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**A critical review of the quantification, analysis and
detection of radionuclides in environment using Diffusive
Gradients in Thin Films (DGT): advances and perspectives**

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Manuscripts

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3 For the attention of:
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5 Pure and Applied Chemistry
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7 Dear Editor
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9 We would like to thank the invitation to submit our research for the "Radioactive waste in the
10 marine environment" special topic
11

12 We would like to submit the accompanying manuscript entitled "A critical review of the
13 quantification, analysis and detection of radionuclides in environment using Diffusive Gradients in
14 Thin Films (DGT): advances and perspectives" by Leonardo Pantoja Munoz and Hemda Garelick for
15 consideration for publication in Pure and Applied Chemistry Journal.
16

17 We are confident that this paper will be of relevance and interest to those concerned with
18 Radioactive waste in the marine environment, specifically with those interested in novel sampling
19 techniques such as DGT. To date there are no reviews focusing on this aspect yet..
20

21 As such, we trust that the paper will have an appeal to the broad readership of Pure and Applied
22 Chemistry Journal.
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26 Sincerely
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3 A critical review of the quantification, analysis and detection of radionuclides in environment using
4 Diffusive Gradients in Thin Films (DGT): advances and perspectives
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14 ABSTRACT 15

16 This critical review explores the quantification, analysis, and detection of radionuclides in the
17 environment using the Diffusive Gradients in Thin Films (DGT) technique.
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19 Radionuclides, unstable isotopes emitting ionising radiation, are present in the environment due to
20 natural and anthropogenic sources for which concerns are raised about their impact on human
21 health and ecosystems. DGT offers a unique passive sampling approach for understanding the
22 behaviour of radionuclides and other trace elements. This review provides insights into method
23 development, real case scenarios, advantages, limitations, and future perspectives of DGT in
24 radionuclide analysis.
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27 In terms of method development, various isotopes have been analysed with varying significance
28 based on origin, concentration, risks, and persistence. Notably, U, Th, Pu, Am, Cm, 99Tc, 226Ra,
29 137Cs, 134Cs, 232U, 237Np, and 152Eu have been measured, revealing their diverse roles in
30 environmental radioactivity. Real case scenarios illustrate applications in uranium mining, water
31 quality monitoring, and metal speciation studies, shedding light on mobility, bioavailability, and
32 ecological impacts. DGT's advantages include in-situ monitoring, time-averaged mean
33 concentrations, and comprehensive speciation insights. Challenges include potential influences from
34 biofouling, temperature changes and specifically the possible degradation of the binding and diffuse
35 layer due to ionising radiation in long term exposures. In addition, the distinction between fully
36 labile free metal ions and partially labile metal-ligand complexes introduces a potential limitation in
37 the DGT technique, hence being an opportunity for future studies. Looking forward, DGT is expected
38 to contribute to radiation dose modelling, environmental risk assessment, and water quality
39 monitoring, with ongoing developments enhancing its utility and accuracy.
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1. INTRODUCTION

1.1. Radionuclides in the environment, sources and human health

Radionuclides are unstable isotopes of elements that emit ionising radiation as they undergo radioactive decay. Many of these radioactive isotopes are naturally present in the environment due to cosmic radiation, geological processes, and natural nuclear reactions (e.g uranium, thorium, and radon) (1). Additionally, anthropogenic activities, such as nuclear power generation, nuclear weapons testing, and industrial practices, have introduced a variety of man-made radionuclides into the environment. These can include isotopes like cesium-137, strontium-90, and iodine-131 (2). The presence of radionuclides in the environment raises concerns about their impact on human and ecosystems health as well as the potential for long-term contamination.

Radionuclides in the environment can pose significant health risks to humans through multiple pathways. Radioactive particles present in the air can be inhaled, potentially leading to an overall radionuclide incorporation as well as irradiation of lung tissue and an increased risk of lung cancer. Moreover, the consumption of contaminated food and water can result in the ingestion of radionuclides, leading to their accumulation within the body and subsequent irradiation of internal organs (3). Additionally, individuals can be externally exposed to radiation by coming into contact with surfaces that have been contaminated with radioactive materials.

Natural radionuclides contribute to the background radiation that humans are exposed to daily. Currently, there is a good understanding of the distribution and behaviour of many naturally occurring radionuclides (4). In addition, events such as the Chernobyl disaster and the Fukushima Daiichi nuclear accident have provided valuable insights into the behaviour of radionuclides following large-scale releases into the environment. As a consequence, regulatory agencies and international organisations have established guidelines and safety standards for permissible levels of exposure to radionuclides to protect human health (5).

Regulatory agencies face several challenges regarding the occurrence of such radionuclides of man-made origin. Some show extended half-lives, resulting in persistent contamination that can endure across generations. Their mobility across diverse environmental compartments such as air, water, and soil, coupled with their propensity to accumulate within biota, show intricate and elusive behavioural patterns that defy straightforward prediction (6). This complex interplay of radionuclides with ecosystems has the potential to disrupt natural processes, plants and animals. The assessment of health repercussions arising from prolonged low-level radiation exposure poses a formidable challenge, and uncertainties persist concerning the precise risks attributed to distinct radionuclides. Crucially, the proper disposal and management of radioactive waste originating from nuclear facilities assume paramount importance in averting enduring environmental contamination of global proportions (7).

1.2. Current techniques for the sampling of radionuclides

The measurement of radionuclides in the environment is crucial for assessing potential radiation exposure, understanding radioactive contamination, and ensuring the safety of ecosystems and human populations. Radionuclide sampling techniques play a pivotal role in capturing accurate and representative data for effective radiological monitoring and risk assessment.

There are several techniques for sampling radionuclides in the environment. Particularly, when sampling is performed within the environment, a spectrum of techniques is employed.

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3 In air sampling, two noteworthy methods stand out. Particulate air sampling involving the use of
4 high-volume air samplers to capture airborne particles on filters, facilitating the analysis of alpha,
5 beta, and gamma-emitting radionuclides. In addition, gaseous radionuclide sampling captures
6 airborne noble gases through specialised adsorption systems or cryogenic techniques (8).
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9 For water sampling, grab sampling collects discrete water samples from various sources such as
10 surface water bodies, groundwater wells, or effluents, enabling the examination of radionuclide
11 concentrations. Automated water samplers, on the other hand, systematically collect water samples
12 at predetermined intervals, offering valuable time-series data for assessing variations in radionuclide
13 levels over time (7).
14

15 Soil sampling encompasses both surface soil sampling, which gathers soil specimens from the upper
16 layer to analyse radionuclide distribution, and core sampling, involving the collection of soil cores to
17 study vertical radionuclide profiles and migration patterns (8). It is important to note that soil
18 sampling can also involve porewater analyses for partition coefficient studies.
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21 Regarding biota sampling, biological tissue sampling involves collecting plant and animal tissues to
22 assess radionuclide uptake and bioaccumulation. Moreover, seawater and sediment biota sampling
23 target marine organisms like fish and benthic creatures, shedding light on the transfer of
24 radionuclides through aquatic food chains (9). Finally, sediment sampling adopts distinct
25 approaches: surface sediment sampling captures sediments from the water-sediment interface,
26 providing insights into radionuclide deposition and interactions, while core sediment sampling
27 extracts sediment cores to delve into historical radionuclide deposition and sediment mixing
28 dynamics.
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31 Regardless of the sampling method chosen, there are a number of challenges to consider when it
32 comes to ensuring reliability and accuracy. One key aspect is selecting sampling locations that truly
33 represent the area of interest, so that any potential bias is avoided. It is also crucial to handle and
34 preserve samples correctly to prevent any changes or decay of the radioactive materials. Rigorous
35 quality control measures are essential to validate both the sampling process and subsequent
36 laboratory analysis. To maintain the integrity of the data, it is important to prevent any
37 contamination between samples and equipment (10).
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40 1.3. DGT as sampling technique, introduction, overview, comparison and advantages

41
42 The Diffusive Gradients in Thin Films (DGT) technique has emerged as a versatile and innovative
43 approach in environmental science for the quantification and assessment of the bioavailability,
44 speciation, and mobility of various trace elements, including radioisotopes, in complex matrices.
45 Developed as a passive sampling method, the DGT technique offers unique advantages in
46 understanding the behaviour of elements in different environmental compartments (11).
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49 The DGT technique operates on fundamental principles of diffusion and sorption, allowing for the
50 precise capture of labile forms of trace elements from the surrounding environment. The technique
51 involves the deployment of a specialised DGT device that consists of two key components: a
52 diffusive layer and a binding phase.
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55 The diffusive layer is a permeable membrane that controls the rate at which trace elements from the
56 surrounding medium diffuse into the DGT device. This mechanism prevents the sampling of analytes
57 without the influence of convection. Its thickness and material properties are designed to mimic the
58 diffusion characteristics of the target elements, ensuring controlled and time-integrated sampling.
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The binding phase of the DGT device is carefully selected based on the chemical properties of the trace elements of interest. This binding phase has a high affinity for specific elements, or groups of elements, allowing selective capture and accumulation. Under normal circumstances, the solute binds strongly to the binding layer, leading to a negligible concentration at the interface between the diffusion and binding layers. Different binding phases can be employed to target different elements, groups or combinations enabling customisation for various applications. The relationship between the accumulated mass of the species in the binding phase (M) and its concentration in solution (C) is expressed as (11):

$$M = \frac{C D A t}{\Delta g}$$

In the equation, A is the exposed surface area of the DGT device, D is the diffusion coefficient of the analyte through the diffusive layer, t is the deployment time and Δg is the thickness of the diffusive layer. The diffusion coefficient is different for each element/species and requires investigation and validation before the device is deployed.

When the DGT device is deployed in the environment, trace elements diffuse through the diffusive layer and accumulate on the binding phase. As accumulation occurs, a concentration gradient develops in the diffusive phase (between the window of the device and the binding phase). After a predetermined exposure time, the DGT device is retrieved, and the accumulated trace elements are eluted from the binding phase for subsequent analysis (12).

The DGT technique offers several notable advantages for trace element measurement and assessment (13):

- In-situ Sampling: DGT enables direct sampling of trace elements in their native environment, providing insights into their behaviour under realistic conditions.
- Time-Integrated Sampling: The technique captures the integrated exposure of trace elements over time, yielding comprehensive data on their bioavailability and mobility.
- Selective Capture: By utilising specific binding phases, the DGT technique can target and accumulate particular trace elements, reducing interference from other elements.
- Speciation Insights: The technique can provide information about the chemical forms and species of radioactive isotopes, aiding in understanding their environmental fate.
- Non-Destructive: DGT is a non-destructive sampling method, preserving the integrity of the sampled environment for further analysis or monitoring.
- Multi-Element Capability: The technique's versatility allows for the simultaneous measurement of multiple trace elements using distinct binding phases within a single deployment.

The DGT technique could be applied across a range of environmental settings, including aquatic systems, soils, sediments, and industrial effluents. Ongoing research focuses on refining DGT methodologies, optimising binding phases for specific elements, and expanding its application to new trace elements. As environmental concerns and regulatory frameworks continue to evolve, the DGT technique holds promise for advancing our understanding of trace element dynamics and informing effective environmental management strategies (12).

There are several reviews highlighting applications of DGT (14,15,12,16). However, so far, no reviews have assessed the use of DGT to measure radionuclides in the environment, their strengths, drawbacks and future use.

2. AIMS

The aim of the review is to present a critical evaluation of quantification, analysis and detection of radionuclides using Diffusive Gradients in Thin Films (DGT) and to discuss applications, advances, drawbacks and future perspectives.

3. METHODS

A search was undertaken in Pubmed (March, 2023), using the terms and categories outlined in Table 1. The abstracts were screened and articles with unrelated topics as well as articles without full text were excluded. After that, all remaining articles were excluded if the methodology did not include the analysis of a radioactive isotope.

Table 1 Search terms, categories and connectors used in the literature search

Category	Search term	Number of hits
Title or Abstract	Beryllium, Carbon, Fluorine, Aluminium, Chlorine, Potassium, Calcium, Cobalt, Krypton, Strontium, Iodine, Xenon, Caesium, Cesium, Gadolinium, Bismuth, Barium, Cadmium, Cobalt, Manganese, Sodium, Zinc, Ruthenium, Cerium, Zirconium, Lanthanum, Iron, Silver	1,952,358
Title or Abstract	Radionuclide, radioactive, radioisotope, radioactivity, radioactive waste, actinide, actinoid, nuclear	659,171
Combine these two with AND		71,856
Title or Abstract	Tritium, Technetium, Polonium, Radon, Thorium, Uranium, Plutonium, Americium, Californium, Europium, Thallium, Radium	69,175
Combine these two with OR		138,463
Title or Abstract	DGT, diffusive gradients in thin films	1,361
Combine these two with AND		42

4. RESULTS

Figure 1 shows the trend on publications regarding the use of DGT for measuring radioisotopes in the environment. The first publication found was in 2001 and since then there has been a small but increasing trend on the application of the technique in the literature.

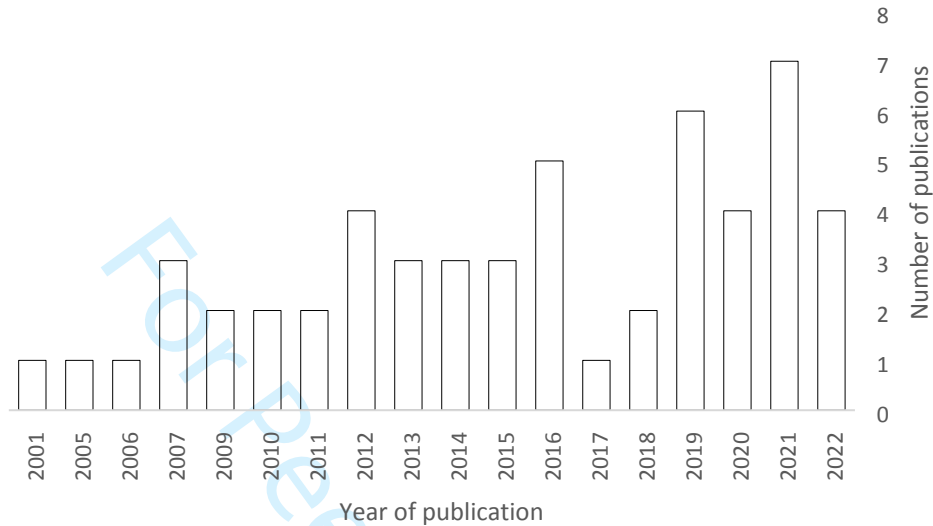


Figure 1 Yearly occurrence of studies related to measurement of radioactive isotopes using Diffuse gradients in thin films sampling technique (DGT)

From the Prisma chart (17) (Figure 2), it can be observed that a total of 38 articles fulfilled the inclusion criteria and therefore were subject to further analysis.

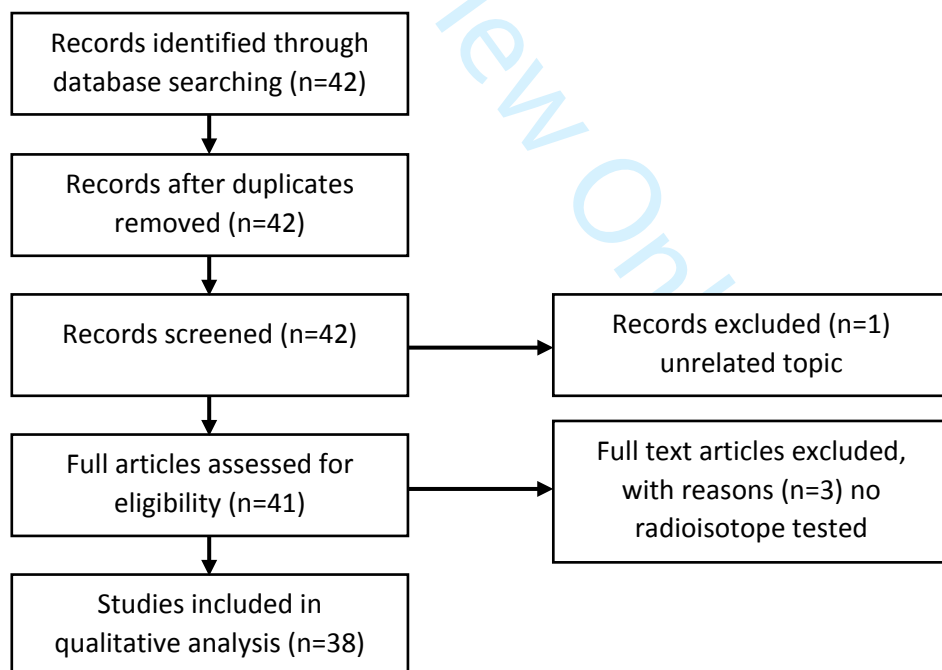


Figure 2 Prisma chart summarising the number of publications found that fulfil the criteria for analysis

Table 2 Summary of the studies on quantification, analysis and detection of radionuclides using Diffusive Gradients in Thin Films (DGT) sampling technique

Elements analysed	Matrix	Det limits	Resin used (diffusive / binding)	Type of analysis	Comments	Ref.
U	Humic acid (HA) and fulvic acid (FA) model solutions	N/R	Polyacrylamide / Chelex-100	Quantitation	Copper competition, pH and ionic strength effects	(18)
U, Th	Phosphate based fertiliser extracts	N/R	Polyacrylamide / Chelex-Metsorb	Quantitation	Comparison to speciation using XANES	(19)
U	Groundwater, surface water	N/R	Polyethersulfone / Metsorb	Quantitation, speciation	Speciation vs geochemical speciation modelling	(20)
U, Pu, Am, and Cm	Spent nuclear fuel pools	N/R	Polyacrylamide / U and Pu KMS-1, Am and Cm IIP-Y3+	Quantitation	N/A	(21)
Pu, Am and U	Marine sediments	N/R	Polyacrylamide / KMS-1 and IIP-Y3+	Quantitation with prior separation	Remobilisation fluxes and bioavailability calculations	(22)
U, Pu and Am	Bulk seawater	N/R	Polyacrylamide / KMS-1 and IIP-Y3+	Quantitation	Comparison DGT-labile fraction vs bulk concentration	(23)
U, Pu and Am	Freshwater and seawater simulants	N/R	Agarose cross-linked polyacrylamide / KMS-1 and IIP-Y3+	Quantitation	Diffusion coefficients reported	(24)
U	Estuarine and marine environments		Polyacrylamide / Chelex-100, Dow-PIWBA, Diphonix, and Lewatit FO 36	Quantitation	Salinity gradients compared	(25)
U	Sediments and porewater	N/R	Polyacrylamide / Chelex-100 resin and DOW PIWBA	Quantitation, mobility and speciation	Comparison to bioaccumulation by <i>Chironomus riparius</i> . Geochemical modelling using CHESS	(26)
Pu	Mineral freshwater	N/R	Polyacrylamide / Chelex-100	Quantitation, bioavailability and speciation	Didactic step by step protocol including a video guide	(27)
U	Experimental solutions	0.02 µg L ⁻¹	Polyacrylamide / Lewatit FO 36	Quantitation	As and U comparison	(28)
U	Wetland soil Uranium mine	N/R	Polyacrylamide and polyethersulfone / Chelex-100	Quantitation, depth profiles	Calculation of depth soil profiles	(29)
U	Synthetic river Water and natural river water	N/R	Polyacrylamide / Dowex, Chelex-100 and DE 81	Quantitation	Comparison between resins	(30)
U	Sediment pore water	9 pg L ⁻¹ U and 1.3 g L ⁻¹ U for DGT and DET respectively	Agarose / Chelex-100 and Spheron-Oxin 1000	Quantitation, isotope ratios	238U/235U isotopic ratio depth profiles	(31)
U	Topsoil and tree core samples		Polyacrylamide / Chelex-100	Quantitation	Other elements analysed: Co, Fe, Pb and Zn, lability and bioavailability is discussed	(32)

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3	U	Model carbonate loaded solutions of natural water	N/R	Agarose / Chelex-100 and Spheron-Oxin with anchored 8-hydroxyquinoline	Quantitation	Comparison between resins	(33)
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8	U	Synthetic solutions	0.79+- 0.08 ng U	Polyacrylamide / Diphonix	Quantitation	Effects of pH (4–9), ionic strength (0.01–1.00 M, as NaNO ₃) and varying aqueous concentrations of Ca ²⁺ (100–500 mg L ⁻¹) and HCO ₃ ⁻ (100–500 mg L ⁻¹)	(34)
9							
10							
11							
12							
13							
14	Pu	Synthetic solutions	N/R	Polyacrylamide / Chelex-100	Quantitation	Special cell used. Diffusion coefficients calculated	(35)
15							
16							
17	U	Contaminated soil pore water and selective extracts	N/R	N/R	Quantitation	Ryegrass uptake correlation to calculate bioavailability	(36)
18							
19							
20	U	Spiked sediment core	9 µg U	Agarose / Spheron-Oxin	Quantitation, depth profiles	Calculation of depth soil profiles. Fe and Mn were also tested	(37)
21							
22							
23	U	Spiked soils	N/R	Polyacrylamide / Chelex-100	Quantitation	Ryegrass uptake correlation to calculate bioavailability. Twelve properties of soil described	(38)
24							
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27							
28	99Tc	Seawater	0.05 and 0.025 Bq L ⁻¹ , for 2- and 4-week DGT deployments	Acrylamide, agarose / TEVA	Quantitation, time-integrated data	Time-integrated data reported. pH range 3-8 and ionic strength range 0.01-1.3 M tested	(39)
29							
30							
31							
32	U	Synthetic and natural waters	N/R	Polyacrylamide / Chelex-100, Metsorb and MnO ₂	Quantitation, speciation	pH (5–9) and ionic strength (0.001–1 mol L ⁻¹ NaNO ₃) and phosphate interference tested. Isotopic ratios measured	(40)
33							
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37	U	Acid mine drainage waters	N/R	Polyacrylamide / Chelex-100	Quantitation	Anions (F ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , Br ⁻ , PO ₄ ³⁻) and cations (Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺) tested. Dissolved Organic Carbon (DOC) and Non Purgeable Organic Carbon (NPOC) tested. Gamma-ray mapping performed	(41)
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47	U	Synthetic water	Diphonix (0.002ug L ⁻¹), Chelex-100 (0.003ug L ⁻¹) and Metsorb (0.003ug L ⁻¹)	Polyacrylamide / Diphonix, Chelex-100 and Metsorb	Quantitation	Diffusion coefficients reported. pH (3-9) and ionic strength (0.001-0.7 M NaNO ₃) tested	(42)
48							
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53	U	Treated acid mine drainage	N/R	Polyacrylamide-agarose / P81, DE81 and Chelex-100	Quantitation, speciation	Ca and Mg measured	(43)
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3	U	Synthetic river water solutions and in local river water	N/R	Polyacrylamide / DE81 and Chelex-100	Quantitation, speciation	Cations (Na+, K+, Ca ²⁺ , Mg ²⁺), anions (Cl ⁻ , SO ₄ ²⁻) measured, Dissolved organic carbon (DOC) Total inorganic carbon (TIC), Total carbon (TC), pH and alkalinity were measured	(44)
4							
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10	U	Synthetic freshwater	Metsorb 0.003 ug L ⁻¹	Polyacrylamide / Metsorb, Chelex-100	Quantitation	pH range 3.0–8.1, speciation modelling (MINEQL) compared	(45)
11							
12	U	Uranium mining site water	N/R	Polyacrylamide / Chelex-100, Metsorb and Diphonix	Quantitation, speciation	Speciation compared to geochemical speciation modelling (PhreeQC)	(46)
13							
14	U and 226Ra	Stream water and soil porewater in a wetland	N/R	Polyacrylamide / Chelex-100	Quantitation, depth profiles	Al, Fe, Mn and Ba measured, speciation done by ultrafiltration compared	(47)
15							
16	U	Uranium mine soil	N/R	Polyacrylamide / Chelex-100	Quantitation	As, Pb, Cd, Ni, Cu, Cr, Mn, Zn, Ba and Rare earths La to Lu measured. Bio- uptake in corn compared. Speciation using sequential extraction compared	(48)
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27	U	Natural and uranium mining influenced waters	PIWBA 0.005 ug L ⁻¹	Polyacrylamide / Chelex-100 and PIWBA	Quantitation, speciation	pH (3-9) and ionic strength (0.001-0.7 M NaNO ₃). Effects of PO ₄ ³⁻ (up to 1.72 X 10 ⁴ M), and HCO ₃ ⁻ (up to 8.20X10 ³ M) tested	(49)
28							
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32	137Cs	Synthetic river water, nuclear industrial discharge water and Chernobyl accident-impacted Berezina River water	1.8 mBq L ⁻¹ (5.9 × 10 ⁻¹⁰ µg L ⁻¹) in 4 week deployment	Polyacrylamide / copper ferrocyanide (CFCN) and Chelex-100	Quantitation, speciation	Stable 133Cs measured	(50)
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40	134Cs and 137Cs	Synthetic river water and nuclear power station discharge water	(60 Bq L ⁻¹)	Polyacrylamide / ammonium molybdophosphate (AMP)	Quantitation	Temperature effect tested	(51)
41							
42	U	Alkaline freshwater	N/R	Polyacrylamide / Metsorb	Quantitation	Long term monitoring, 7 day intervals over 5 months. Comparison with total uranium and 235/238U isotopic ratios. Particulate matter and dissolved organic matter tested	(52)
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52	Pu	Organic-rich natural water	N/R	Polyacrylamide / Chelex-100	Quantitation	Diffusion coefficients reported. dissociation rate constant of plutonium complexes with NOM reported	(53)
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232U, 237Np and 152Eu	Synthetic water	N\R	Polyacrylamide / Chelex-100	Quantitation	High pH range (7 to 13) and 0.005 mol L ⁻¹ NaCl tested	(54)
226Ra	Surface water and sediments of phosphate production wastewater	0.5 pg L ⁻¹ (0.018 Bq L ⁻¹)	Polyacrylamide / Chelex-100 and MnO ₂	Quantitation	Sequential extraction compared	(55)

N\R = Not reported, N\A = Not applicable

Table 2 presents an overview of the publications chosen for the review, as well as a summary of the isotopes analysed, the matrix in which the isotopes were measured, the detection limits, type of resin and conditions measured.

5. CRITICAL EVALUATION AND DISCUSSION

This investigation found that 38 research articles have used the DGT sampling technique to analyse radioactive isotopes. Such research can be divided in two classes: Method development and their deployment in real case scenarios.

5.1. Method development:

A range of elements and isotopes have been investigated using the DGT technique, including U, Th, Pu, Am, Cm, 99Tc, 226Ra, 137Cs, 134Cs, 232U, 237Np, and 152Eu. The significance of these isotopes varies due to factors such as their man-made origin, concentration, environmental risks, speciation and persistence. Each of these radioisotopes plays a unique role in environmental radioactivity and poses distinct challenges and concerns.

The following list provides a non-quantitative evaluation of the importance of measuring these isotopes using DGT and rank them based on several factors such as origin, concentration, risks, and persistence. It's important to note that the ranking provided can vary depending on specific environmental contexts and concerns, and ongoing research may lead to updates in the significance of measuring these radioisotopes. Additionally, the choice of radioisotopes to measure depends on regional factors, nuclear activities, and monitoring objectives.

1. Uranium (U):

Importance: High. Uranium is a naturally occurring element and a key component in nuclear fuel. Its measurement is crucial due to its presence in soil, water, and sediments, especially in regions with uranium mining or nuclear activities. Monitoring U helps assess radiological risk and environmental contamination.

2. Thorium (Th):

Importance: High. Similar to U, thorium is a naturally occurring radioactive element that contributes to environmental radioactivity. Its measurement aids in understanding its distribution in soil and water and its potential influence on human exposure.

3. Plutonium (Pu) and Americium (Am):

Importance: High. Pu and Am are primarily man-made isotopes generated through nuclear reactions. Their measurement is crucial for assessing the legacy of nuclear weapons testing, nuclear accidents, and nuclear waste disposal. These isotopes have long half-lives and can pose significant radiological risks.

4. Curium (Cm) and Neptunium (Np):

Importance: Moderate. Cm and Np are also man-made isotopes produced in nuclear reactors and are present in radioactive waste. Their measurement contributes to understanding the behaviour of transuranic elements in the environment and potential pathways of exposure.

5. Technetium-99 (^{99}Tc):

Importance: Moderate. ^{99}Tc is a by-product of nuclear fission and has a long half-life. Its measurement is relevant for nuclear waste management and understanding its transport in the environment.

6. Radium-226 (^{226}Ra):

Importance: Moderate. ^{226}Ra is a decay product of uranium and thorium. Its measurement is important in assessing the impact of uranium mining, as well as understanding its behaviour in water and its potential health risks.

7. Cesium-137 (^{137}Cs) and Cesium-134 (^{134}Cs):

Importance: Moderate. Cs isotopes are released during nuclear accidents and atmospheric nuclear testing. Their measurement aids in studying the dispersion of radioactive contaminants in the environment and evaluating their radiological impact.

8. Uranium-232 (^{232}U):

Importance: Low. ^{232}U is a decay product of thorium and contributes to the overall radiological impact of thorium decay chains. Its measurement is relevant for understanding the behaviour of thorium series isotopes.

9. Europium-152 (^{152}Eu):

Importance: Low. ^{152}Eu is used in nuclear fuel and as a tracer in environmental studies. Its measurement contributes to assessing potential releases from nuclear facilities.

The following is a list of other Important Radioisotopes that have not been measured using DGT and therefore would be significant to measure in the future:

1. Strontium-90 (^{90}Sr): A fission product released from nuclear reactors, ^{90}Sr can enter the human food chain through plants and animals, potentially impacting human health.
2. Iodine-131 (^{131}I): Released during nuclear accidents, ^{131}I poses a significant health risk due to its accumulation in the thyroid gland.
3. Radon-222 (^{222}Rn): A naturally occurring radioactive gas, ^{222}Rn is a major contributor to indoor radon exposure and can vary widely in concentration.
4. Uranium -236, 238/235 (^{236}U , $^{238}/^{235}\text{U}$): ^{236}U is a relatively novel ocean tracer. In addition, calculation the ratio of $^{238}/^{235}\text{U}$ can help to point to the source of the U
5. Carbon-14 (^{14}C): Present in nuclear waste and used in carbon dating, ^{14}C is important for understanding long-term environmental processes. At present, it is challenging to measure ^{14}C in the environment, it is for that reason that DGT could be used as a long term pre-concentration technique to improve the detection limits and reduce analysis time when ^{14}C is measured.

While studies have predominantly focused on quantitation, there is a growing body of research exploring other aspects such as speciation, mobility, bioavailability, depth profiles, isotope ratios,

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3 and the analysis of time-integrated data, including remobilisation fluxes. Diverse environmental
4 conditions and matrices have been investigated, including humic acid and fulvic acid model
5 solutions, various types of water (groundwater, surface water, spent nuclear fuel pools, seawater),
6 sediments (marine, estuarine, synthetic), soils (topsoil, wetland soil, uranium mine soil), and specific
7 sites impacted by nuclear activities.
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10 In the pursuit of accurate measurements, numerous diffuse layer and binding layer combinations
11 have been employed, showcasing the adaptability of DGT. These combinations include
12 polyacrylamide as well as agarose cross-linked polyacrylamide with various binding agents like
13 Chelex-100, Metsorb, KMS-1, IIP-Y3+, Dow-PIWBA, Lewatit FO 36, Dowex, DE 81, Spheron-Oxin
14 1000, Spheron-Oxin with anchored 8-hydroxyquinoline, Diphonix and TEVA...
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16 The scope of investigations has extended beyond mere quantitation, including more comprehensive
17 studies involving competition between metals, pH and ionic strength effects, comparisons with
18 speciation (XANES and ultrafiltration) and speciation models (CHESS, MINEQL and PhreeQC),
19 bioaccumulation analysis, isotope ratio assessments, and remobilisation flux calculations.
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22 Additionally, the applicability of the DGT technique has been demonstrated across a wide range of
23 environmental matrices, ranging from aquatic systems (groundwater, surface water, estuarine and
24 marine environments) to terrestrial settings (soils, wetland soil, tree cores), and even including
25 specific contexts such as uranium mining sites and nuclear industrial discharge waters. This diversity
26 underscores the versatility of DGT in addressing various research questions related to radionuclide
27 behaviour and environmental impacts.
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30 5.2. Real case scenarios

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32 Research is primarily related to uranium mining, water quality monitoring, and metal speciation. So
33 far, the focus has been to use the passive sampling technique to investigate ions and trace metals to
34 assess their mobility, bioavailability, and potential environmental impacts. The studies highlight the
35 advantages and limitations of DGT compared to traditional methods, providing insights into metal
36 behaviour, speciation, and transport in different environmental contexts.
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39 The research can be classified as

40 1. Uranium Mining and Environmental Impacts:

- 41 • Various studies use DGT to assess uranium behaviour, mobility, and bioavailability in
42 environments impacted by mining activities.
- 43 • In-situ methodologies combining DGT and other techniques are used to evaluate metal
44 resupply and distribution in soil profiles downstream of former uranium mines.
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48 2. Water Quality Monitoring:

- 49 • DGT is employed for long-term monitoring of water quality and metal concentrations,
50 including radionuclides, trace metals, and actinides, in natural waters.
- 51 • The technique is compared to traditional sampling methods, highlighting its advantages in
52 providing time-averaged mean concentrations and accurate measurements.
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55 3. Metal Speciation and Bioavailability:

- 56 • DGT is used to assess metal speciation and lability in sediments and pore waters,
57 contributing to an understanding of metal mobility and potential risks to biota.
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- Studies investigate the relationship between metal concentrations measured by DGT and their bioaccumulation in vegetation, suggesting potential ecological impacts.

4. Comparisons with Existing Techniques:

- DGT is compared to traditional sampling methods, such as grab sampling and sequential extraction, in terms of accuracy, efficiency, and ability to provide meaningful insights into metal behaviour. The technique's advantages include its ability to measure time-averaged mean concentrations, assess labile fractions, and offer a more comprehensive understanding of metal speciation and mobility.

The following common advantages have been found when the passive samplers have been deployed in real case scenarios. DGT allows for in-situ, passive monitoring of metal concentrations and speciation. The technique provides insights into metal mobility, bioavailability, and potential ecological impacts. DGT complements traditional sampling methods, offering a more comprehensive understanding of metal behaviour in different environmental contexts. High-resolution profiles of metals in soil pore water and sediment can be obtained using DGT, providing valuable information for risk assessment.

However, some drawbacks have also been found. DGT measurements may be influenced by factors such as changes in temperature, and biofilm growth. Calibration challenges can arise if large changes in temperature and concentration occur simultaneously. It is noteworthy to mention that such disadvantages are also found when measuring any element (non-radioactive) in similar environmental conditions. Some limitations, specific for radionuclides, are associated with DGT deployment durations and potential degradation of binding agents over longer periods. To address these concerns, Turner et al. (2014) conducted a study involving the measurement of uranium over a 5-month period. This study yielded valuable insights and recommendations, such as the use of protective cages and the measurement of other physical parameters like temperature and pH that are specific to the environment. Based on their findings, they concluded that with the implementation of appropriate measures, DGT samplers can be employed for long-term deployments (52).

In addition, free metal ions are generally considered fully labile. This means that they have a high affinity for the binding phase of the DGT device and are efficiently captured. However, the interpretation of DGT data becomes more complex when dealing with metal-ligand species interactions. Many metal species, including radionuclides, in natural waters form complexes with ligands, and these metal-ligand species exist in a dynamic equilibrium. Some of these complexes may be partially labile, meaning they can interact with the DGT binding phase, but not as effectively as free metal ions.

This distinction between fully labile free metal ions and partially labile metal-ligand complexes introduces a potential limitation in the DGT technique. DGT may not be able to completely detect or quantify the extent of partially labile species present in the environment. Therefore, the interpretation of DGT data requires careful consideration of the underlying speciation dynamics and the potential biases introduced by the assumption of perfect sink conditions.

Importantly, the following ligand-metal interactions have been identified for some of the radionuclides (Table 3) (56,57):

Table 3, Radioisotope - ligand interactions

Isotope/ ligand	Carbonate	Hydroxide	Organic matter	Sulphate
Uranium (U)	carbonate complexes in basic conditions	hydroxide complexes in basic conditions	NA	NA
Thorium (Th)	carbonate complexes in basic conditions	hydroxide complexes in basic conditions	NA	NA
Plutonium (Pu) and Americium (Am)	NA	NA	interact with natural organic matter forming complexes	NA
Curium (Cm) and Neptunium (Np)	carbonate complexes in basic conditions	NA	interact with natural organic matter affecting their speciation	NA
Technetium-99 (99Tc)	NA	NA	NA	NA
Radium-226 (226Ra)	NA	NA	NA	sulphate complexes in sulphate-rich conditions
Cesium-137 (137Cs) and Cesium-134 (134Cs)	weak complexes with carbonate	NA	NA	NA
Uranium-232 (232U)	Similar to other uranium isotopes, uranium-232 form carbonate complexes	NA	NA	NA
Europium-152 (152Eu)	No specific ligand-metal interactions have been found			

Several studies have addressed this challenge and examined the extent to which DGT measurements accurately reflect the true metal speciation. For instance, research by dos Anjos et al. (2017) and Mongin et al. (2011) have highlighted instances where DGT may not fully capture the presence of partially labile metal-ligand species. This underscores the importance of interpreting DGT data in the context of the specific speciation parameters and metal-ligand interactions present in the environment under study (58,59).

Although there are only a limited number of studies that have tackled the ligand-metal challenges specific to radionuclides, noteworthy investigations have made progress in this regard. For instance, researchers have tested variations in pH and organic matter, as well as ionic strength (54,45,18,34,39,41,42), all of which can influence metal-ligand interactions. A particularly significant study by Drozdal et al. (2016) investigated the interplay of uranium speciation in conditions with different pH ranges, varying levels of phosphate, and the presence of carbonate and ionic strength. The findings suggested that neither phosphate (PO_4^{3-}) nor bicarbonate (HCO_3^-) had a significant impact on the quantitative measurement of uranium using the DGT-PIWBA method. Only when confronted with high concentrations of calcium ions and sulphate ions did the uptake of uranium by DGT-PIWBA experience reduction. The study concluded that an exhaustive laboratory

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3 characterization of the DGT binding phase layer is a prerequisite before starting in-situ fieldwork to
4 ensure the accuracy of results and their interpretation (49).
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6 It is important to note that the interactions between radionuclides and ligands can vary in different
7 environmental matrices, such as water, soil, sediments, and biological tissues. Further research is
8 needed to fully understand the specific ligand-metal interactions for each radionuclide in different
9 environmental contexts. Therefore, the interpretation of DGT results is essential for understanding
10 how the technique captures and reflects the speciation of metals in complex environmental
11 samples. Researchers must carefully evaluate DGT data in conjunction with knowledge of speciation
12 parameters, potential biases, and the assumptions made regarding perfect sink conditions to derive
13 meaningful insights into the speciation dynamics of metals in natural systems.
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16 5.3. Future Perspectives 17

18 DGT is expected to play a significant role in improving radiation dose modelling, understanding
19 metal speciation, and assessing environmental risks associated with mining activities. DGT could
20 prove valuable for sampling and pre-concentration of alkaline radioactive earth metals, including
21 strontium (Sr). Moreover, DGT can effectively concentrate neutral anionic species like iodine (I),
22 acting as a versatile pre-concentration technique depending on the DGT binding phase. This
23 highlights DGT's adaptability in enhancing sampling and pre-concentration for diverse metal ions and
24 anionic species. The technique's potential for long-term water quality monitoring and its application
25 to various environmental projects, such as nuclear waste disposal, highlight its importance in future
26 research. Further developments in DGT technology and methodologies are anticipated to enhance
27 its applicability and accuracy in various environmental studies.
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31 6. CONCLUSIONS 32

33 This review underscores the significance of the Diffusive Gradients in Thin Films (DGT) technique as a
34 valuable tool for the quantification, analysis, and detection of radionuclides in diverse environmental
35 settings. Through a comprehensive analysis of method development and real case scenarios, it
36 becomes evident that DGT offers a holistic approach to understanding the behaviour of
37 radionuclides and other trace elements. The ranking of isotopes based on importance highlights the
38 wide-ranging implications of radionuclide presence, spanning from natural occurrences to
39 anthropogenic activities. The technique's versatility is evident in its applications, ranging from
40 uranium mining assessments to water quality monitoring and metal speciation studies. By offering
41 insights into mobility, bioavailability, and potential ecological impacts, DGT stands as a powerful tool
42 in unravelling the complex interactions between radionuclides and their surroundings. While
43 challenges and limitations exist, such as potential influences from biofouling, calibration difficulties
44 and metal-ligand interactions, ongoing developments in DGT technology and methodologies hold
45 promise for overcoming these obstacles and enhancing the technique's accuracy and applicability.
46 As regulatory frameworks and environmental concerns continue to evolve, DGT's role in advancing
47 our understanding of radionuclide behaviour and informing effective environmental management
48 strategies is poised to expand, contributing significantly to safeguarding human health and
49 preserving ecological integrity.
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For Peer Review Only

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3 A critical review of the quantification, analysis and detection of radionuclides in environment using
4 Diffusive Gradients in Thin Films (DGT): advances and perspectives
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14 ABSTRACT 15

16 This critical review explores the quantification, analysis, and detection of radionuclides in the
17 environment using the Diffusive Gradients in Thin Films (DGT) technique.
18

19 Radionuclides, unstable isotopes emitting ionising radiation, are present in the environment due to
20 natural and anthropogenic sources for which concerns are raised about their impact on human
21 health and ecosystems. DGT offers a unique passive sampling approach for understanding the
22 behaviour of radionuclides and other trace elements. This review provides insights into method
23 development, real case scenarios, advantages, limitations, and future perspectives of DGT in
24 radionuclide analysis.
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27 In terms of method development, various isotopes have been analysed with varying significance
28 based on origin, concentration, risks, and persistence. Notably, U, Th, Pu, Am, Cm, 99Tc, 226Ra,
29 137Cs, 134Cs, 232U, 237Np, and 152Eu have been measured, revealing their diverse roles in
30 environmental radioactivity. Real case scenarios illustrate applications in uranium mining, water
31 quality monitoring, and metal speciation studies, shedding light on mobility, bioavailability, and
32 ecological impacts. DGT's advantages include in-situ monitoring, time-averaged mean
33 concentrations, and comprehensive speciation insights. Challenges include potential influences from
34 biofouling, temperature changes and specifically the possible degradation of the binding and diffuse
35 layer due to ionising radiation in long term exposures. In addition, the distinction between fully
36 labile free metal ions and partially labile metal-ligand complexes introduces a potential limitation in
37 the DGT technique, **hence therefore being an opportunity for future studies**. Looking forward, DGT is
38 expected to contribute to radiation dose modelling, environmental risk assessment, and water
39 quality monitoring, with ongoing developments enhancing its utility and accuracy.
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1. INTRODUCTION

1.1. Radionuclides in the environment, sources and human health

Radionuclides are unstable isotopes of elements that emit ionising radiation as they undergo radioactive decay. Many of these radioactive isotopes are naturally present in the environment due to cosmic radiation, geological processes, and natural nuclear reactions (e.g uranium, thorium, and radon) ((US), 1999). Additionally, anthropogenic activities, such as nuclear power generation, nuclear weapons testing, and industrial practices, have introduced a variety of man-made radionuclides into the environment. These can include isotopes like cesium-137, strontium-90, and iodine-131 (Qin-Hong , Jian-Qing, & Jin-Sheng , 2010). The presence of radionuclides in the environment raises concerns about their impact on human and ecosystems health as well as the potential for long-term contamination.

Radionuclides in the environment can pose significant health risks to humans through multiple pathways. Radioactive particles present in the air can be inhaled, potentially leading to ante overall radionuclide incorporation as well as the irradiation of lung tissue and an increased risk of lung cancer. Moreover, the consumption of contaminated food and water can result in the ingestion of radionuclides, leading to their accumulation within the body and subsequent irradiation of internal organs (Fritz & Patton, 2006). Additionally, individuals can be externally exposed to radiation by coming into contact with surfaces that have been contaminated with radioactive materials.

Natural radionuclides contribute to the background radiation that humans are exposed to daily. Currently, there is a good understanding of the distribution and behaviour of many naturally occurring radionuclides (Belli & Indovina , 2020). In addition, events such as the Chernobyl disaster and the Fukushima Daiichi nuclear accident have provided valuable insights into the behaviour of radionuclides following large-scale releases into the environment. As a consequence, regulatory agencies and international organisations have established guidelines and safety standards for permissible levels of exposure to radionuclides to protect human health (Hirose, 2020).

Regulatory agencies face several challenges regarding- the occurrence of such radionuclides of man-made origin. Some show extended half-lives, resulting in persistent contamination that can endure across generations. Their mobility across diverse environmental compartments such as air, water, and soil, coupled with their propensity to accumulate within biota, show intricate and elusive behavioural patterns that defy straightforward prediction (Deblonde, Kersting, & Zavarin, 2020). This complex interplay of radionuclides with ecosystems has the potential to disrupt natural processes, jeopardising plants and animals, thereby fostering genetic mutations and undermining biodiversity. The assessment of health repercussions arising from prolonged low-level radiation exposure poses a formidable challenge, and uncertainties persist concerning the precise risks attributed to distinct radionuclides. Crucially, the proper disposal and management of radioactive waste originating from nuclear facilities assume paramount importance in averting enduring environmental contamination of global proportions (Salbu, et al., 2018).

1.2. Current techniques for the sampling of radionuclides

The measurement of radionuclides in the environment is crucial for assessing potential radiation exposure, understanding radioactive contamination, and ensuring the safety of ecosystems and human populations. Radionuclide sampling techniques play a pivotal role in capturing accurate and representative data for effective radiological monitoring and risk assessment.

There are several techniques for sampling radionuclides in the environment. Particularly, when sampling is performed within the environment, a spectrum of techniques is employed.

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3 In air sampling, two noteworthy methods stand out. Particulate air sampling involving the use of
4 high-volume air samplers to capture airborne particles on filters, facilitating the analysis of alpha,
5 beta, and gamma-emitting radionuclides. In addition, gaseous radionuclide sampling captures
6 airborne noble gases through specialised adsorption systems or cryogenic techniques (Paretzke,
7 Deluca, & Wambersie, 2006).
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10 For water sampling, grab sampling collects discrete water samples from various sources such as
11 surface water bodies, groundwater wells, or effluents, enabling the examination of radionuclide
12 concentrations. Automated water samplers, on the other hand, systematically collect water samples
13 at predetermined intervals, offering valuable time-series data for assessing variations in radionuclide
14 levels over time (Salbu, et al., 2018).
15

16 Soil sampling encompasses both surface soil sampling, which gathers soil specimens from the upper
17 layer to analyse radionuclide distribution, and core sampling, involving the collection of soil cores to
18 study vertical radionuclide profiles and migration patterns (Paretzke, Deluca, & Wambersie, 2006). It
19 is important to note that soil sampling can also involve porewater analyses for partition coefficient
20 studies.
21
22

23 Regarding biota sampling, biological tissue sampling involves collecting plant and animal tissues to
24 assess radionuclide uptake and bioaccumulation. Moreover, seawater and sediment biota sampling
25 target marine organisms like fish and benthic creatures, shedding light on the transfer of
26 radionuclides through aquatic food chains (Koralan, et al., 2023). Finally, sediment sampling adopts
27 distinct approaches: surface sediment sampling captures sediments from the water-sediment
28 interface, providing insights into radionuclide deposition and interactions, while core sediment
29 sampling extracts sediment cores to delve into historical radionuclide deposition and sediment
30 mixing dynamics.
31
32

33 Regardless of the sampling method chosen, there are a number of challenges to consider when it
34 comes to ensuring reliability and accuracy. One key aspect is selecting sampling locations that truly
35 represent the area of interest, so that any potential bias is avoided. It is also crucial to handle and
36 preserve samples correctly to prevent any changes or decay of the radioactive materials. Rigorous
37 quality control measures are essential to validate both the sampling process and subsequent
38 laboratory analysis. To maintain the integrity of the data, it is important to prevent any
39 contamination between samples and equipment (Salbu B. , 2009).
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43 1.3. DGT as sampling technique, introduction, overview, comparison and advantages

44 The Diffusive Gradients in Thin Films (DGT) technique has emerged as a versatile and innovative
45 approach in environmental science for the quantification and assessment of the bioavailability,
46 speciation, and mobility of various trace elements, including radioisotopes, in complex matrices.
47 Developed as a passive sampling method, the DGT technique offers unique advantages in
48 understanding the behaviour of elements in different environmental compartments (Davison &
49 Zhang , In situ speciation measurements of trace components in natural waters using thin-film gels,
50 1994).
51
52

53 The DGT technique operates on fundamental principles of diffusion and adsorption, allowing for the
54 precise capture of labile forms of trace elements from the surrounding environment. The technique
55 involves the deployment of a specialised DGT device that consists of two key components: a
56 diffusive layer and a binding phase.
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3 The diffusive layer is a permeable membrane that controls the rate at which trace elements from the
4 surrounding medium diffuse into the DGT device. This mechanism prevents the sampling of analytes
5 without the influence of convection. Its thickness and material properties are designed to mimic the
6 diffusion characteristics of the target elements, ensuring controlled and time-integrated sampling.
7

8
9 The binding phase of the DGT device is carefully selected based on the chemical properties of the
10 trace elements of interest. This binding phase has a high affinity for specific elements, or groups of
11 elements, allowing selective capture and accumulation. Under normal circumstances, the solute
12 binds strongly to the binding layer, leading to a negligible concentration at the interface between
13 the diffusion and binding layers. Different binding phases can be employed to target different
14 elements, groups or combinations enabling customisation for various applications.
15

16
17 The relationship between the accumulated mass of the species in the binding phase (M) and its
18 concentration in solution (C) is expressed as (Davison & Zhang, In situ speciation measurements of
19 trace components in natural waters using thin-film gels, 1994):

$$M = \frac{CDA t}{\Delta g}$$

20
21
22
23 In the equation, A is the exposed surface area of the DGT device, D is the diffusion coefficient of the
24 analyte through the diffusive layer, t is the deployment time and Δg is the thickness of the diffusive
25 layer. The diffusion coefficient is different for each element/species and requires investigation and
26 validation before the device is deployed.
27

28
29 When the DGT device is deployed in the environment, trace elements diffuse through the diffusive
30 layer and accumulate on the binding phase. As accumulation occurs, a concentration gradient
31 develops in the diffusive phase (between the window of the device and the binding phase) within the
32 device. After a predetermined exposure time, the DGT device is retrieved, and the accumulated
33 trace elements are eluted from the binding phase for subsequent analysis (Menegário, Yabuki, Luko,
34 Williams, & Blackburn, 2017).
35

36
37 The DGT technique offers several notable advantages for trace element measurement and
38 assessment (Davison, Diffusive Gradients in Thin-Films for Environmental Measurements, 2016):

- 39 • In-situ Sampling: DGT enables direct sampling of trace elements in their native environment,
40 providing insights into their behaviour under realistic conditions.
- 41 • Time-Integrated Sampling: The technique captures the integrated exposure of trace
42 elements over time, yielding comprehensive data on their bioavailability and mobility.
- 43 • Selective Capture: By utilising specific binding phases, the DGT technique can target and
44 accumulate particular trace elements, reducing interference from other elements.
- 45 • Speciation Insights: The technique can provide information about the chemical forms and
46 species of radioactive isotopes, aiding in understanding their environmental fate.
- 47 • Non-Destructive: DGT is a non-destructive sampling method, preserving the integrity of the
48 sampled environment for further analysis or monitoring.
- 49 • Multi-Element Capability: The technique's versatility allows for the simultaneous
50 measurement of multiple trace elements using distinct binding phases within a single
51 deployment.
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56
57 The DGT technique could be applied across a range of environmental settings, including aquatic
58 systems, soils, sediments, and industrial effluents. Ongoing research focuses on refining DGT
59 methodologies, optimising binding phases for specific elements, and expanding its application to
60 new trace elements. As environmental concerns and regulatory frameworks continue to evolve, the

DGT technique holds promise for advancing our understanding of trace element dynamics and informing effective environmental management strategies (Menegário, Yabuki, Luko, Williams, & Blackburn, 2017).

There are several reviews highlighting applications of DGT (Zhang, Ding, Xu, Tang, & Wong, 2014; Ji, Challis, & Brinkmann, 2022; Menegário, Yabuki, Luko, Williams, & Blackburn, 2017; Davison & Zhang, Progress in understanding the use of diffusive gradients in thin films (DGT) – back to basics, 2011). However, so far, no reviews have assessed the use of DGT to measure radionuclides in the environment, their strengths, drawbacks and future use.

2. AIMS

The aim of the review is to present a critical evaluation of quantification, analysis and detection of radionuclides using Diffusive Gradients in Thin Films (DGT) and to discuss applications, advances, drawbacks and future perspectives.

3. METHODS

A search was undertaken in Pubmed (March, 2023), using the terms and categories outlined in Table 1. The abstracts were screened and articles with unrelated topics as well as articles without full text were excluded. After that, all remaining articles were excluded if the methodology did not include the analysis of a radioactive isotope.

Table 1 Search terms, categories and connectors used in the literature search

Category	Search term	Number of hits
Title or Abstract	Beryllium, Carbon, Fluorine, Aluminium, Chlorine, Potassium, Calcium, Cobalt, Krypton, Strontium, Iodine, Xenon, Caesium, Cesium, Gadolinium, Bismuth, Barium, Cadmium, Cobalt, Manganese, Sodium, Zinc, Ruthenium, Cerium, Zirconium, Lanthanum, Iron, Silver	1,952,358
Title or Abstract	Radionuclide, radioactive, radioisotope, radioactivity, radioactive waste, actinide, actinoid, nuclear	659,171
Combine these two with AND		71,856
Title or Abstract	Tritium, Technetium, Polonium, Radon, Thorium, Uranium, Plutonium, Americium, Californium, Europium, Thallium, Radium	69,175
Combine these two with OR		138,463
Title or Abstract	DGT, diffusive gradients in thin films	1,361
Combine these two with AND		42

4. RESULTS

Figure 1 shows the trend on publications regarding the use of DGT for measuring radioisotopes in the environment. The first publication found was in 2001 and since then there has been a small but increasing trend on the application of the technique in the literature.

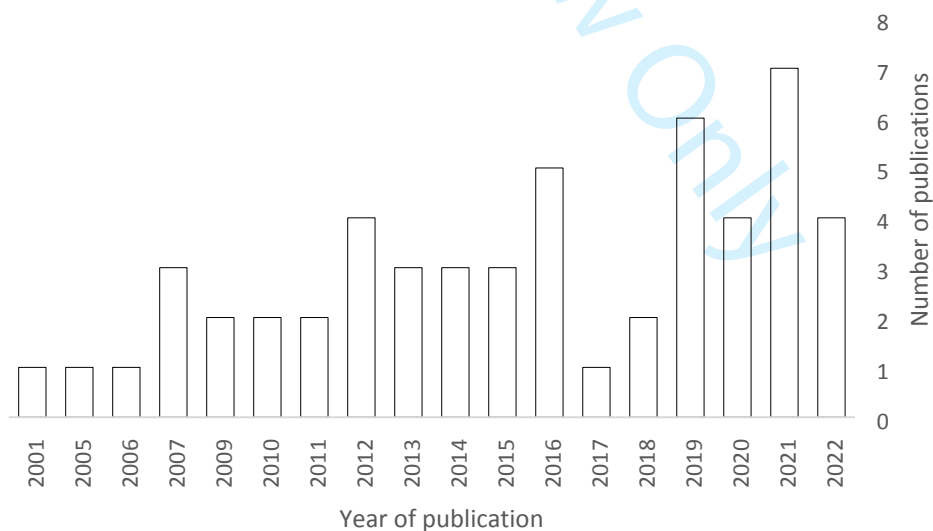


Figure 1 Yearly occurrence of studies related to measurement of radioactive isotopes using Diffuse gradients in thin films sampling technique (DGT)

From the Prisma chart (Page, et al., 2021) (Figure 2), it can be observed that a total of 38 articles fulfilled the inclusion criteria and therefore were subject to further analysis.

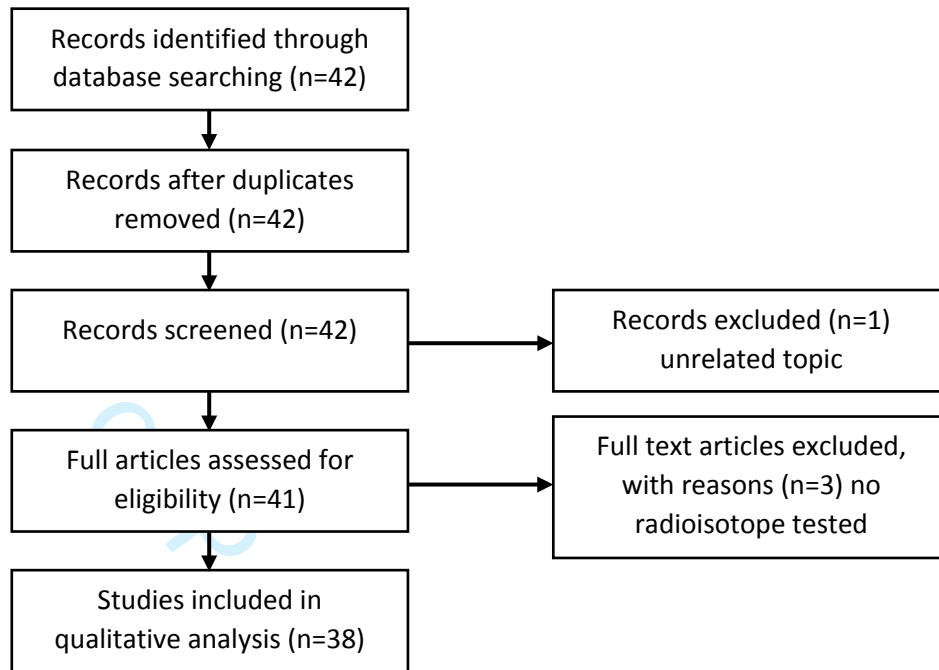


Figure 2 Prisma chart summarising the number of publications found that fulfil the criteria for analysis

Table 2 Summary of the studies on quantification, analysis and detection of radionuclides using Diffusive Gradients in Thin Films (DGT) sampling technique

Elements analysed	Matrix	Det limits	Resin used (diffusive / binding)	Type of analysis	Comments	Ref.
U	Humic acid (HA) and fulvic acid (FA) model solutions	N/R	Polyacrylamide / Chelex-100	Quantitation	Copper competition, pH and ionic strength effects	22
U, Th	Phosphate based fertiliser extracts	N/R	Polyacrylamide / Chelex-Metsorb	Quantitation	Comparison to speciation using XANES	28
U	Groundwater, surface water	N/R	Polyethersulfone / Metsorb	Quantitation, speciation	Speciation vs geochemical speciation modelling	29
U, Pu, Am, and Cm	Spent nuclear fuel pools	N/R	Polyacrylamide / U and Pu KMS-1, Am and Cm IIP-Y3+	Quantitation	N/A	30
Pu, Am and U	Marine sediments	N/R	Polyacrylamide Polyethersulfone / KMS-1 and IIP-Y3+	Quantitation with prior separation	Remobilisation fluxes and bioavailability calculations	31
U, Pu and Am	Bulk seawater	N/R	Polyacrylamide Polyethersulfone / KMS-1 and IIP-Y3+	Quantitation	Comparison DGT-labile fraction vs bulk concentration	32
U, Pu and Am	Freshwater and seawater simulants	N/R	Agarose cross-linked polyacrylamide / KMS-1 and IIP-Y3+	Quantitation	Diffusion coefficients reported	33

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3	U	Estuarine and marine environments		Polyacrylamide / Chelex-100, Dow-PIWBA, Diphonix, and Lewatit FO 36	Quantitation	Salinity gradients compared	34
4							
5							
6							
7	U	Sediments and porewater	N/R	Polyacrylamide /Chelex-100 resin and DOW PIWBA	Quantitation, mobility and speciation	Comparison to <i>Chironomus riparius</i> . Geochemical modelling using CHESS	35
8							
9							
10							
11	Pu	Mineral freshwater	N/R	Polyacrylamide / Chelex-100	Quantitation, bioavailability and speciation	Didactic step by step protocol including a video guide	36
12							
13							
14							
15	U	Experimental solutions	0.02 µg L ⁻¹	Polyacrylamide / Lewatit FO 36	Quantitation	As and U comparison	37
16							
17	U	Wetland soil Uranium mine	N/R	Polyacrylamide and polyethersulfone / Chelex-100	Quantitation, depth profiles	Calculation of depth soil profiles	38
18							
19							
20	U	Synthetic river Water and natural river water	N/R	Polyacrylamide / Dowex, Chelex-100 and DE 81	Quantitation	Comparison between resins	39
21							
22							
23							
24	U	Sediment pore water	9 pg L ⁻¹ U and 1.3 g L ⁻¹ U for DGT and DET respectively	Agarose / Chelex-100 and Spheron-Oxin 1000	Quantitation, isotope ratios	238U/235U isotopic ratio depth profiles	40
25							
26							
27							
28	U	Topsoil and tree core samples		Polyacrylamide / Chelex-100	Quantitation	Other elements analysed: Co, Fe, Pb and Zn, lability and bioavailability is discussed	41
29							
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33	U	Model carbonate loaded solutions of natural water	N/R	Agarose / Chelex-100 and Spheron-Oxin with anchored 8-hydroxyquinoline	Quantitation	Comparison between resins	42
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36							
37	U	Synthetic solutions	0.79+- 0.08 ng U	Polyacrylamide / Diphonix	Quantitation	Effects of pH (4–9), ionic strength (0.01–1.00 M, as NaNO ₃) and varying aqueous concentrations of Ca ²⁺ (100–500 mg L ⁻¹) and HCO ₃ ⁻ (100–500 mg L ⁻¹)	23
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42							
43	Pu	Synthetic solutions	N/R	Polyacrylamide / Chelex-100	Quantitation	Special cell used. Diffusion coefficients calculated	43
44							
45							
46	U	Contaminated soil pore water and selective extracts	N/R	N/R	Quantitation	Ryegrass uptake correlation to calculate bioavailability	44
47							
48							
49							
50	U	Spiked sediment core	9 pg U	Agarose / Spheron-Oxin	Quantitation, depth profiles	Calculation of depth soil profiles. Fe and Mn were also tested	45
51							
52							
53	U	Spiked soils	N/R	Polyacrylamide / Chelex-100	Quantitation	Ryegrass uptake correlation to calculate bioavailability. Twelve properties of soil described	46
54							
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57	99Tc	Seawater	0.05 and 0.025 Bq L ⁻¹ , for 2- and 4-week DGT	Acrylamide, agarose / TEVA	Quantitation, time-integrated data	Time-integrated data reported. pH range 3-8 and ionic strength range 0.01-1.3 M tested	24
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deployments

U	Synthetic and natural waters	N/R	Polyacrylamide / Chelex-100, Metsorb and MnO ₂	Quantitation, speciation	pH (5–9) and ionic strength (0.001–1 mol L ⁻¹ NaNO ₃) and phosphate interference tested. Isotopic ratios measured	47
U	Acid mine drainage waters	N/R	Polyacrylamide / Chelex-100	Quantitation	Anions (F ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , Br ⁻ , PO ₄ ³⁻) and cations (Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺) tested. Dissolved Organic Carbon (DOC) and Non Purgeable Organic Carbon (NPOC) tested. Gamma-ray mapping performed	25
U	Synthetic water	Diphonix (0.002ug L ⁻¹), Chelex-100 (0.003ug L ⁻¹) and Metsorb (0.003ug L ⁻¹)	Polyacrylamide / Diphonix, Chelex-100 and Metsorb	Quantitation	Diffusion coefficients reported. pH (3-9) and ionic strength (0.001-0.7 M NaNO ₃) tested	26
U	Treated acid mine drainage	N/R	Polyacrylamide-agarose / P81, DE81 and Chelex-100	Quantitation, speciation	Ca and Mg measured	48
U	Synthetic river water solutions and in local river water	N/R	Polyacrylamide / DE81 and Chelex-100	Quantitation, speciation	Cations (Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺), anions (Cl ⁻ , SO ₄ ²⁻) measured, Dissolved organic carbon (DOC) Total inorganic carbon (TIC), Total carbon (TC), pH and alkalinity were measured	49
U	Synthetic freshwater	Metsorb 0.003 ug L ⁻¹	Polyacrylamide / Metsorb, Chelex-100	Quantitation	pH range 3.0–8.1, speciation modelling (MINEQL) compared	21
U	Uranium mining site water	N/R	Polyacrylamide / Chelex-100, Metsorb and Diphonix	Quantitation, speciation	Speciation compared to geochemical speciation modelling (PhreeQC)	50
U and 226Ra	Stream water and soil porewater in a wetland	N/R	Polyacrylamide / Chelex-100	Quantitation, depth profiles	Al, Fe, Mn and Ba measured, speciation done by ultrafiltration compared	51
U	Uranium mine soil	N/R	Polyacrylamide / Chelex-100	Quantitation	As, Pb, Cd, Ni, Cu, Cr, Mn, Zn, Ba and Rare earths La to Lu measured. Bio- uptake in corn compared. Speciation using sequential extraction compared	52
U	Natural and uranium mining influenced waters	PIWBA 0.005 ug L ⁻¹	Polyacrylamide / Chelex-100 and PIWBA	Quantitation, speciation	pH (3-9) and ionic strength (0.001-0.7 M NaNO ₃). Effects of PO ₄ ³⁻ (up to 1.72 X 10 ⁴ M), and HCO ₃ ⁻ (up to 8.20X10 ³ M) tested	27

137Cs	Synthetic river water, nuclear industrial discharge water and Chernobyl accident-impacted Berezina River water	1.8 mBq L ⁻¹ (5.9×10^{-10} µg L ⁻¹) in 4 week deployment	Polyacrylamide / copper ferrocyanide (CFCN) and Chelex-100	Quantitation, speciation	Stable 133Cs measured	53
134Cs and 137Cs	Synthetic river water and nuclear power station discharge water	(60 Bq L ⁻¹)	Polyacrylamide / ammonium molybdophosphate (AMP)	Quantitation	Temperature effect tested	54
U	Alkaline freshwater	N/R	Polyacrylamide / Metsorb	Quantitation	Long term monitoring, 7 day intervals over 5 months. Comparison with total uranium and 235/238U isotopic ratios. Particulate matter and dissolved organic matter tested	17
Pu	Organic-rich natural water	N/R	Polyacrylamide / Chelex-100	Quantitation	Diffusion coefficients reported. dissociation rate constant of plutonium complexes with NOM reported	55
232U, 237Np and 152Eu	Synthetic water	N\R	Polyacrylamide / Chelex-100	Quantitation	High pH range (7 to 13) and 0.005 mol L ⁻¹ NaCl tested	20
226Ra	Surface water and sediments of phosphate production wastewater	0.5 pg L ⁻¹ (0.018 Bq L ⁻¹)	Polyacrylamide / Chelex-100 and MnO ₂	Quantitation	Sequential extraction compared	56

N\R = Not reported, N\A = Not applicable

Table 2 presents an overview of the publications chosen for the review, as well as a summary of the isotopes analysed, the matrix in which the isotopes were measured, the detection limits, type of resin and conditions measured.

5. CRITICAL EVALUATION AND DISCUSSION

This investigation found that 38 research articles have used the DGT sampling technique to analyse radioactive isotopes. Such research can be divided in two classes: Method development and their deployment in real case scenarios.

5.1. Method development:

A range of elements and isotopes have been investigated using the DGT technique, including U, Th, Pu, Am, Cm, 99Tc, 226Ra, 137Cs, 134Cs, 232U, 237Np, and 152Eu. The significance of these isotopes varies due to factors such as their man-made origin, concentration, environmental risks, speciation, and persistence. Each of these radioisotopes plays a unique role in environmental radioactivity and poses distinct challenges and concerns.

The following list provides a non-quantitative evaluation of the importance of measuring these isotopes using DGT and rank them based on several factors such as origin, concentration, risks, and

1
2
3 persistence. It's important to note that the ranking provided can vary depending on specific
4 environmental contexts and concerns, and ongoing research may lead to updates in the significance
5 of measuring these radioisotopes. Additionally, the choice of radioisotopes to measure depends on
6 regional factors, nuclear activities, and monitoring objectives.
7

8
9 1. Uranium (U):

10 Importance: High. Uranium is a naturally occurring element and a key component in nuclear fuel. Its
11 measurement is crucial due to its presence in soil, water, and sediments, especially in regions with
12 uranium mining or nuclear activities. Monitoring U helps assess radiological risk and environmental
13 contamination.
14

15
16 2. Thorium (Th):

17 Importance: High. Similar to U, thorium is a naturally occurring radioactive element that contributes
18 to environmental radioactivity. Its measurement aids in understanding its distribution in soil and
19 water and its potential influence on human exposure.
20

21
22 3. Plutonium (Pu) and Americium (Am):

23 Importance: High. Pu and Am are primarily man-made isotopes generated through nuclear reactions.
24 Their measurement is crucial for assessing the legacy of nuclear weapons testing, nuclear accidents,
25 and nuclear waste disposal. These isotopes have long half-lives and can pose significant radiological
26 risks.
27

28
29 4. Curium (Cm) and Neptunium (Np):

30 Importance: Moderate. Cm and Np are also man-made isotopes produced in nuclear reactors and
31 are present in radioactive waste. Their measurement contributes to understanding the behaviour of
32 transuranic elements in the environment and potential pathways of exposure.
33

34
35 5. Technetium-99 (^{99}Tc):

36 Importance: Moderate. ^{99}Tc is a by-product of nuclear fission and has a long half-life. Its
37 measurement is relevant for nuclear waste management and understanding its transport in the
38 environment.
39

40
41 6. Radium-226 (^{226}Ra):

42 Importance: Moderate. ^{226}Ra is a decay product of uranium and thorium. Its measurement is
43 important in assessing the impact of uranium mining, as well as understanding its behaviour in water
44 and its potential health risks.
45

46
47 7. Cesium-137 (^{137}Cs) and Cesium-134 (^{134}Cs):

48 Importance: Moderate. Cs isotopes are released during nuclear accidents and atmospheric nuclear
49 testing. Their measurement aids in studying the dispersion of radioactive contaminants in the
50 environment and evaluating their radiological impact.
51

52
53 8. Uranium-232 (^{232}U):

54 Importance: Low. ^{232}U is a decay product of thorium and contributes to the overall radiological
55 impact of thorium decay chains. Its measurement is relevant for understanding the behaviour of
56 thorium series isotopes.
57
58
59
60

9. Europium-152 (¹⁵²Eu):

Importance: Low. ¹⁵²Eu is used in nuclear fuel and as a tracer in environmental studies. Its measurement contributes to assessing potential releases from nuclear facilities.

The following is a list of other Important Radioisotopes that have not been measured using DGT and therefore would be significant to measure in the future:

1. Strontium-90 (⁹⁰Sr): A fission product released from nuclear reactors, ⁹⁰Sr can enter the human food chain through plants and animals, potentially impacting human health.
2. Iodine-131 (¹³¹I): Released during nuclear accidents, ¹³¹I poses a significant health risk due to its accumulation in the thyroid gland.
3. Radon-222 (²²²Rn): A naturally occurring radioactive gas, ²²²Rn is a major contributor to indoor radon exposure and can vary widely in concentration.
- 3.4. Uranium -236, 238/235 (²³⁶U, ^{238/235}U): ²³⁶U is a relatively novel ocean tracer. In addition calculation the ratio of ^{238/235}U can help to point to the source of the U
- 4.5. Carbon-14 (¹⁴C): Present in nuclear waste and used in carbon dating, ¹⁴C is important for understanding long-term environmental processes. At present, it is challenging to measure ¹⁴C in the environment, it is for that reason that DGT could be used as a long term pre-concentration technique to improve the detection limits and reduce analysis time when ¹⁴C is measured.

While studies have predominantly focused on quantitation, there is a growing body of research exploring other aspects such as speciation, mobility, bioavailability, depth profiles, isotope ratios, and the analysis of time-integrated data, including remobilisation fluxes. Diverse environmental conditions and matrices have been investigated, including humic acid and fulvic acid model solutions, various types of water (groundwater, surface water, spent nuclear fuel pools, seawater), sediments (marine, estuarine, synthetic), soils (topsoil, wetland soil, uranium mine soil), and specific sites impacted by nuclear activities.

In the pursuit of accurate measurements, numerous diffuse layer and binding layer combinations have been employed, showcasing the adaptability of DGT. These combinations include polyacrylamide as well as agarose cross-linked polyacrylamide with various binding agents like Chelex-100, Metsorb, KMS-1, ~~CM~~ IIP-Y3+, Dow-PIWBA, Lewatit FO 36, Dowex, DE 81, Spheron-Oxin 1000, Spheron-Oxin with anchored 8-hydroxyquinoline, Diphonix and TEVA, and some combinations, as well as agarose cross-linked polyacrylamide.

The scope of investigations has extended beyond mere quantitation, including more comprehensive studies involving competition between metals, pH and ionic strength effects, comparisons with speciation (XANES and ultrafiltration) and speciation models (CHESS, MINEQL and PhreeQC), bioaccumulation analysis, isotope ratio assessments, and remobilisation flux calculations.

Additionally, the applicability of the DGT technique has been demonstrated across a wide range of environmental matrices, ranging from aquatic systems (groundwater, surface water, estuarine and marine environments) to terrestrial settings (soils, wetland soil, tree cores), and even including specific contexts such as uranium mining sites and nuclear industrial discharge waters. This diversity underscores the versatility of DGT in addressing various research questions related to radionuclide behaviour and environmental impacts.

5.2. Real case scenarios

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2
3 Research is primarily related to uranium mining, water quality monitoring, and metal speciation. So
4 far, the focus has been to use the passive sampling technique to investigate ions and trace metals to
5 assess their mobility, bioavailability, and potential environmental impacts. The studies highlight the
6 advantages and limitations of DGT compared to traditional methods, providing insights into metal
7 behaviour, speciation, and transport in different environmental contexts.
8
9

10 The research can be classified as

11
12 1. Uranium Mining and Environmental Impacts:

- 13 • Various studies use DGT to assess uranium behaviour, mobility, and bioavailability in
14 environments impacted by mining activities.
- 15 • In-situ methodologies combining DGT and other techniques are used to evaluate metal
16 resupply and distribution in soil profiles downstream of former uranium mines.
17
18

19 2. Water Quality Monitoring:

- 20 • DGT is employed for long-term monitoring of water quality and metal concentrations,
21 including radionuclides, trace metals, and actinides, in natural waters.
- 22 • The technique is compared to traditional sampling methods, highlighting its advantages in
23 providing time-averaged mean concentrations and accurate measurements.
24
25

26 3. Metal Speciation and Bioavailability:

- 27 • DGT is used to assess metal speciation and lability in sediments and pore waters,
28 contributing to an understanding of metal mobility and potential risks to biota.
- 29 • Studies investigate the relationship between metal concentrations measured by DGT and
30 their bioaccumulation in vegetation, suggesting potential ecological impacts.
31
32

33 4. Comparisons with Existing Techniques:

- 34 • DGT is compared to traditional sampling methods, such as grab sampling and sequential
35 extraction, in terms of accuracy, efficiency, and ability to provide meaningful insights into
36 metal behaviour. The technique's advantages include its ability to measure time-averaged
37 mean concentrations, assess labile fractions, and offer a more comprehensive
38 understanding of metal speciation and mobility.
39
40
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42 The following common advantages have been found when the passive samplers have been deployed
43 in real case scenarios. DGT allows for in-situ, passive monitoring of metal concentrations and
44 speciation. The technique provides insights into metal mobility, bioavailability, and potential
45 ecological impacts. DGT complements traditional sampling methods, offering a more comprehensive
46 understanding of metal behaviour in different environmental contexts. High-resolution profiles of
47 metals in soil pore water and sediment can be obtained using DGT, providing valuable information
48 for risk assessment.
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51 However, some drawbacks have also been found. DGT measurements may be influenced by factors
52 such as **biofouling**, changes in temperature, and biofilm growth. Calibration challenges can arise if
53 large changes in temperature and concentration occur simultaneously. It is noteworthy to mention
54 that such disadvantages are also found when measuring any element (non-radioactive) in similar
55 environmental conditions. Some limitations, specific for radionuclides, are associated with DGT
56 deployment durations and potential degradation of binding agents over longer periods. To address
57 these concerns, Turner et al. (2014) conducted a study involving the measurement of uranium over a
58 5-month period. This study yielded valuable insights and recommendations, such as the use of
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protective cages and the measurement of other physical parameters like temperature and pH that are specific to the environment. Based on their findings, they concluded that with the implementation of appropriate measures, DGT samplers can be employed for long-term deployments (Turner G. S., et al., 2014).

In addition, free metal ions are generally considered fully labile. This means that they have a high affinity for the binding phase of the DGT device and are efficiently captured. However, the interpretation of DGT data becomes more complex when dealing with metal-ligand species interactions. Many metal species, including radionuclides, in natural waters form complexes with ligands, and these metal-ligand species exist in a dynamic equilibrium. Some of these complexes may be partially labile, meaning they can interact with the DGT binding phase, but not as effectively as free metal ions.

This distinction between fully labile free metal ions and partially labile metal-ligand complexes introduces a potential limitation in the DGT technique. DGT may not be able to completely detect or quantify the extent of partially labile species present in the environment. Therefore, the interpretation of DGT data requires careful consideration of the underlying speciation dynamics and the potential biases introduced by the assumption of perfect sink conditions.

Importantly, the following ligand-metal interactions have been identified for some of the radionuclides (Table 3) (Vyas & Mistry, 75–82; Sokolik, Ovsianikova, & Kimlenko, 2002):

Table 3, Radioisotope - ligand interactions

Isotope/ ligand	Carbonate	Hydroxide	Organic matter	Sulphate
Uranium (U)	carbonate complexes in basic conditions	hydroxide complexes in basic conditions	NA	NA
Thorium (Th)	carbonate complexes in basic conditions	hydroxide complexes in basic conditions	NA	NA
Plutonium (Pu) and Americium (Am)	NA	NA	interact with natural organic matter forming complexes	NA
Curium (Cm) and Neptunium (Np)	carbonate complexes in basic conditions	NA	interact with natural organic matter affecting their speciation	NA
Technetium-99 (99Tc)	NA	NA	NA	NA
Radium-226 (226Ra)	NA	NA	NA	sulphate complexes in sulphate-rich conditions

Cesium-137 (137Cs) and Cesium-134 (134Cs)	weak complexes with carbonate	NA	NA	NA
Uranium-232 (232U)	Similar to other uranium isotopes, uranium-232 form carbonate complexes	NA	NA	NA
Europium-152 (152Eu)	No specific ligand-metal interactions have been found			

Several studies have addressed this challenge and examined the extent to which DGT measurements accurately reflect the true metal speciation. For instance, research by dos Anjos et al. (2017) and Mongin et al. (2011) has highlighted instances where DGT may not fully capture the presence of partially labile metal-ligand species. This underscores the importance of interpreting DGT data in the context of the specific speciation parameters and metal-ligand interactions present in the environment under study (Mongin, et al., 2011; dos Anjos, Abate, & Grassi, 2017).

Although there are only a limited number of studies that have tackled the ligand-metal challenges specific to radionuclides, noteworthy investigations have made progress in this regard. For instance, researchers have tested variations in pH and organic matter, as well as ionic strength (Stockdale & Bryan, 2013; Hutchins, et al., 2012; Zhaoa, Cornett, & Chakrabarti, 2020; Turner S. , Mills, Burnett, Amos, & Fones, 2015; French, Zhang, Pates, Bryan, & Wilson, 2005; Martin, et al., 2019; Drozdak, Leermakers, Gao, Phrommavanh, & Descostes, Evaluation and application of Diffusive Gradients in Thin Films (DGT) technique using Chelex®-100, Metsorb™ and Diphonix® binding phases in uranium mining environments, 2015), all of which can influence metal-ligand interactions. A particularly significant study by Drozdak et al. (2016) investigated the interplay of uranium speciation in conditions with different pH ranges, varying levels of phosphate, and the presence of carbonate and ionic strength. The findings suggested that neither phosphate (PO₄³⁻) nor bicarbonate (HCO₃⁻) had a significant impact on the quantitative measurement of uranium using the DGT-PIWBA method. Only when confronted with high concentrations of calcium ions and sulphate ions did the uptake of uranium by DGT-PIWBA experience reduction. The study concluded that an exhaustive laboratory characterization of the DGT binding phase layer is a prerequisite before starting in-situ fieldwork to ensure the accuracy of results and their interpretation (Drozdak, Leermakers, Gao, Phrommavanh, & Descostes, Novel speciation method based on Diffusive Gradients in Thin Films for in situ measurement of uranium in the vicinity of the former uranium mining sites, 2016).

It is important to note that the interactions between radionuclides and ligands can vary in different environmental matrices, such as water, soil, sediments, and biological tissues. Further research is needed to fully understand the specific ligand-metal interactions for each radionuclide in different environmental contexts. Therefore, the interpretation of DGT results is essential for understanding how the technique captures and reflects the speciation of metals in complex environmental samples. Researchers must carefully evaluate DGT data in conjunction with knowledge of speciation parameters, potential biases, and the assumptions made regarding perfect sink conditions to derive meaningful insights into the speciation dynamics of metals in natural systems.

5.3. Future Perspectives

DGT is expected to play a significant role in improving radiation dose modelling, understanding metal speciation, and assessing environmental risks associated with mining activities. [DGT could](#)

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4 prove valuable for sampling and pre-concentration of both alkaline and alkaline radioactive earth
5 metals, including strontium (Sr). Moreover, DGT can effectively concentrate neutral anionic species
6 like iodine (I), acting as a versatile pre-concentration technique depending on the DGT binding
7 phase. This highlights DGT's adaptability in enhancing sampling and pre-concentration for diverse
8 metal ions and anionic species. The technique's potential for long-term water quality monitoring and
9 its application to various environmental projects, such as nuclear waste disposal, highlight its
10 importance in future research. Further developments in DGT technology and methodologies are
11 anticipated to enhance its applicability and accuracy in various environmental studies.

12 13 14 6. CONCLUSIONS

15 This review underscores the significance of the Diffusive Gradients in Thin Films (DGT) technique as a
16 valuable tool for the quantification, analysis, and detection of radionuclides in diverse environmental
17 settings. Through a comprehensive analysis of method development and real case scenarios, it
18 becomes evident that DGT offers a holistic approach to understanding the behaviour of
19 radionuclides and other trace elements. The ranking of isotopes based on importance highlights the
20 wide-ranging implications of radionuclide presence, spanning from natural occurrences to
21 anthropogenic activities. The technique's versatility is evident in its applications, ranging from
22 uranium mining assessments to water quality monitoring and metal speciation studies. By offering
23 insights into mobility, bioavailability, and potential ecological impacts, DGT stands as a powerful tool
24 in unravelling the complex interactions between radionuclides and their surroundings. While
25 challenges and limitations exist, such as potential influences from biofouling, calibration difficulties
26 and metal-ligand interactions, ongoing developments in DGT technology and methodologies hold
27 promise for overcoming these obstacles and enhancing the technique's accuracy and applicability.
28 As regulatory frameworks and environmental concerns continue to evolve, DGT's role in advancing
29 our understanding of radionuclide behaviour and informing effective environmental management
30 strategies is poised to expand, contributing significantly to safeguarding human health and
31 preserving ecological integrity.
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