

Technical Document:

**The use of nuclear spectrometry techniques in assessing the impact of
mining and milling sites on human health and the environment.**

INTERNATIONAL ATOMIC ENERGY AGENCY

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FOREWORD

The number of pollution sources is constantly increasing throughout the world as a consequence of the growing industrial development. Mining and milling operations, apart from the direct disruption of the landscape, bring a significant contribution to the pollution of the environment due to accidental releases of the main products of mineral extraction and the accumulation of large amounts of mining wastes.

To achieve a comprehensive characterization of environmental problems, many factors have to be taken into account and only designing a proper assessment program including interdisciplinary research can produce a proper interpretation and contribute to solving a particular problem. At different stages of any environmental assessment large amount of data on the nature, concentration and distribution pathways of the investigated contaminants of concern is required.

This technical report aims to provide recommendations to achieve a cost-effective sampling program and to highlight the capabilities of several nuclear and nuclear-related techniques in gathering information on the contents of common inorganic contaminants and radiation hazards resulting from mining and milling operations in the exploitation of both radioactive and non-radioactive mineral resources.

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1 Introduction

The growing demands for energy and resources required for a higher standard of living lead to a significant increase in waste production and thus, in environmental pollution. Determining the nature and extent of environmental problems at a site involves a complete understanding of the study area both in terms of the natural state and the contamination problem. Major components of a site characterization include field investigations, laboratory analysis of collected samples, data synthesis and interpretation analysis. In order to get a comprehensive characterization of environmental problems, many factors have to be taken into account, including understanding of the process originating the polluting materials and their nature, the type of reactions occurring with the environmental areas, the transport of chemical species in the environment and the potential or already revealed hazardous impacts to life forms.

Within this context, analytical methods are required to monitor the levels of concentration of the identified contaminants of concern (COC) at different stages of the conducted survey.

1.1 The impact of mining / milling activities in the environment

The exploitation of our Earth resources has had a long and fascinating history since the gathering of stone materials for tool-making to the sophisticated mining and extractive industries [1]. The metals utilized in manufacturing are obtained from either the mining of ore bodies in the rocks of the earth's crust or from the recycling of scrap metal originally derived from geological sources.

Ore bodies are naturally occurring concentrations of minerals with sufficiently high concentrations of metals as to make them economically worthwhile exploited. However, it has been estimated that more than 70% of all the material excavated in mining operations world-wide is discarded. Therefore, apart from the direct disruption of the landscape, one of the more environmental troublesome by-products of mineral extraction consists of mining wastes or tailings.

Generally, the greatest part of metals contained in the ores is extracted during the mineral processing to obtain the economically valuable product. However, due to the incomplete metal extraction from the original material, the mining wastes generated during this processing step could present also a substantially enriched metal content.

The waste material plays an important role in controlling how readily metals are liberated from the wastes into the environment. The size of particles produced by mineral processing can dramatically influence their environmental impact. For instance, solid tailings, due to their fine grain size resulting from crushing and grinding, are likely to be more reactive than geologically similar waste rocks, and hence are likely to have greater potential metal mobility.

On the other hand, the techniques employed to enhance the mineral recovery (mineral processing) can also influence on the environmental impact, mainly due to the potentially polluting chemicals that are used. For example, sodium cyanide, copper sulphate and different kind of surfactants have been widely used to extract lead and zinc from ores [2]. Many of these processing solutions are recycled as much as possible in order to minimize water and reagent usage. However, disposal of these solutions is unavoidable once their extractive capacities have been exhausted, becoming an additional pollution source in mining operations.

In addition to the commonly recognized hazardous substances associated with metal mining, radiation risks also require responsible management at uranium mines and mills. Radon and other short-lived radio-nuclides from the radon progeny, as well as ore dust are released by the ventilation system of operating uranium mines. Radio-nuclides are also discharged by the mine water streams and can affect the quality of the waters in neighboring water sources and be further up taken by terrestrial plants. Rock materials stored around U mine are subject to weathering processes and wind transfer, thus impacting the topsoil in surrounding areas.

Radiation hazards can also be increased by other activities leading to a substantial increase in the concentration of naturally occurring radio-nuclides (NOR) in the environment. Mining and milling of phosphates, rare earth elements, zirconium and titanium minerals, among other activities, are known to increase the concentration of NORs.

Most of metallic mineral deposits beneath the Earth's surface contain sulphide minerals, which are largely chemically stable to geological conditions. But when they are exposed by erosion or by mining activities to atmospheric oxygen and water, they can become quite unstable [3]. The chemical weathering of sulphide minerals represents a series of linked geochemical and microbiologically-mediated reactions through which metals are released from ores and mining wastes into the environment.

One of the most crucial properties of metals, which differentiate them from organic pollutants, is that they are not biodegradable in the environment [4]. As a result, they tend to persist in the various reservoirs of natural systems such as water, soils and sediments, or they accumulate in biological systems, leading to an important hazard to environment and to life forms, including human health.

In any case a typical feature of the weathering of mining wastes, apart from the possible acidic water formation, is the release of metals from the mineral matrix into the environment. It must be kept in mind that not all the metal content in an earth material is usually susceptible to alteration and weathering reactions and thus, only a part of it could be problematic for the key compartments of the natural environment. Figure 1 illustrates the pathways and relationships between total metal content in mining wastes and potential toxicity to organisms.

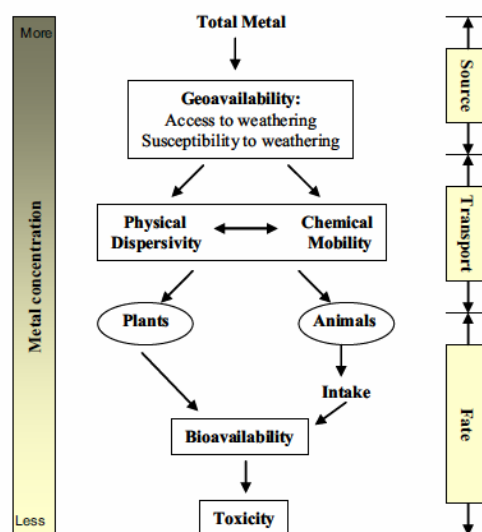


Figure 1: Diagram showing the pathways and relationships between total metal in an earth material and toxicity. (Figure adapted from [1])

In general, the term “geo-availability” defines the portion of a chemical element’s total content in an earth material that can be liberated to the surface or near-surface environment (or biosphere) through mechanical, chemical, or biological processes [1]).

There are a lot of factors that can affect the concentration of geo-available metals, including the characteristics of the earth material itself (total metal content, mineral type, grain size, texture, structure, pH and redox conditions, impurities) and the weathering agents (climate and topographic relief).

Dispersal refers to the ability to spread via non-chemical paths (physical processes), and mostly occur via transport through air (e.g., smelter emissions, wind erosion). Mobility of metals is based on chemical processes, which include chemical interactions with the surface or near-surface environment, and the capacity to migrate within fluids after dissolution. Mobility greatly depends on the physicochemical characteristics and binding forms of the elements in the solid matrix [5]. The more labile interaction between metal-solid phases the higher potential metal mobility and thus, higher environmental impact.

Bioavailability can be defined [6] as the degree to which a contaminant in a potential source is free for uptake (movement into or onto an organism). It is a function of geo-availability, dispersal and mobility but it also depends on the biological specificity and individual susceptibility of the organism. Generally, the bioavailability is a prerequisite for toxicity but does not necessarily results in toxicity. Toxicity implies an adverse effect on an organism and it varies widely with species and genotypes within species. Some individuals are genetically adapted to tolerating anomalous high concentrations of certain metals. It is therefore difficult to generalise about toxicity [7]. As it can be seen in Figure 2, bioavailability is generally a requirement for uptake in plants, whereas animals may intake (ingest, inhale, etc.) toxicants that subsequently pass through their bodies without any systemic uptake.

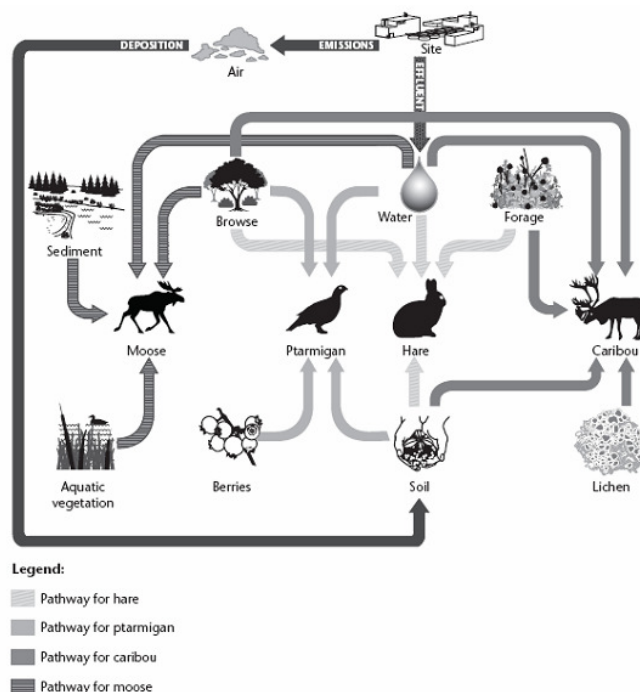


Figure 2: Diagram showing the bioavailability pathways for vegetation and animal species

1.2 Common contaminants of concern associated to mining / milling operations and sampling media.

There is an extensive range of elements that may be considered contaminants arising from mining/milling sites. The contaminants of concern will vary depending on the type of mining/milling facility, the composition of the host rock bearing the ore, the type of milling process and the characteristics of the receiving environment. The most common hazardous inorganic elements regulated and or monitored at mining sites are Aluminium, Arsenic, Copper, Cadmium, Chromium, Lead, Manganese, Mercury, Nickel, and Zinc. However, a number of other elements should also be considered. Iron and sulphates shall be monitored due to their relevance to the development and monitoring of acid rock drainage. Phosphorous and nitrogen can substantially influence the productivity of aquatic species. Molybdenum and selenium can pose substantial risk depending on the characteristics of the ecosystem receiving them.

Facilities associated with the mining and milling of ores known to be associated with elevated levels of natural radio-nuclides [8], such uranium, phosphate, rare earth elements etc, should evaluate their waste materials and receiving environments for radio nuclides associated with the uranium-238 decay series products.

Organic contaminants, such as those used in the milling process or resulting from hydrocarbon spills, as well as sewage releases can also pose risks, however, this document is restricted to the monitoring of inorganic elements. A summary of the most common analyzed samples to monitor the contents of contaminants of interest is provided.

- Air samples:

Radio-nuclides, radon gas, heavy metals and particulate matter (PM) can be released from underground ventilation systems. Waste rock and tailings storage areas as well as surface mining operations and the uranium milling processes are significant sources of air pollution. Milling operations release nitrogen oxides (NO_x), volatile organic compounds (VOCs), carbon dioxide (CO₂) and PM. Acid plants producing acid for milling operations release large amounts of sulphur dioxide (SO₂) - a major contributor to the formation of acid rains [9]. Monitoring of radio-nuclides in air around U mines include Rn, Rn short-lived progeny, Pb-210, Po-210.

- Water samples:

In addition to the leaching of contaminants from tailings management facilities (TMFs) and waste-rock storage sites, uranium mines and mills release radioactive (principally uranium), hazardous (e.g. heavy metals) and conventional (e.g. total suspended solids) contaminants to groundwater and surface water through discharges of mill and mine waters, and general run-off from mine sites. The radio-nuclides to be monitored in waters shall be defined depending on the chemical properties of the water and can include U, Ra, Pb-210, Po-210 with different priorities.

Acid mine waters typically have pH values in the range 2-4 and high concentrations of the metals associated with the iron sulphides, and both these properties lead to an overall degradation of the water quality and the inability to support aquatic life. The release of these components into natural water is a widespread and persistent world-wide problem, and examples can be found in many countries [10, 11, 12].

- Soil, sediment, tailings

The tailings consist of ground rock particles, water, and mill chemicals, and radioactive and otherwise hazardous contaminants, such as heavy metals. Uranium mining operations produce also waste rock, which can contain both radio-nuclides and heavy metals, such as nickel, copper, arsenic, molybdenum, selenium and cadmium. Depending on the type of rock, these wastes may be acidic with the result that radio-nuclides and heavy metals may be leached out of the waste and contaminate surface and ground water. Surface mines can generate up to 40 tones of waste rock for every ton of uranium ore produced, while underground mines produce about one tone of waste rock per tone of ore. Specific attention must be paid to uranium, radium -226, lead-210, polonium-210, and Th-230 for solid materials, such as U-ore dust and tailings in uranium mining.

Tailings and waste rocks contain high concentration of metals which can have toxic and carcinogenic properties. Monitoring of these elements is important to protect the human health [13]. Soil and sediment analysis could be useful to study the impact of metal dispersal coming from the mining wastes. Determination of total metal contents in surface samples or in depth profiles could be useful for such purposes.

As mentioned in the previous section, the mobility and availability of heavy metals in the mining wastes strongly depends on their physicochemical characteristics and specific chemical forms of binding in the solid matrix. Consequently, toxic effects and biogeochemical pathways can only be assessed on the basis of the determination of these forms. As an approximation, the speciation studies involving soil and sediment analysis are often based on the use of extraction procedures (single or sequential) which enable broader forms or phases to be measured and which are, in most cases, sufficient for the purpose of environmental policy. Leaching tests are applied to waste materials to provide information about the release of specific components under reference conditions, or under conditions that may approximate more closely or simulate the actual field situation under consideration [14].

- Flora

Because of their capacity to act as efficient interceptors and accumulators of chemicals, vegetation species are widely employed as passive monitors in areas contaminated by heavy metals, such as those affected by mining operations. Therefore, the implementation and improvement of suitable analytical tools to determine chemical composition is also required. In the last decade, the use of higher plants for the clean-up of metal contaminated environments (known as phyto-remediation technology) has gained popularity among government agencies worldwide, as an alternative or complementary cost-effective non-invasive technology to the engineering based remediation methods. In addition, some vegetation species have also demonstrated their potential use to prevent water erosion, to stabilize mine wastes and thus, to reduce effects of metal pollution (phyto-stabilization). Nevertheless, to increase the efficiency of such technologies, it is important to learn more about the specific plant physiological processes involved, including plant metal uptake, translocation and tolerance mechanisms, plant-microbe interactions and other rhizosphere processes [15].

- Fauna

Taking into account that the metals are not biodegradable and tend to accumulate in biological tissues, the determination of this type of pollutants in the fauna of areas

affected by mining operations is also a common practice to evaluate the impact of mining operations.

1.3 Objectives of Environmental Investigations or Monitoring Programs for Mining and Milling activities

Environmental monitoring may be completed for many purposes, the most common being:

- *Characterization of spatial distribution of contaminant(s) of uncontrolled tailings/waste disposal at abandoned historical mine sites.*

Relatively little attention has been given until the last several decades to deposition of wastes from mining industry. In the past, often the mining wastes were dumped indiscriminately, deposited in inadequate facilities or were simply released into the nearest water course [16]. As a result of these practices, a number of historic (meaning those operated prior to the last decades) mining and mineral processing sites that were abandoned once the practice became non-profitable, are now potential or ongoing sources of environmental contamination. [17, 18, 19].

Many governments face the problem of designing and implementing cost-effective programs aimed to remediate the state of pollution in such sites. Different types of remediation strategies are conducted, being some of the more common:

- Reshaping the landscape of the area: Large volumes of tailings are often re-distributed and relocated as to fill areas of the landscape that can ensure their immobilization and minimize the dispersal of the pollutants. In some cases, even abandoned mines are somehow secured and conditioned as to make possible the visit of tourists.
- Finding alternatives uses for the tailings. New technological developments make possible the re-utilization of the tailings as to extract some valuable material.
- Physical / Chemical / Phytoremediation: Different types of procedures are developed to achieve a stronger immobilization and to minimize the dispersal of the pollutants.

Together with statistical treatment of data and field investigations, chemical analysis is needed to assess the potential risk of contaminants for the environment and thus, to choose the best remediation process in each particular case [20, 21, 22]. A Consultancy Meeting organized by the IAEA [23] outlined technical recommendations and recommendations in regard to the instrumentation and associated statistical interpretation tools required to design a model mobile unit to be used in monitoring the environmental pollution in sites evaluated for remediation actions.

[Horst, please, review, complement]

- *In new operating mines*

The increased concern of public opinion has led to the establishment of national regulations imposing the need of performing a constant monitoring survey of the accumulated tailings and accidental releases of products in ongoing mining and milling activities.

Substantial improvements in tailings and waste rock management as well as increased expectations with respect to the control and treatment of mine and mill waste waters has

greatly reduced the environmental impacts associated with new modern mining methods. However, environmental monitoring is still required to ensure that mitigation measures are adequate and that environmental impacts are minimized as much as possible, throughout the complete life-cycle of a mining operation.

This need for full life-cycle monitoring and assessment involves the collection, laboratory and data analyses, and scientific interpretation of large amounts of data on mine and milling related contaminants for the purposes of assessing different issues, including:

- Environmental characterization to serve as a baseline for a proposed or new operation.
- The characterization of wastes emissions and/or effluents released to the environment to verify compliance with regulations. For most of the cases actual regulatory compliance limits are restricted to license limits on controlled points of release for atmospheric emissions (e.g., stack limits) and points of release for liquid effluents. To demonstrate compliance with these release limits sites are required to have emission and effluent monitoring programs. An additional regulatory limit associated with uranium mines is the maximum additional acceptable radiation dose to the public. Hence, uranium mining operations are commonly required to have monitoring programs designed to demonstrate that members of the public are not exposed to radiation doses exceeding the regulatory limit.
- To confirm the effectiveness of mitigation actions (e.g., stack scrubbers, liners or other barriers, effluent treatment) by measuring environmental levels and to provide public assurance of the effectiveness of containment and effluent control.
- The assessment of the level of risk to human health and safety, and the potential effects in the environment and non-human biota of contaminants arising from or that may arise from a mine/milling operation

The last two issues are usually evaluated as part of Environmental Risk Assessments, which are described in the following section.

1.4 Environment Risk Assessment

Several national regulations have been approved to impose as a compulsory pre-requisite for any new investment in the mining sector to carry out an environment risk assessment (ERA). ERA is a pre-condition to ensure that proposed new mining operations are implemented in an environmentally responsible manner. The latter is accomplished by providing site-specific planning documents that serve for the purposes of:

- Identifying the greatest risks to the environment associated with the proposed activity,
- Outlining mitigation measures during the design stage and their further implementation,
- Assessing the performance of the mitigation measure during operations and decommissioning through the use of specifically designed performance and environmental monitoring programs.

The ERA should provide clear conceptual site models to aid in mentally and visually clarifying the major exposure pathways to be addressed within a monitoring program. Conceptual models can range from broad facility-wide models exhibiting generic project-environment interactions (see Figure 3) to site-specific focused representations

of specific contaminants and/or physical stressors and their environmental pathways to be considered for environmental monitoring exposure to specific biota. A number of examples of conceptual models are provided elsewhere [24].

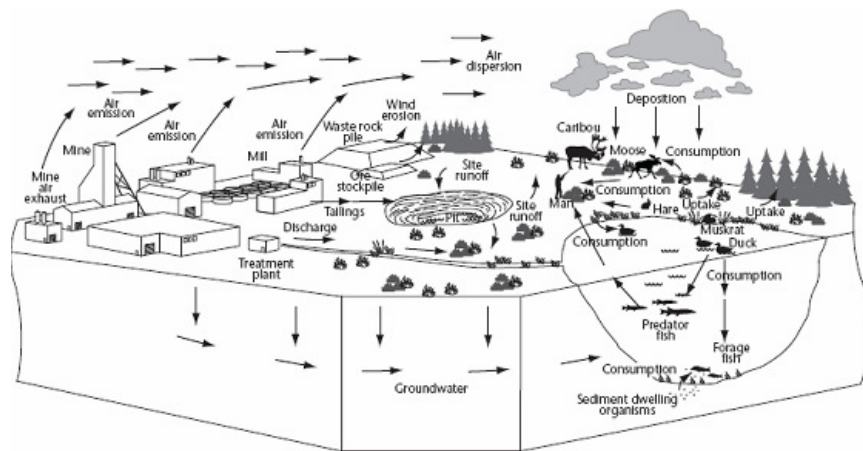


Figure 3: Diagram showing the interrelation between mining/milling operations and the environment.

The environmental monitoring program for a mining/milling operation should be focused on abiotic and biotic elements of the environment most exposed and potentially at risk from the mining activity. This requires the completion of some form of ERA, providing a framework for identifying the potential for contaminant transport and exposure to human and non-human biota and a means to predict the magnitude, probability, and significance of the identified effects associated with the mining operation. If an environmental monitoring program is to be appropriately designed to identify issues arising from normal operating conditions and reasonably foreseeable upset events, the ERA should at a minimum:

- a) identify and provide rationale for selecting the contaminants of concern (See Section 1.2);
- b) identify the sources or points of release of the contaminants from the mining operation;
- c) identify the potential receptors (human and non-human biota) of concern for the specific site;
- d) provide conceptual models of the environment compartments the COC may migrate through and therefore result in exposure to receptors.

The above minimal requirements represent a conceptual qualitative ERA. Ideally, a more quantitative ERA must also:

- e) incorporate predicted or actual average and upper bound concentrations, activity levels and total loads of COCs which may be released;
- f) predict the level of exposure of the relevant COCs to the site-specific receptors
- g) assess the potential risk of the exposure to the receptor using a scientifically supportable toxicity or dose benchmark; and
- h) identify and, whenever possible, quantify the uncertainties in the assessment of the environmental risk.

This approach allows the monitoring program to be focused in a cost effective and environmentally protective manner on most at risk elements of the abiotic and biotic environment for a specific site. Additional information and guidance to design ERAs can be obtained elsewhere [24, 25, 26]

1.5 Main requirements to analytical techniques

In view of the considerable number of samples to be analyzed as part of monitoring programs some features are preferred when selecting an analytical method:

- Multi-element capability, allowing gathering as much information as possible, since there is not always a-priori knowledge of the kind of information that can be of relevance.
- Simple sample preparation.
- High throughput and low cost per determination.
- A wide dynamic range is required to compare element composition of samples collected at non-polluted sites (baseline values) with those from polluted areas (higher contents of COC).
- The achieved accuracy, precision, and detection limits shall be sufficient for the given purpose.

In order to investigate, control and regulate a contaminated site the possibility to perform an initial screening survey of the contaminated sites using in-situ techniques is an important alternative allowing to improve the sampling strategies and to reduce the costs of the analytical survey, since the amount of samples sent for more accurate laboratory analysis can be optimized. By in-situ technique it is understood that the analytical instrument is taken to and placed over or in contact with the sampling area. In-situ characterization has been adopted as a tool in decision making policies through site-specific risk assessment [27]. In this context, the in-situ nuclear spectrometry techniques and other nuclear-related methods, have reached a high level of analytical performance and offer certain advantages over other more traditional characterization procedures, such as:

- Fast determination of contaminant concentrations/activities in many spots/areas across the contaminated site without time-consuming sample collection and preparation procedures.
- Fine tuning of the contaminant spatial distribution, with immediate real time identification of areas of interest ('hot-spot' areas), allowing further investigation of these areas with a better spatial resolution sampling.
- Cost reduction for the investigation of all the stages of an assessment, and remediation process.

Finally it is also interesting to remark the significance of obtaining information on spatial distribution within the object in some environmental studies. For instance the study of metal distribution at micrometric scale in soil and sediment profiles is useful to study the input and migration of contaminants in areas contaminated by heavy metals [28].

There is no universal technique fulfilling all the requirements and usually a combination of different analytical methods is necessary. More detailed information on the most common nuclear and nuclear-related techniques used for the determination of metals is presented in section 3 of this report.

2 Introduction to Basic Study Design and Statistical Considerations

As it was mentioned in section 1.3 environmental studies may be completed at historical, operating, or for proposed new facilities for a wide range of reasons. Care must be taken to ensure that the study is appropriately designed to support the required objective.

A brief introduction to study designs is provided in this section. Those unfamiliar with the complexity of scientifically defensible study designs are encouraged to consult other sources for additional guidance on study design and analyses [29, 30, 31, 32, 33, 34]. Different software tools have been developed to facilitate the development of a defensible sampling plan based on statistical sampling theory and the statistical analysis of sample results to support decision making. One example of such tool is the Visual Sample Plan (VSP) provided in the public domain of the Pacific North West Laboratory [35].

The greatest difficulty with developing study designs for investigations in the natural environment is the lack of control and great variability within the environment itself. Environmental investigations most commonly involve the collection of sub-samples (sample populations) from the total population of interest (target population or N) from a given media (e.g., air water, sediment). The use of a statistically defensible sampling design increases the chance that a set of samples is collected in a manner that is representative of the total sample population, thus allowing for the extrapolation of the observations or information from the small sub-sample to the total population and to estimate the uncertainty with which one can assume such extrapolation.

For example it may be determined that it is desirable to know the contaminant concentration in the fish in a pond receiving run-off from a waste rock pile. In this case all of the fish in the pond can be referred to as the study target population or N. Since it is not practical (nor desirable!) to collect and analyse all of the fish one could collect a single fish for analyses. However, the question arises as to how representative of the target population as a whole would be the analytical results from this single fish? What confidence can we have in using the results from this single fish when we know that any two adjacent soil or sediment samples, two leaves from the same plant, or two fish collected from the same location will contain different concentrations of any given radionuclide or metal of interest? Even under natural undisturbed baseline conditions, these differences can vary substantially.

However, if multiple replicates, in this case fish, are randomly collected from the desired sample media and analyzed one obtains a distribution of values. The larger the distribution the greater is the variability of the analyte of interest measured in the sample population. With multiple samples it is now possible to calculate the mean (arithmetic or geometric) of the concentration in the sample population as well as an estimate of the variability associated with this mean.

There may be a number of sources contributing to this variation in the sample results including:

- laboratory uncertainties (spread of the values that can be attributed reasonably to the results obtained);
- variations in the field sampling protocols; and
- true spatial, temporal or individual variations in the field sampled population.

The latter represents the natural variability or differences of the parameter being measured that is present from place-to-place, time-to-time, or individual-to-individual

that results from the various natural processes influencing the target population [36] [Malcolm, please provide reference on Whicker et. al. 2006]. In most instances, though not necessarily all, this natural variation heavily outweighs other forms of variability associated with environmental studies. The objective of statistical sample designs is to design a program in such a manner that this variability can be captured and quantified in a manner that allows the results from the sample population to be used to confidently represent the total population.

2.1 Types of Sampling Designs

Sampling designs depend on the nature of the studied problem, on the nature, concentration and distribution pathways of the investigated contaminants of concern, among other factors (see Figure4).

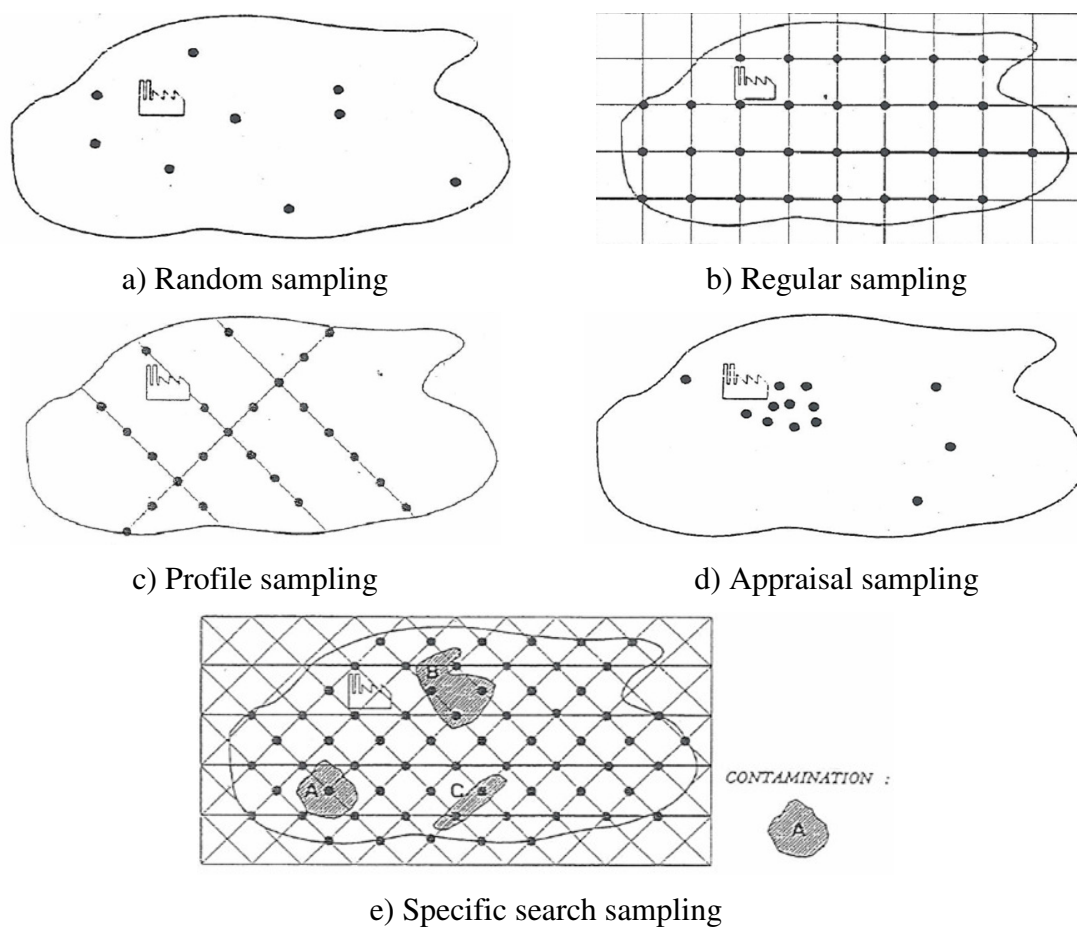


Figure 4: Different sampling plans

A simple classification of sampling designs is provided below.

2.1.1 Haphazard and Judgmental Designs

The term haphazard designs is applied to studies which incorporate little thought into decisions associated with sampling locations and replication. Samples are often located and timed based on the convenience of the investigator and generally produce heavily biased and unrepresentative results. This approach is only appropriate when the target population is completely homogenous and the estimated parameter of interest is evenly

distributed amongst the target population. Such conditions rarely if ever occur in the natural environment.

Judgmental designs are based on professional judgment, not statistical theory. The selection of sampling units (i.e., the number and location and/or timing of collecting samples) is based on the designer's personal knowledge of the feature or condition under investigation. As a result, conclusions about the target population are limited, and depend entirely on the validity and accuracy of the designer's personal knowledge. In addition no probabilistic statements may be made; therefore it is not possible to assess the accuracy or bias of any estimated parameters.

2.1.2 Probability Based Sampling Designs:

- *Simple Random Sampling*

In simple random sampling designs every sampling unit in a population (N) has an equal chance of being one of the samples (n_i) selected for measurement. In addition, the selection of one unit has no influence over the probability of selection for another unit. This sampling design is appropriate for the estimation of means and totals if the population does not contain major trends, cycles or patterns of contamination.

Simple random sample designs are often applied to the collection of soil samples for contaminants associated with particle deposition where the deposition can be expected to have been relatively evenly distributed within the total sample area (i.e., no wind plume gradient within sample grid). The specific sample locations are selected using a random number generator for the coordinates of the overall sampling grid.

The advantages of this approach are:

- Statistically unbiased estimates of the mean, proportions, and variability.
- Easy to understand and easy to implement
- Sample size calculations and data analysis are very straightforward.

- *Stratified Sampling*

As the name implies, stratified sampling involves the subdivision of the total sampling area into various non-overlapping strata or sub-populations known or believed to be more homogeneous such that there will be less variation among sampling units in the same stratum than among sampling units in different strata. Strata may be determined on the basis of spatial or temporal proximity of the units, or on the basis of pre-existing information (e.g., historical information or preliminary survey) or "professional judgement" about the site or process being investigated. Random sampling is then completed within each of the selected strata.

Stratified sampling designs are best for parameter estimation where the target population is heterogeneous and this heterogeneity can be captured within defined strata. This sampling design has potential for achieving greater precision in estimates of the mean and variance, and allows computation of reliable estimates for population subgroups of special interest. Greater precision can be obtained if the measurement of interest is strongly correlated with the variable used to make the strata. For example, a study investigating the total contaminant load and distribution within a water body could benefit from a stratified design based on particle size and/or organic carbon content as many metal contaminants are strongly correlated to these sediment characteristics.

- *Systematic and Grid Sampling*

This method involves taking measurements or samples at locations and/or times corresponding to a spatial or temporal pattern. An initial location or time should be chosen at random, and then the remaining sampling locations are selected based on regular intervals over an area (grid) or time (systematic).

Systematic and grid sampling is used to search for hot spots and to infer means, percentiles, or other parameters and is also useful for estimating spatial patterns or trends over time. This design provides a practical and easy method for designating sample locations and ensures uniform coverage of a site, unit, or process. However, this design is inappropriate if the parameter being measured varies either spatially or temporally along the same pattern as the study design.

- *Double Sampling*

Double sampling involves using a related parameter as a proxy for the desired parameter of interest if the latter is more difficult or costly to sample. This approach often involves completing a large number of measurements or samples analysis using the less expensive or more efficient technique, which are further compared with the results of a smaller subset of samples that have been analyzed using the more extensive or expensive analyses. If a strong correlation can be demonstrated between the two sets of results then the revealed relationship can be used to make inferences to the entire sample set of the desired parameter.

This is a procedure often used in radioecology. A large number of in situ radiation measurements is completed using hand portable devices, while a smaller subset of samples is submitted to laboratory analysis to identify the radionuclides and to determine activity concentrations. The relationship between the radiation measured and the radio-nuclides present can be used to estimate radionuclide activity levels throughout the study area. This approach is extremely beneficial when laboratory costs are high and is becoming even more attractive as improved portable detectors are being developed.

2.2 Number of Replicate Samples and Compositing

Determination of the required number of sample replicates will vary depending on the parameter being estimated, (e.g., mean or variance), the required precision for the estimate, and the natural variation inherent in the population being sampled. The required precision will depend on the specific study design objective. Knowledge of the inherent variation within the total population can only be obtained from historical studies or past experience or requires preliminary sample surveys. The specific means of calculating sample size is also dependent on the type of study designs. Guidance on study design specific determination of the desired number of replicates can be obtained from the sources identified at the beginning of this section.

In composite sampling several sampling units (now referred to as sub-samples) are physically combined and mixed in an effort to form a single homogeneous sample, which is then analyzed. Compositing can be acceptable when the goal is to estimate the population mean and information on spatial or temporal variability is not required and is often incorporated as an element into the previously mentioned study designs. It can also be used when trying to capture or estimate a rare trait such as rare species in benthic macro-invertebrate surveys.

Compositing can result in substantial cost savings as the number of chemical analyses is reduced. As such it is best used when analyses costs are large relative to sampling costs, however, it should only be used when there are no safety hazards associated with the increased handling from combining the samples or potential biases such as can arise if the contaminant of interest can be lost through volatilization or degassing.

2.3 Interpretation of Data

The specific data analyses to be applied to environmental data will depend on the objective of the study and the selected study design. The planned statistical procedures should be incorporated into the study design from the beginning. The raw data sets should be screened and validated using the following steps:

- routinely check data during processing screening for errors in station codes and other data transcription errors (using filters or pivots in database or spreadsheet software) and whenever possible use digital transfer methods to minimize human transcription errors;
- rapid tests of consistency within sample areas can be achieved by visual examination of simple plots with statistical testing for outliers; and
- comparisons against historical datasets can be done rapidly by simple visual plots or statistical control charts tests can be used

Outliers require specific attention as they can heavily influence data analyses and associated conclusions.

Five basic steps should be applied when addressing outliers [37]:

- Identify extreme values that may be potential outliers;
- Apply statistical test for identifying outliers;
- Scientifically review statistical outliers and decide on their disposition;
- Conduct data analyses with and without statistical outliers; and
- Document the entire process.

It is important to remember that an outlier may be a valid representative of the sample population and should not be automatically attributed to sampling, analytical or handling errors. Identified outliers should be traced back through the handling and analytical procedures to see if the error can be identified. Often a simple call to the analytical laboratory or a trace back to the original laboratory sheets can provide the correct value. The result should be reviewed to determine whether the value can be scientifically supported as a real but extreme (low or high) value. The data analyses should be completed with and without the outliers to determine their influence on the analyses and the whole process should be documented.

A common problem arising when managing analytical chemistry data is the presence of censored data sets. Censored datasets arise when the results from a chemical analysis fall below the detection limit (DL) of the analytical procedure. These measurements are usually reported as non-detects, (rather than as zero or not present) with (hopefully!) the appropriate limit of detection documented. When information is limited to this, all that can be said about the measurement is that it is located somewhere between zero and the detection limit. Data sets incorporating detected and non-detected results are referred to as censored data.

Censored data sets can be managed in a number of different ways with no general procedure being suitable for all scenarios. The US EPA QA/G-9 has provided some general guidelines considered to be adequate for most instances though they recommend

they be used with caution (see Table 1). Detailed information on data censoring can be consulted elsewhere [38]. In any case, it is recommended to report the percentage of non-detects and the method selected for managing them.

Percentage of Non-detects	Statistical Analysis Method
< 15%	Replace non-detects with DL/2, DL, or a very small number.
15% - 50%	Trimmed mean, Cohen's adjustment, Winsorized mean and standard deviation
> 50% - 90%	Use tests for proportions

Table 1 Summary of procedures and methods for dealing with non-detect values.

In most instances minimum data analyses requirements will involve the reporting of basic statistics associated with estimates of central tendency such as the geometric or arithmetic mean and the associated variation around the mean. Appropriately designed studies can allow for statistical hypotheses testing to detect differences between sample populations either spatially or temporally (e.g., Before vs After, Control vs Exposure or more complex Before-After –Control-Impact) using single or multiple Analyses of Variance (ANOVA) procedures. Studies designed to detect change of contaminant concentrations over time can be analyzed using combinations of graphical procedures, regression analyses with significance testing for slope. Correlation and various pattern analyses procedures such as but definitely not limited to principal component analyses can be used to explore data sets are detect patterns or correlations meriting further follow-up investigations. In all instances the statistical tests to be completed on the data should be identified during the study design phase to ensure that the selected design produces results which will meet the statistical assumptions inherent to the statistical analytical procedures.

2.4 Integration of sampling and interpretation in study design.

One particular case of integration of some of the methods described before is that based on Geo-statistics theory that is applied at the Commission for the Implementation of Analytical Methods (CETAMA) at the Commission of Atomic Energy of France (CEA) [39].

Geo-statistics relates to study any quantitative phenomenon that develops in a structured way in space and / or time. This approach was initially developed for the estimation of mineral reserves in the 50s by a professor at the University of Witwatersrand in South Africa, D. G. Krige [40]. It was found that there was a discrepancy between the estimates of ore made on the basis of analysis derived from ad hoc surveys and the ore actually recovered after the mining operations. This difference, related to the difference between the medium and the extent of exploitation (mining blocks several meters side) has been formalized by G. Matheron, a French engineer of the Corps des Mines, giving the "support effect" and the theoretical basis of Geo-statistics [41]. Its effectiveness has been proved after the estimation of many deposits. Since the 80's the areas of application of Geo-statistics have continuously spread to other fields, such as oil exploration, hydrogeology and to environmental assessment, particularly of polluted sites. Two typical cases of successful implementation of the Geo-statistics approach are the remediation of areas subjected to radiological contamination, and the dismantling and decommissioning of nuclear facilities. For such cases, it is possible to optimize the sampling, to create graphic representations of surface and in depth contamination, to

estimate the probability of exceeding regulatory levels and to assess the volumes of waste or contaminated materials while quantifying the uncertainties. The sequence of actions included in a study on radiological contamination using the Geo-statistical approach is illustrated in Figure 5.

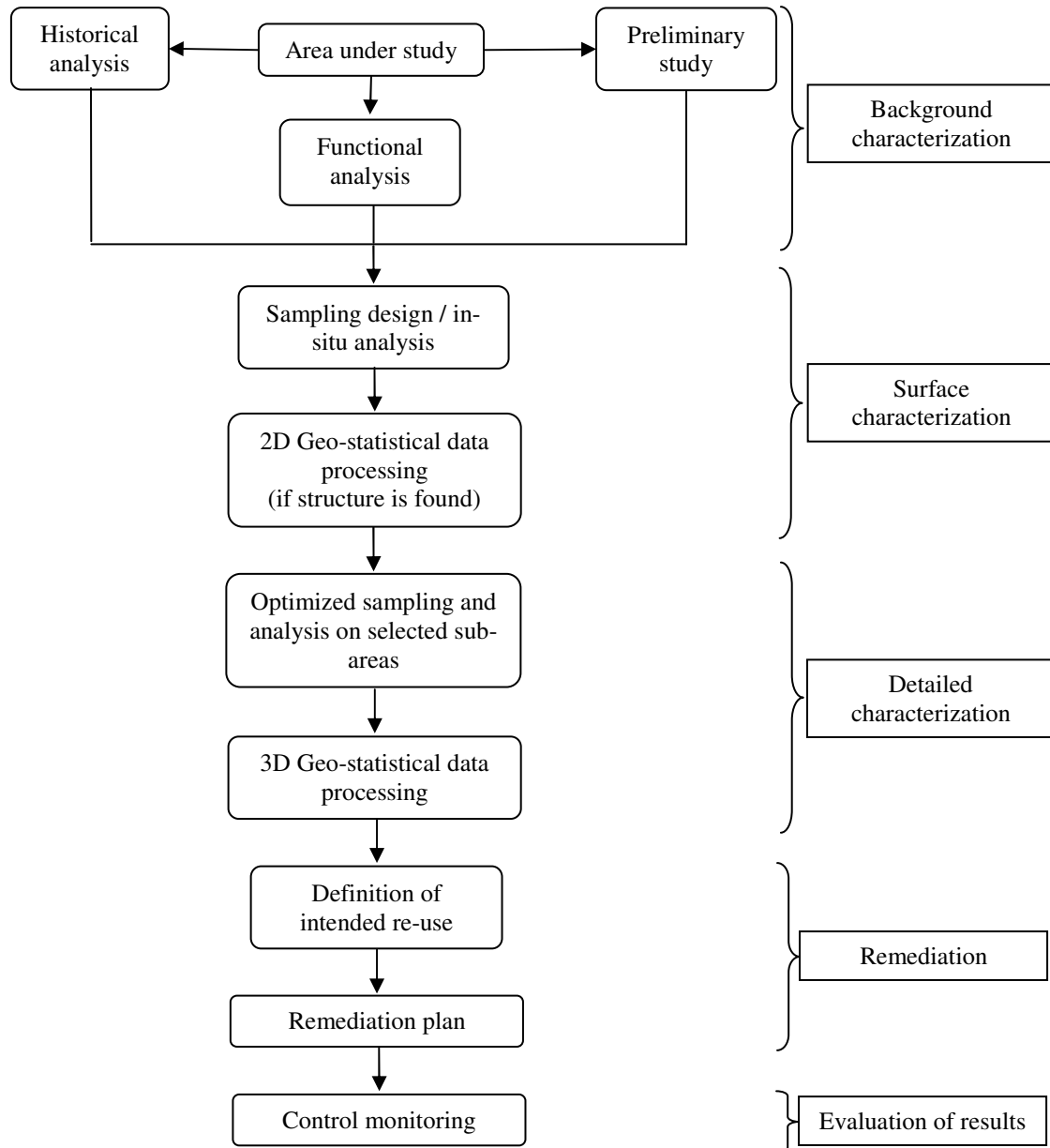


Figure 5: Application of Geo-statistical approach to the study of a radiological contaminated site.

The sequence can be illustrated for the case of intending a remediation of a parcel of land in the vicinity of a mining sector where increased levels of radiation dose have been reported. Figure 6 illustrates the results of the sequence of actions and the software developed and used for this purpose by CEA of Fontenay-aux-Roses, France.

As a first action, the site was inspected with a vehicle equipped with a plastic scintillation detector and a geographic positioning system. The measured count rate was recorded and the results were represented in a map. Later on an interpolation by Kriging was done as to provide an estimate of the dose over the whole area.

A sampling plan based on the observed results and the expected probability of exceeding a given result value allows to select an optimal number of drilling spots to collect samples for further gamma spectrometry laboratory analysis and to produce an estimate of the 3D distribution of the contamination.

[Dubot, please review this last section and include modifications as you might consider]

3 The use of Nuclear and Nuclear-related techniques in gathering analytical data

3.1 Common advantageous features

There are different opinions on whether a given technique can be classified as “nuclear” or as “nuclear-related”, but under these generic labels a large group of techniques have been conventionally classified. All the methods aimed to measure radioactivity, either natural or induced are defined as nuclear techniques, since the measured radiation is originated by a nuclear interaction or phenomena. Techniques based in using some type of ionizing radiation to induce some interactions in the inspected samples and the further measurement of a response signal related to a particular property of the sample are often classified as nuclear-related. Within such category can be classified most of the x-ray spectrometry techniques and ion beam analysis techniques. Mass spectrometry is sometimes classified as nuclear-related technique, based on the understanding that the ratios of different isotopes of chemical elements are determined after separating the isotopes by their differences in isotope masses (nuclei masses).

Nuclear and nuclear-related analytical techniques have proven to be a suitable tool in gathering information for the characterization of objects in solving different kind of applications. Some advantageous features are common for a large group of nuclear and nuclear-related analytical techniques:

The basic principle of detection often ensures a high selectivity. The natural spread of values of energy of a given radiation emission in most of the cases for alpha, gamma and x-ray characteristic emission is so narrow that the selectivity of the analysis is mainly limited by the energy resolution of the used detector in energy dispersive spectrometers. Such methods have as an additional advantage the possibility of detecting more than one analyte in a single measurement, depending on the energy range of the detector efficiency. In high resolution gamma spectrometry the radiation can be effectively detected within a broad range of energies, thus allowing determining the activity of different radio-nuclides in a single measurement. In energy-dispersive x-ray spectrometry the characteristic radiations that are effectively excited and detected serve to identify the elements present in the sample and to assess their concentrations or weight fractions in the analyzed sample.

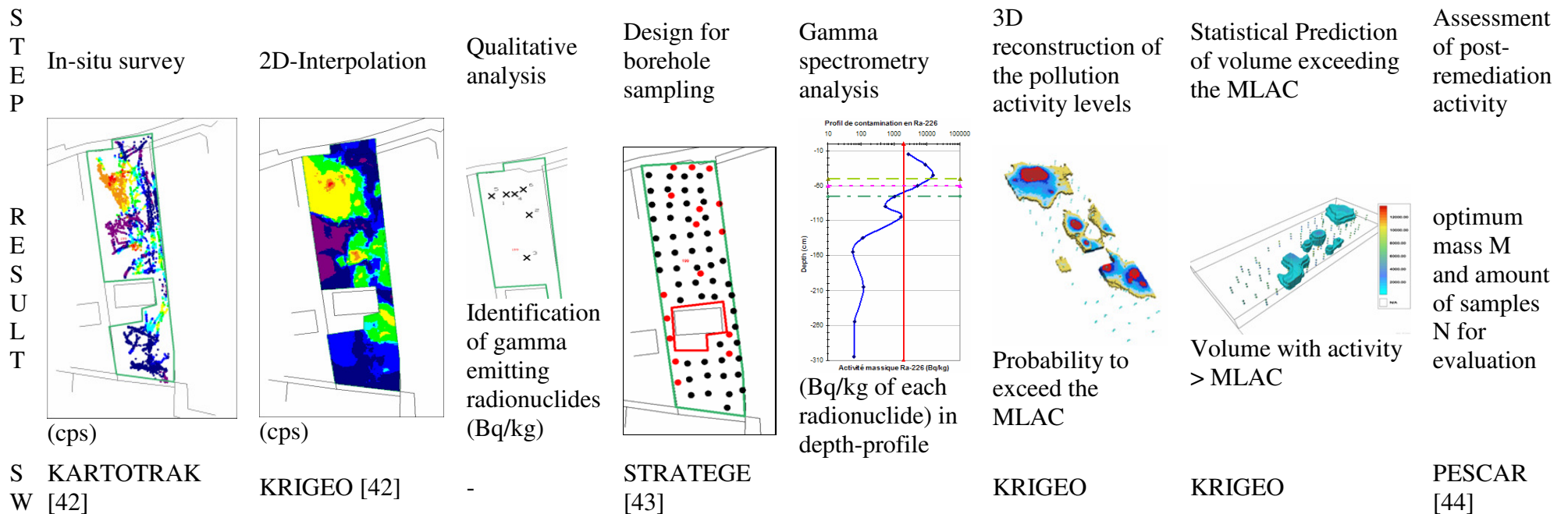


Figure 6. Main actions in optimized sampling - analytical work for site remediation
Notes: SW - Software, MLAC – Maximum Level of activity concentration (Bq/kg)

[Dubot, please review this representation and include modifications as you might consider]

Many techniques are applicable to a wide working range of the measurand property value. The lower limit of the working range (detection limit) is usually dependent on the instrument sensitivity, the time required for the measurement and by the fluctuations of the noise signal (background and spectral interferences, if any). The upper limit of the working range depends on the maximal input rate capability of the instrument, which is in turn inversely proportional to the time required for processing the response signal to a single event.

Another attractive feature of some nuclear and nuclear-related techniques is the possibility of performing the analysis without needing a complex sample preparation procedure. This feature has a great impact in minimizing the costs and time required for the analysis and in avoiding contamination of the sample. The calibration procedure of such methods is basically required to determine the instrument response for a particular measurement conditions set (detection efficiency, sample geometry and mass and excitation conditions if applicable) and sample properties (sample shape, aggregation state).

Some recent developments in nuclear instrumentation have made possible the release of portable instruments. The design of thermoelectrically cooled semiconductor detectors has led to a significant reduction in the weight and size of gamma and x-ray detectors. The advances in programmable electronic devices allowed the significant improvement of spectrometers in terms of compactness and speed of signal processing. Handheld spectrometers for x-ray fluorescence analysis combine these features with the use of miniaturized x-ray tubes and absorbing filters to improve the x-ray production in the sample and provide an instrumental response comparable to laboratory instruments.

3.2 Capabilities of Nuclear and Nuclear-Related Techniques

As already stated in section 1.5, a combination of different analytical techniques is required to get all the information needed for the study of hazardous elements dispersal around mining environments. This section provides a relation of the capabilities and shortcomings of the techniques most commonly used for the determination of such contaminants. Fundamentals and theoretic aspects of these techniques can be found in detail in specialized literature, whereas references to different cases of application are provided in a Table at the end of the section.

3.2.1 Analysis of radio-nuclides:

Preliminary in-situ radiological assessment is usually carried out by measuring the radiation dose rates using scintillation or gas detectors. The developments of compact portable gamma spectrometers and transportable Liquid Scintillation Counting (LSC) instruments made possible the application of these techniques to in-situ measurements.

Most of the measurement tasks required for monitoring radio-nuclides associated to Uranium exploitation can be accomplished with either high resolution High Purity Germanium (HPGE) detectors for gamma-spectrometry or with LSC instruments equipped with alpha/beta separation sample preparation modules and its corresponding procedures for individual measurement of the activity of alpha or beta emitting radio-nuclides.

Radon monitoring by means of etch track detector method is well applicable as integrated methodology in frame of corresponding detectors dynamical range. Other Radon measurement methods based on integrating approach could be used as a base for recognition purposes.

Studying of air particulate matter require of collection on filters using high volume air sampling system or by long term spontaneous gravimetric deposition in dry-deposition (tablet) or wet-deposition systems.

LSC technique is applicable for radon and thoron progeny measurements by using high volume air collectors, allowing covering a wide range of applications from the background levels found in open atmosphere to the high levels of concentration present in the mine ventilation systems.

A good review on the most commonly used techniques for the analysis of NORM is provided in [45]. Several texts provide detailed information on alpha-particle spectrometry [46, 47], radium isotopes analysis [48] gamma spectrometry in radio-elemental mapping [49] and radon analysis [50, 51] as well.

3.2.2 Chemical analysis:

- *Atomic spectroscopic techniques*

Metal determination in liquid samples has been usually carried out by means of atomic spectroscopy techniques, such as Flame and Electro-Thermal Atomic Absorption (FAAS, ETAAS, respectively) and Inductively Coupled Plasma Optical Emission and Mass Spectrometry (ICP-OES and ICP-MS). Each of these techniques has its advantages and limitations and therefore few laboratories rely on using only one technique, but more often on using some combinations of them. Table 2 summarises the comparative benefits of these techniques and typical detection limits for aqueous solutions.

Table 2: Comparison of analytical performance characteristics of the main techniques used for element analysis

	FAAS	ETAAS	ICP-OES	ICP-MS
Single/Multiple elements	S	S	M	M
Linearity Range	10 ²	10 ³	10 ³	10 ⁸
Relative precision (%)	> 10	3-5	1-10	< 5
Trueness	Moderate	Good	Moderate	Good
Costs order	\$	\$\$	\$\$	\$\$\$
Element	Detection limits: mg·L ⁻¹ (mg·Kg ⁻¹)			
Al	<1	<0.05	<1	<0.1
Cr	<1	<0.05	<1	<0.1
Mn	<1	<0.05	<0.1	<0.05
Co	<1	<0.05	<1	<0.05
Ni	<1	<0.05	<1	<0.1
Cu	<1	<0.05	<0.1	<0.05
Zn	<0.1	<0.05	<0.1	<0.1
As(1)	>1	<0.1	<1	<0.1
Se(1)	>1	<0.1	<1	<0.1
Cd	<0.1	<0.05	<1	<0.05
Sn(1)	>1	<0.1	<1	<0.1
Hg(2)	>1	<0.1	<1	<0.1
Pb	<1	<0.05	<1	<0.05

Notes: (1) Improved by hydride generation (HG),
(2) Improved by cold vapour (CV)

Liquid samples related to mining operations, such as mine waters and extraction solutions, usually have a complex matrix (high contents of salts). The direct measurement using conventional atomic spectroscopic techniques is hampered by complex interferences and a separation and/or pre-concentration procedure is often required before the measurement. The analysis of solid samples requires of a previous dissolution which is usually carried out by means of a wet digestion procedure. In both cases disturbances of the measured concentrations might arise either because of element losses due to incomplete digestion of samples or contamination issues [52]. The development of specific procedures becomes often economically unaffordable in environmental studies involving the analysis of different elements in large amounts of samples of different nature and type and the use of nuclear spectrometry techniques constitutes a feasible alternative.

- *Activation Analysis*

Both Instrumental Neutron Activation Analysis (INAA) and Photon Activation Analysis (PAA) comply with the features of multi-element capability, simple sample preparation and a wide dynamic range for the calibrations. With detection limits in the range of 0.1 – 1 mg/Kg and a minute sample size requirement (~ 0.1 g) the techniques have been widely applied for the analysis of elements at low concentrations in samples related to environmental studies since the 1960's [53]. Due to its large neutron fluxes research reactors have been widely applied for NAA in many analytical applications [54]. The main drawbacks are the time delay, the remaining activity in the samples and a relatively high cost per determination. Local policies have led to the decommissioning of nuclear research reactors in some countries during the last years.

- *X-Ray spectrometry techniques*

X-Ray fluorescence spectrometry (XRS) techniques comply with the features of multi-element capability, simple sample preparation, high throughput and low cost per determination. For this reason, several techniques have been widely applied for the analysis and characterization of samples related to the earth [55]. In addition, the possibility to perform in situ analysis with field-portable X-ray Fluorescence (XRF) spectrometers has become a common and standardized technique for on-site screening and fast turnaround analysis of contaminant elements in environmental samples [56].

One of the shortcomings of conventional XRF has been the poor elemental sensitivity for some important pollutant elements (such as Cd, Pb, among others) compared to the other atomic absorption spectroscopic techniques. Nevertheless, the recent development of digital signal processing based spectrometers in combination with enlarged X-ray production using better designs for excitation-detection has added the advantage of increasing instrumental sensitivity, thus allowing the improvement of precision, detection limits and productivity [57]. Besides the application of XRS to the analysis of solid samples, liquid samples can be analyzed by total reflection X-ray fluorescence spectrometry (TXRF) which requires of only a few micro-litres of sample and benefits from limits of detection in the $\mu\text{g/L}$ level.

The rapid development of micro-focusing optics has also promoted the possibility of irradiating a focused area of about 20 - 30 micrometers, thus obtaining information on micrometric scale [58]. The use of synchrotron radiation as excitation source (SRXRF) offers better spatial resolution (down to micrometer) and the high intensity, monochromaticity and high degree of linear polarization in the storage ring plane, allow

obtaining quantitative information on the elemental distributions with absolute detection limits at femtogram scale [59]. Micro-XRF is very useful for the analysis of spatial distribution of elements in environmental samples.

Moreover, with the evolution of synchrotron radiation sources an advent of new and interesting types of analytical methods such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) have also been effectively applied to the determination of speciation and complexation of elements in solid environmental samples [60]. In the case of single crystals or on powdered crystalline materials the structural information can be obtained by X-ray diffraction spectrometry (XRD or μ -XRD).

- *SEM-EDS analysis:*

To get morphological and composition information on the samples of interest (usually individual particles), electron microscopy techniques have been also applied including scanning electron microscopy (SEM), electron probe microanalysis (SEM-EDS) and transmission electron microscopy (TEM). Originally SEM was mainly used to obtain high-resolution images and the chemical analysis was performed by x-ray microprobe. Most of the current instruments allow performing both chemical and topography studies, the differences remaining in practical arrangements.

Due to the nanometer size of the electron beam, electron microscopic images have the best spatial resolution down to the sub micrometer ranges. Elemental detection limits in SEM-EDS are usually not too low (typically 0.1%) and the application of the technique is limited to the analysis of major constituents. Most recent developments include faster and more efficient image processing, including the possibility of gathering element distribution maps and particle identification. The development of ultra-light entrance window detectors allowed detecting light elements such as C, N, and O [61].

- *Infrared and Raman spectrometry*

In infrared spectroscopy (IR), the specific absorption of IR radiation in the wavelength range of 2-200 μm is measured. As a result of IR radiation absorption the quantised vibration states of the molecule or the crystal are changed giving rise to changes in the dipole moment in the structure. By means of IR spectroscopy isolated vibrations assigned to chemical bindings, weak molecular interactions as well as coupled vibrations due to condensed structures and strong solid-state interactions can be studied. Thus IR spectroscopy can be successfully applied for the structural analyses of both organic and mineral materials. IR spectroscopy was originally developed for the analysis of bulk sample composition. Fourier transformation IR microscopy offers the possibility of analyzing individual particles with diameters of $<5\ \mu\text{m}$. To isolate the areas of the sample to be analyzed knife-blade apertures are applied. This image masking technique on the FT IR microscope is quick and accurate. Both micro FT IR spectrometry and micro Raman spectrometry have been applied for the analysis of environmental particles [62].

Table 3 provides some examples of the application of the above mentioned techniques for the analysis of different kind of samples related to environmental monitoring in mining and milling sites. Additional information on each application could be found in more detail in the provided references.

Table 3. Some examples of application of nuclear and nuclear-related analytical techniques to environmental monitoring studies.

Sample	Analyte	Technique	Results	Reference
Mining tailing particles	Uranium	SEM-EDS	Measurement of 600 individual particles resulted in an abundance of detectable uranium-rich particles (>5wt%U)	[63]
Mining tailing particles	Minerals	XRD	Quartz, illite, chlorite, kaolinite and gypsum were the minerals identified in the bulk samples. Considering the concentration of As in the tailings, the nominal concentration of a possible As-bearing mineral should be ~5%. The presence of hematite and Fe, Ni and primary As sulfide minerals was determined in the heavy fraction (13.08g/cm ³).	[64]
Mining particles	Secondary uranium minerals	Micro-Raman spectrometry	K and/or Na uranyl sulphate Na ₆ (UO ₂)(SO ₄) ₄ (H ₂ O) ₂ (zippeite group) were detected in the uranium minerals. U was also present in the form of a trioxide UO ₃ ; but in much lower content than sulphate. Few particles with U ₃ O ₈ and uraninite UO ₂ were also detected. Primary minerals was in this mine the uraninite UO ₂ and coffinite (U,Th)(OH) ₄ x(SiO ₄) _{1-x} .	[65]
Mining tailings	Ca-As precipitates	SEM	Ca-arsenates were observed as amorphous masses of Ca-sulphates, and Fe hydroxides and as coatings of Ca sulphates and Ca-arsenates on gypsum crystals	[66]
Mining tailings	Fe(II), Fe(III), Mn(II), As(V), As(III), U(VI)	XANES	The mixture of Fe(II) and Fe(III) compounds (majority of Fe ₃ O ₄) was predominant in all samples and Fe(II) was slightly increased along the depth profiles. Mn(II) was increased along the depth profiles. As(V) compounds were predominant in all samples and As(III) was slightly increased along the depth profiles. U(VI) compounds were predominant in the tailings, increasing core depth shift to lower oxidation state compounds down the core because of the predominance of anoxic conditions compared with the top layers of tailings samples.	[67]

Table 3 (cont.). Some examples of application of nuclear and nuclear-related analytical techniques to environmental monitoring studies.

Sample	Analyte	Technique	Results	Reference
Ore concentrates	Metals (multielemental)	XRF	Results showed large differences in elemental mass fractions between samples from different mines. Higher concentrations of Na, Ce, Cu, Zn, Mg and Mn were found.	[68]
Overbank and stream sediments	Metals (multielemental)	EDXRF	Geochemical variations in vertical profiles of these two kinds of sediments allow observing noticeable heavy metal pollution (especially Fe, Pb and Zn) in both kind of sediments but especially in the overbank sediments (13%Fe, 6%Pb, 6% Zn).	[69]
Sediment depth profiles	Pb and Zn	μ -XRF	The metal accumulation layers were observed using such approach and this information can serve to understand the sedimentary processes that occur in the different zones of the mining district and identify sediments providing from different depositional processes.	[70]
Metal-bearing waters	Metals (multielemental)	WDXRF	Preconcentration of elements from liquid samples was performed by means of a simple dried residue process. Suitable limits of detection were attained (<0.1mg/L) according to the present regulatory requirements established by the US-EPA (TCLP) and German standard method (DIN-38414-S4)	[71]
Spring and creek mining waters	U	TXRF	The uranium concentration was found in a wide range from below DL (< 17.4 μ g/l) to 25 mg/l. The reason of the difference of the uranium concentration could be the chemical cleaning procedure on the environmental base.	[63]

Table 3 (cont.). Some examples of application of nuclear and nuclear-related analytical techniques to environmental monitoring studies.

Sample	Analyte	Technique	Results	Reference
Vegetation samples	Pb, Zn	μ -XRF	The analysis of the data revealed that the lower leaves of sunflowers grown on the mining land plots accumulated significant quantities of Zn and Zn compared to the control specimens. Two-dimensional elemental mapping of the leaves showed that both metals accumulated in the main vein of the leaves and the leaf margin.	[72]
Vegetation samples	Metals (multielemental)	WDXRF, EDXRF	Different sample preparation strategies and instrumental XRF configurations were evaluated for the determination of metals in vegetal species related to metal contamination.	[73]
Mining tailings, milling tailings	Ra-226, Ra-228, Th, Ac, Pa	Gross alpha counting and emanometry	Determination of 226Ra and 228Ra as well as thorium, actinium and protactinium in different sample types	[74]
Mining tailings, milling tailings	Ra-226	Alpha spectrometry	Determination of 226Ra and 228Ra as well as thorium, actinium and protactinium in different sample types	[75]
Uranium mining waters	Different gamma emitters	Gamma Spectrometry	Ra and Th nuclides, 238U and 227Ac	[76]
Mining or milling tailings body	Radon in soil gas vs. radon flow	LSC based method	Classification of radon source and radon flow	[77]
Abandoned mine areas	Different radionuclides	Various techniques	Measurements of ambient radiation doses and determination of radionuclide concentrations in mining waste and soils	[78]
Air particulate matter	Radon and thoron progeny (Po-218,Pb-214, Bi-214, Pb-212)	High volume sample, LSC	Radon and thoron effective equivalent concentration (EEC), Radon in air equilibrium factor	[79]

4 Conclusions

To achieve a comprehensive characterization of environmental impact arising from mining and milling activities require of a proper assessment program based on an interdisciplinary approach. At different stages of any environmental assessment large amount of data on the nature, concentration and distribution pathways of the investigated contaminants of concern is required.

Nuclear analytic techniques allow determining the contents and distribution of common inorganic contaminants and radiation hazards resulting from mining and milling operations in the exploitation of both radioactive and non-radioactive mineral resources. The basic principles of detection often ensure a high selectivity, with the additional advantages of detecting more than one analyte in a single measurement, a wide working range and not needing in many cases a complex sample preparation procedure. The recent developments in nuclear instrumentation have made possible the release of portable instruments with sensitivity comparable to that achieved with laboratory instruments, thus allowing the use of in-situ techniques as a cost-effective approach to determine the spatial distribution of the contaminants and radiation hazard.

5 Recommendations

The contributors to this report considered relevant to formulate the following recommendations to the International Atomic Energy Agency and to its Member States:

Recommendations to the Member States

- Member States should consider incorporating sound environmental risk assessment programs as part of the mining and ore processing projects, including the monitoring of the levels of concentration of contaminants of concern at different stages of the projects.
- The main stakeholders in mining industry should be aware of the advantages of designing and implementing cost-effective programs aimed to minimize the impact or to remediate the state of pollution in mining-milling sites. The use of a combination of in-situ and laboratory based nuclear analytic techniques, together with advanced statistical or geo-statistical sampling strategies allows maximizing the efficacy and to reduce the costs of these environmental assessment programs.
- The creation of a mobile unit for environmental monitoring, to be shared by several countries in a particular region, is an alternative to minimize the costs related to analytical services and environmental assessment programs.

Recommendations to the International Atomic Energy Agency

- The IAEA should recognize the importance of further development in the procedures for comprehensive characterization of sites subjected to past, present or future mining and milling operations, and consequently increase promotion among Member States of the advantages and benefits of their implementation in sound environmental assessment programs.

- The participants recommend considering to develop a mobile unit combining several nuclear analytical techniques with advanced geo-positioning and geo-statistics based tools for sampling optimization and interpretation of the analytical results. Such Unit could be used for demonstration in typical scenarios in different countries as well as for training purposes.
- The IAEA should play an important role to facilitate the access to and for the utilization of advanced tools for the monitoring of environmental impact arising from mining-milling operations, as well as to support the cooperation among specialists from different disciplines, by organizing Schools, Workshops, Technical Meetings and/or Coordinated Research Programs.
- The IAEA should support sound National and Regional Technical Cooperation projects related to establishing procedures for monitoring the impact of mining-milling operations involving an effective utilization of nuclear spectrometry-based analytical techniques.

6 Contributors to drafting and review

This report summarizes the results of discussions held on several topics by the participants of a consultancy meeting on Applications and trends in the use of nuclear spectrometry techniques for assessing the impact of mining and milling sites on human health and the environment (Vienna, Austria, November 23 - 25, 2010). Contributions to the drafting of this report were made by:

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