-90	X				X	250	1000	0.02
Ru-103		X				500	1440	0.2
Ru-106		X				500	1440	0.7
Ta-182		X				500	1440	0.3
Tc-99	X			X		500	360	0.015
Te-131m		X				500	1440	0.5
Te-132		X				500	1440	0.09
U-232	X		X			50	5000	0.004
U-233	X		X			50	5000	0.004
U-234	X		X			50	5000	0.004
U-235	X		X			50	5000	0.004
U-236	X		X			50	5000	0.004
U-238	X		X			50	5000	0.004
Y-91	X				X	250	1000	0.03
Zn-65		X				500	1440	0.2
Zr-95		X				500	1440	0.2

NOTE: (*) Not evaluable by any of the proposed techniques.

the consumed drinking-water would yield an individual dose of 0.01 mSv, can be assessed as established in 2.1.

Applying this criterion to the complete list of radionuclides derived previously, Table 4 is obtained. In Table 4, the results of activity concentration levels together with the proposed detection limits, the half-life of the radionuclides and the stage of the NPP where they appear are gathered.

4.2. - Recommended measurement method

It must be considered that groundwater radiological monitoring is carried out in laboratories, by discrete sampling. In situ radiological monitoring is almost impractical.

For the purposes of groundwater monitoring, the methodologies envisaged by the safety authorities to laboratories shall be taken into account by considering also the risks, safety and costs. Comparable and fit-for-purpose results are an essential requirement for any decision based on radioactivity measurements, so it is essential that laboratories devoted to this monitoring use appropriate nuclide-specific measurement methods.

Having defined the table of radionuclides (Table 4) that can be determined in groundwater at any stage of the life of a NPP and the reasonably achievable detection limits, it is worth considering the operational achievability of these limits by conventional radioactivity measuring laboratories and through which techniques. It should also be highlighted that, for operational reasons and also in terms of financial costs and consumption of laboratory consumables and reagents, it is important that the analyses can be run using the smallest possible sample quantity and optimizing the time needed to obtain meaningful results.

Depending on the radionuclide emissions to be determined, three spectrometric techniques are routinely used: alpha, beta and gamma spectrometry. Additionally, proportional counter and scintillator techniques are commonly found. Beyond these, mass accelerators, are not considered because, although very powerful for some radionuclides, they are not as widespread as those mentioned above.

Although it is not one of the objectives of this paper to conduct an exhaustive analysis of the spectrometric techniques, for which there is extensive documentation [48,49], some recommendations can be made.

Direct gamma spectrometry using High Purity Germanium (HPGe) semiconductor detectors (although not exclusively) is a very powerful technique that allows the simultaneous determination of a large number of gamma-emitting radionuclides in a sample without the need for any treatment beyond evaporation if the volume required to reach the requested DL is very high. Simplicity in obtaining the emission record is not always accompanied by simplicity in interpreting this record and thus providing the required activity concentration values for all radionuclides present in the sample. The overlapping of emissions from different radionuclides and coincidence effects are the most common issues in gamma spectrometry. If we also consider that a large number of radionuclides are beta or alpha emitters and then emit gamma radiation, it is clear that this technology, as can be seen in Table 5, can be used to determine the activity concentration required for most radionuclides present in the sample. Unfortunately, the detection efficiency of these devices is low in comparison to the other techniques described here, which means that the detection limits that are achieved with these HPGe devices are the highest ones making use of the same sample volume and measurement time.

In some cases, when interferences with other emitters render a radionuclide undetectable, this gamma spectrometry technique is applied by previous and exhaustive sample preparation consisting of isolating the element corresponding to the radionuclide(s) to be determined from the sample; a process called radionuclide isolation. This complexity, highly consuming of laboratory and time resources, is compensated by a straightforward interpretation of the results.

In the case of those radionuclides undetectable by gamma spectrometry - a situation that can occur for several reasons, the most common being: emission of gamma particles whose energy is outside the operating range of the equipment, non-existent gamma emissions, emissions with such a low probability that the DL required for that radionuclide is not achievable by this technique, or because interferences with other emitters make them undetectable - alpha/beta spectrometry, or counters are the techniques to be used.

Alpha spectrometry, performed - although not exclusively - with implanted silicon detectors (PIPS), is a technique which requires the isolation of the element corresponding to the radionuclide(s) to be determined from the sample containing it, before proceeding to its measurement. In this case, the complexity of this process is balanced by a simple interpretation of the results and by a high detection efficiency, which means that the DLs obtained by this technique are generally low for relatively small sample quantities, as shown in Table 5.

Beta-spectrometry using the liquid scintillation technique is a technique that also requires radionuclide separation to isolate the chemical element to which it pertains before measurement. This complexity, the production of mixed (chemical and radioactive) residues that needs to be properly managed and highly consuming of laboratory and time resources, is offset by an easy analysis of the results, and by a high detection efficiency, which means that the DLs obtained by this technique are generally low with relatively small sample quantities, as we show in Table 5. However, since beta emissions present a continuous spectrum, reading the record is not as simple as in the case of alpha spectrometry; the possible occurrence of interferers, the existence of extinction, among other possible issues, mean that well-qualified personnel are required to perform the reading interpretation.

Regarding the use of counters, e.g., proportional counters, these have the advantage, in terms of equipment, of being extremely robust, relatively inexpensive and with very low maintenance and operating costs. However, it will always require radiochemical isolation of the element to be measured. In addition, since these equipments do not provide a spectrum, but only a certain number of counts, it is very difficult to determine the existence of interferers. However, their detection efficiency is high and provides low detection limits.

At this point, it is worth mentioning that while some radionuclides can be measured by different techniques, the choice of which

depends on the sample size available, the required detection limits and the possible presence of other radionuclides in the sample that can interfere in its determination; some other radionuclides present a particularly complex determination and other factors such as the time needed to provide the results and the economic costs must also be taken into consideration; so that correlation factors are evoked for their assessment.

From such considerations, we propose, for each radionuclide, the procedure that appears to be the most appropriate for its determination.

Whenever a radiochemical isolation must be carried out, it is necessary to know the yield of the isolation, i.e., the percentage of the element present in the sample that could be extracted by the chemical procedure followed. There are different ways to control this yield. Among them, the most common are the use of a well-known quantity of a radioactive tracer belonging to the same element as the radionuclide to be determined, but whose emissions do not interfere with those of the radionuclide to be determined and, which will be detected in the test-sample by the same or another measurement technique as the radionuclide sought. A second alternative is the use of a well-known quantity of a stable carrier usually belonging to the same element as the radionuclide to be determined and which will be determined in the test-sample by conventional measurement techniques (for example atomic absorption, mass spectrometry or gravimetric analysis). There are other procedures, such as the preparation of two test-samples in parallel, one traced with the radionuclide to be determined and the other without, are rarely recommended, although they are occasionally the only option.

The use of a radioactive tracer, which is determined in the test-sample together with the unknown radionuclide(s), is the most common technique in the case of alpha spectrometry analysis.

Any of these tracing techniques are the usual practice for obtaining the value of the radiochemical yield in the cases of radionuclides determined by liquid scintillation, and in the case of counters, depending on the radionuclide to be detected.

The existence of uncertainties linked to the process of the radiochemical yield determination, volume determination as well as those derived from the necessary process of equipment calibration, which in turn include the determination of some corrective factors - which for the sake of brevity are not dealt with in this text - among which are quenching curves, sum effect corrections, density corrections and self-absorption, make it difficult to provide a general expression for the uncertainties of determination of activity concentration and also for those of the detection limits. In the last few years, several contributions provide directly applicable numerical expressions for these parameters [50–53]. Together with this, a great normative effort is being made at international level to reach a consensus on these expressions of use [37,54,55–57] which is, essential in order to achieve comparability of the results provided, both during plant operation and decommissioning, by the different actors participating in these processes.

Throughout the lifetime of the plant, the radionuclides that are to be measured in groundwater are those shown in Table 4. Table 5 shows all of them, together with the DL achieved, the technique proposed to achieve this DL, and also a proposal of the volume of samples required as well as the suitable measurement time. The criteria for proposing the techniques are: 1.- That the proposed DLs are achievable with the proposed technique. 2.- That these DLs can be achieved with the technique using reasonable sample volumes and measurement times. 3.- When these conditions are met by more than one technique, the one that requires the least investment of time and resources is proposed.

In Table 5 a realistic DL is also given, obtained using conventional but specific detection equipment, as used in the UPV/EHU low activity measurement laboratory. This laboratory is accredited by ENAC (Spanish accreditation body belonging to ILAC) under the ISO/IEC 17025 [58] standard, for 90% of the determinations shown in Table 5. Naturally, the reported DLs are approximate, as they will depend not only on the equipment used, the amount of sample used to prepare the test-sample and the measurement time, but also on the background of the measurement, the performance of the radiochemical isolation (if any) and the measurement geometry (in the case of gamma spectrometry). Regardless, they correspond to the values we routinely obtain in our laboratory.

The equipment used are as follow:

For gamma spectrometry, HPGe, detectors from Canberra and Mirion suppliers, with detector efficiencies between 110 and 60% relative to NaI(Tl). Measurements are performed near-contact.

For alpha spectrometry, Canberra PIPS detectors of one inch diameter and nominal efficiencies of 25%. Measurements are performed at a 5 mm source-detector distance.

Used for beta spectrometry, PerkinElmer 1220 Quantulus ultra-low background Liquid Scintillation Counting (LSC) equipment. Efficiencies vary from 20% to 100% according to the energy of the emitter, type of cocktail and vial used, sample-cocktail ratio and quenching.

Completing the set, the counters are gas flow proportional counters from Canberra and Berthold, with detector diameters of two inches and nominal efficiencies of 40% and 25% for beta and alpha particles from Am-241 and Sr-90.

In view of Table 5, one main conclusion of this paper is that a large part of the radionuclides to be determined can be obtained using conventional radiometric techniques. Only some of them, such as Cs-135 and Pm-147, require more sophisticated techniques, such as mass spectrometry.

It should also be mentioned that some of these radionuclides require adaptation of the methods used, i.e., for the determination of Am-241 by alpha-spectrometry, Am-243 is routinely used as a tracer. So, if Am-243 is also to be determined, a double determination, with and without tracer, will have to be carried out. In a further example, there are radionuclides that are inseparable by these conventional measurement techniques, such as Pu-239 and Pu-240, so the joint value of both is provided. Although there are more examples that mirror the complexity of some of these determinations, it is not the aim of this paper to analyse them in depth, but to show that the radio analytical conventional methods allow, for most radionuclides, to reach the hereby proposed maximum detection limits considered reasonable when making a radiological characterization of groundwater throughout the different stages of the life of a NPP. Alternatively, for the radionuclides not detectable by radiometric techniques, but also for those difficult to determine, the use of correlation factors is an option that, although not providing a precise value of the content of the radionuclides, does a reliable

understanding of whether the values reached by their activity concentration are adequate for the proposed purpose.

Examination of Table 5 shows that about 50% of the analyses can be performed with just 500 ml of water in a non-destructive analysis by gamma ray spectrometry. Alpha spectrometry is needed for only five of the nuclide analyses and it needs a maximum of 100 ml for each radionuclide analysis (500 ml for all radionuclide assessments) and requires the highest counting times, which amount to about 3 days. For those determinations requiring LSC or beta counters, less than 3500 ml of water is needed in total, consuming counting times of less than one day, except for Pu-241. In summary, less than 7500 ml is needed to achieve the assessment of activity concentrations above proposed detection limits for the vast majority of radionuclides employing radiometric techniques. Interestingly, only in two cases, more than 1 day of counting time would be required to achieve the proposed detection limits by gamma ray spectrometry.

5. Conclusions

From the initial consideration of groundwater as a part of the land, dose criteria is established as 0.1 mSv/y, assuming the worst-case scenario of water ingestion and using the most restricted value of effective dose from those appearing in different national and international regulations.

Based on previous studies and existing literature, a directory of the most important radionuclides that may be potentially released into the environment during the different phases of the life of a nuclear power plant, from the beginning of its operation to the final stages of its decommissioning, is presented. Concerning the aim of this paper, only radionuclides with half-life longer than 24 h are considered.

For each radionuclide, the activity concentration responsible for independently producing one tenth of the dose criterion of 0.1 mSv/y for members of the public is calculated following the methodology proposed by the WHO.

The most appropriate value for the detection limit to be reached in the measurement of each of these radionuclides' activity concentrations when routine determinations are performed in the framework of the radiological monitoring plans in the environment and in the nuclear power plants themselves are established. In this paper, we address the proposal of these detection limits as 10% of the activity concentration level responsible for 10% of the dose criteria, and the corresponding table containing these detection limit values is provided.

Finally, a brief notice regarding the analytical methodologies and resources necessary to undertake the determination of these radionuclides is realized. This analysis shows that the vast majority of these radionuclides can be determined within the proposed detection limits using conventional methods, commonly used in radiological averaging laboratories equipped with standard radiometric equipment (alpha, beta and gamma spectrometry and proportional counters), with average sample volumes (500 ml in most cases) and average counting times (maximum 3 days of counting in the case of alpha spectrometry).

For those radionuclides that are difficult to determine by radiometric means, such as Cs-135 or Pm-147, alternative methods such as mass spectrometry are recommended. Otherwise, the use of correlation factors is preferred when only an estimation of their activity concentration rather than their precise values is adequate for the proposed purpose.

Author contribution statement

R. Idoeta: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

M. Herranz: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

C. Olondo: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

S. Petisco-Ferrero: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

S. Rozas: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] IAEA. Site Evaluation for Nuclear Installations, Safety Standard Series SSR-1, International Atomic Energy Agency, Vienna, 2019.
- [2] EU, Council Directive 2013/59/EURATOM of 5 December 2013 Laying Down Basic Safety Standards for Protection against the Dangers Arising from Exposure to Ionising Radiation, and Repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom, Official Journal of the European Union L13, 2014, 1-73, <http://data.europa.eu/eli/dir/2013/59/oj>.
- [3] IAEA, Radiological Characterization of Shut Down Nuclear Reactors for Decommissioning Purposes, in: Technical Report Series 389, International Atomic Energy Agency, Vienna, 1998.
- [4] NRC, NUREG - 1575 - Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM), Rev. 1, U.S. Nuclear Regulatory Commission (2000).
- [5] EU, EURATOM, Consolidated Version of the Treaty on the European Atomic Energy Community (EURATOM), Official Journal of the European Union C203, 2016, pp. 1–112. http://data.europa.eu/eli/treaty/euratom_2016/oj.

- [6] EC, 2000/473/Euratom Commission recommendation of 8 June 2000 on the application of Article 36 of the Euratom Treaty concerning the monitoring of the levels of radioactivity in the environment for the purpose of assessing the exposure of the population as a whole, Official Journal of the European Communities L191 (2000) 37–46. <http://data.europa.eu/eli/reco/2000/473/oj>.
- [7] A. Bond, M. Bussell, P. O'Sullivan, J. Palermo, Environmental impact assessment and the decommissioning of nuclear power plants - a review and suggestion for a best practicable approach, *Environ. Impact Assess. Rev.* 23 (2003) 197–217, [https://doi.org/10.1016/S0195-9255\(02\)00091-4](https://doi.org/10.1016/S0195-9255(02)00091-4).
- [8] NRC, NUREG-1757 - Consolidated Decommissioning Guidance - Decommissioning Process for Materials Licensees, Vol. 1, Rev. 2, U.S. Nuclear Regulatory Commission (2006).
- [9] O. Kuras, P.B. Wilkinson, P.I. Meldrum, L.S. Oxby, S. Uhlemann, J.E. Chambers, A. Binley, J. Graham, N.T. Smith, N. Atherton, Geoelectrical monitoring of simulated subsurface leakage to support high-hazard nuclear decommissioning at the Sellafield Site, UK, *Sci. Total Environ.* 566–567 (2016) 350–359, <https://doi.org/10.1016/j.scitotenv.2016.04.212>.
- [10] H.W. Seo, J.Y. Oh, W.G. Shin, Proposal for the list of potential radionuclides of interest during NPP site characterization or final status surveys, *Nucl. Eng. Technol.* 53 (2021) 234–243, <https://doi.org/10.1016/j.net.2020.06.007>.
- [11] S. Turhan, E. Özçatak, H. Taşkın, A. Varinlioğlu, Determination of natural radioactivity by gross alpha and beta measurements in groundwater samples, *Water Res.* 47 (2013) 3103–3108, <https://doi.org/10.1016/j.watres.2013.03.030>.
- [12] NRC, NUREG-1757 - Consolidated Decommissioning Guidance, Vol. 2, Rev. 2, U.S. Nuclear Regulatory Commission (2022).
- [13] IAEA, Database on Discharges of Radionuclides to the Atmosphere and Aquatic Environment, 2022. <https://www.iaea.org/resources/databases/database-on-discharges-of-radionuclides-to-the-atmosphere-and-aquatic-environment>.
- [14] A. Baeza, A.M. Brogueira, M.C.V. Carreiro, E. García, J.M. Gil, C. Miró, M.M. Sequeira, M.M.R. Teixeira, Spatial and temporal evolution of the levels of tritium in the Tagus river in its passage through Cáceres (Spain) and the Alentejo (Portugal), *Water Res.* 35 (2001) 705–714, [https://doi.org/10.1016/S0043-1354\(00\)00302-X](https://doi.org/10.1016/S0043-1354(00)00302-X).
- [15] H. Sato, M. Gusyeve, D. Veremenko, G. Laptev, N. Shibasaki, Y. Onda, M. Zhleznyak, S. Kirieiev, K. Nanba, Evaluating changes in radionuclide concentrations and groundwater levels before and after the cooling pond drawdown in the Chernobyl Nuclear Power Plant vicinity, *Sci. Total Environ.* 872 (2023) 161997, <https://doi.org/10.1016/j.scitotenv.2023.161997>.
- [16] IAEA, Quantification of Radionuclide Transfer in Terrestrial and Freshwater Environments for Radiological Assessments, in: TECDOC No. 1616, International Atomic Energy Agency, Vienna, 2009.
- [17] O. Fallatah, M. Ahmed, B. Gyawali, A. Alhawsawi, Factors controlling groundwater radioactivity in arid environments: an automated machine learning approach, *Sci. Total Environ.* 830 (2022), 154707, <https://doi.org/10.1016/j.scitotenv.2022.154707>.
- [18] R.B. Codell, J.O. Duguid, in: John E. Till (Ed.), Chapter "Transport of Radionuclides in Groundwater" from Book: Radiological Risk Assessment and Environmental Analysis, Oxford Academic, 2008, <https://doi.org/10.1093/acprof:oso/9780195127270.003.0005>.
- [19] L. Elango, M. Thirumurugan, F. Sunny, M. Chopra, 2016, in: M. Thangarajan, V. Singh (Eds.), Chapter "Modeling of Radionuclide Transport in Groundwater" from Book: Groundwater Assessment, Modeling, and Management, Taylor & Francis, 2016.
- [20] K.H. Birdshell, A.V. Wolsberg, D. Hollis, T.A. Cherry, K.M. Bower, et al., Groundwater flow and radionuclide transport calculations for a performance assessment of a low-level waste site, *J. Contam. Hydrol.* 46 (2000) 99–129, [https://doi.org/10.1016/S0169-7722\(00\)00129-7](https://doi.org/10.1016/S0169-7722(00)00129-7).
- [21] R. Testoni, R. Levizzari, M. De Salve, Radionuclide transport in shallow groundwater, *Prog. Nucl. Energy* 85 (2015) 277–290, <https://doi.org/10.1016/j.pnucene.2015.06.023>.
- [22] CSN, Guía de Seguridad 7.9 Manual de Cálculo de Dosis en el Exterior de las Instalaciones Nucleares, Colección Guías de Seguridad del CSN, 2006.
- [23] EC, Commission Recommendation of 18 December 2003 on Standardised Information on Radioactive Airborne and Liquid Discharges into the Environment from Nuclear Power Reactors and Reprocessing Plants in Normal Operation (2004/2/Euratom), Official Journal of the European Communities L002 (2004) 36–46. <http://data.europa.eu/eli/reco/2004/2/oj>.
- [24] W.W. Meinke, T.H. Essig, NUREG-1301 - Offsite Dose Calculation Manual Guidance : Standard Radiological Effluent Controls for Pressurized Water Reactors - Generic Letter 89-01, Supplement No. 01, U.S. Nuclear Regulatory Commission (1991).
- [25] W.W. Meinke, T.H. Essig, NUREG - 1302 - Offsite Dose Calculation Manual Guidance: Standard Radiological Effluent Controls for Boiling Water Reactors, Generic Letter 89-01, Supplement No. 1, U.S. Nuclear Regulatory Commission (1991).
- [26] NRC, NUREG/CR-2907 - Radioactive Effluents from Nuclear Power Plants, Annual Report. 2019, Vol. 25, U.S. Nuclear Regulatory Commission (2021).
- [27] WHO, Guidelines for Drinking-Water Quality, Fourth ed., World Health Organization, Geneva, 2022.
- [28] CEU, Council Directive 2013/51/EURATOM of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption, Official Journal of the European Union L 296 (2013) 12–21. <http://data.europa.eu/eli/dir/2013/51/oj>.
- [29] CEU, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal of the European Communities L330 (1998) 32–54. <http://data.europa.eu/eli/dir/1998/83/oj>.
- [30] CSN, Instrucción IS-13, de 21 de marzo de 2007, del Consejo de Seguridad Nuclear, sobre Criterios Radiológicos para la Liberación de Emplazamientos de Instalaciones Nucleares, Boletín Oficial del Estado 109 (2007)19703–19704.
- [31] IAEA, Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards, IAEA Safety Standards Series No. GSR Part 3, International Atomic Energy Agency, Vienna, 2014.
- [32] DOE, National Primary Drinking Water Regulations, 40 CFR Part 141, U.S. Environmental Protection Agency, 2010.
- [33] JCGM, JCGM 100:2008 Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement, 2008.
- [34] IUPAC, Nomenclature in evaluation of analytical methods including detection and quantification capabilities, *International Union of Pure and Applied Chemistry* 67 (1995) 1699–1723, https://doi.org/10.1007/978-3-642-27833-4_5326-1.
- [35] ISO, ISO 11843-1:1997 Capability of Detection — Part 1: Terms and Definitions, International Organization for Standardization, Geneva, 1997.
- [36] L.A. Currie, Limits for qualitative detection and quantitative determination: application to radiochemistry, *Analytical Chemistry* 40 (1968) 586–593, <https://doi.org/10.1021/ac60259a007>.
- [37] ISO, ISO 11929-1:2021 Determination of the Characteristic Limits (Decision Threshold, Detection Limit and Limits of the Coverage Interval) for Measurements of Ionizing Radiation - Fundamentals and Application - Part 1: Elementary Applications, International Organization for Standardization, Geneva, 2021.
- [38] K. Eckerman, J. Harrison, H.-G. Menzel, C.H. Clement, ICRP Publication 119: Compendium of Dose Coefficients Based on ICRP Publication 60, *Ann. ICRP* 42 (2013), 1–130, <https://doi.org/10.1016/j.icrp.2013.05.003>.
- [39] IAEA, Environmental and Source Monitoring for Purposes of Radiation Protection, in: Safety Guide, Vol. 7, International Atomic Energy Agency, Vienna, 2019.
- [40] Engineering ToolBox, Gases Solved in Water - Diffusion Coefficients, 2008. https://www.engineeringtoolbox.com/diffusion-coefficients-d_1404.html.
- [41] S. Thierfeldt, A. Deckert, Radionuclides Difficult to Measure in Waste Packages. Final report, in: BS-Nr. 9203-6, Brenk Systemplanung, Aachen, 1995.
- [42] E.E. Lewis, Nuclear Power Reactor Safety, in: Wiley-Interscience Publication, Wiley, 1977.
- [43] ANSI, American National Standard: Radioactive Source Term for Normal Operation of Light Water Reactors, in: ANSI/ANS-18.1-1999, American Nuclear Society, Illinois, 1999.
- [44] IAEA, Objectives and Design of Environmental Monitoring Programmes for Radioactive Contaminants, in: Safety Standard Series, Vol. 41, International Atomic Energy Agency, Vienna, 1975.
- [45] NEA, The Decommissioning and Dismantling of Nuclear Facilities: Status, Approaches, Challenges, OECD Nuclear Energy Agency, 2002.
- [46] NEA, Regulating the Decommissioning of Nuclear Facilities: Relevant Issues and Emerging Practices, OECD Nuclear Energy Agency No 6401, 2008.
- [47] ENRESA, Private Communication, 2022.
- [48] IAEA, Measurement of Radionuclides in Food and the Environment. Tech. Rep. Ser. 295, International Atomic Energy Agency, Vienna, 1989.
- [49] NRC, Report No. 058-A Handbook of Radioactivity Measurements Procedures, Second ed., National Council on Radiation Protection and Measurements, NCRP Reports, 1985.

- [50] D. Calmet, M. Herranz, R. Idoeta, Characteristic limits in radioactivity measurement: from Currie's definition to the international standard ISO-11929 publication, *J Radioanal Nuclear Chem* 276 (2008) 299–304, <https://doi.org/10.1007/s10967-008-0502-4>.
- [51] M. Herranz, R. Idoeta, F. Legarda, Evaluation of uncertainty and detection limits in radioactivity measurements, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 595 (2008) 526–534, <https://doi.org/10.1016/j.nima.2008.07.105>.
- [52] M. Herranz, R. Idoeta, F. Legarda, Analysis of uncertainties and detection limits for the double measurement method of ⁹⁰Sr and ⁸⁹Sr, *Radiation Measurements* 46 (2011) 680–686, <https://doi.org/10.1016/j.radmeas.2011.06.055>.
- [53] M. Herranz, R. Idoeta, A. Abelairas, F. Legarda, Uncertainties in ⁶³Ni and ⁵⁵Fe determinations using liquid scintillation counting methods, *Appl. Radiat. Isot.* 70 (2012) 1863–1866, <https://doi.org/10.1016/j.apradiso.2012.02.027>.
- [54] ISO, ISO 22515:2021 Water Quality - Iron-55 - Test Method Using Liquid Scintillation Counting, International Organization for Standardization, Geneva, 2021.
- [55] ISO, ISO 10704:2019 Water Quality - Gross Alpha and Gross Beta Activity - Test Method Using Thin Source Deposit, International Organization for Standardization, Geneva, 2019.
- [56] ISO, ISO 9698:2019 Water Quality - Tritium - Test Method Using Liquid Scintillation Counting, International Organization for Standardization, Geneva, 2019.
- [57] ISO, ISO 13166:2020 Water Quality — Uranium Isotopes — Test Method Using Alpha-Spectrometry, International Organization for Standardization, Geneva, 2020.
- [58] ISO, ISO/IEC 17025:2017 General Requirements for the Competence of Testing and Calibration Laboratories, International Organization for Standardization, Geneva, 2018.