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ENVIRONMENTAL SAMPLING AND ANALYSIS
AS A SAFEGUARDS TOOL

N. A. Wogman
R. W. Perkins
G. R. Holdren

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Pacific Northwest Laboratory
Richland, Washington 99352

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ENVIRONMENTAL SAMPLING AND ANALYSIS AS A SAFEGUARDS TOOL

1.0 ABSTRACT

Environmental sampling and radionuclide analysis of the resulting material can be utilized as a supplemental approach in safeguarding practices and particularly for detection of undeclared nuclear activities.

The production of nuclear weapons could be pursued by uranium enrichment processes to produce highly enriched U-235 or by nuclear reactor operations followed by chemical separations to produce Pu-239. The application of either of these processes results in the production of signature materials, some of which will be released to the environs.

Results from the operations of the Hanford production facilities are discussed and indicate the type of signatures that may be expected from plutonium production facilities. These include noble gas emissions from the reactors and chemical separations processes, the production of radionuclides in reactor cooling water followed by their subsequent release to the Columbia River, and the release of mildly contaminated process water from the chemical processing facilities. These signature materials are carried by both gaseous and liquid effluents and enter various compartments of the environment. The types of signature materials which are most likely to be released and the environmental compartments where they are likely to be accumulated are discussed, together with examples of the quantities which have been released during past separations.

There are numerous processes by which natural uranium may be enriched to produce highly enriched U-235. The most definitive signature of such processes is always a modification in uranium isotope ratios, and materials showing either enriched or depleted uranium in gaseous and liquid effluents provide the best

indication that uranium enrichment processes are taking place. Therefore, techniques for sampling and analysis of airborne, waterborne, or deposited uranium in environmental matrices provide a means of detecting uranium enrichment which may lead to proliferation products.

2.0 INTRODUCTION

A safeguards program for detection of illicit nuclear weapons production could be enhanced by including the collection and analysis of environmental materials, including aerosols, water, soil, and biota. For example, a proliferant state could pursue nuclear weapons production based on uranium enrichment processes or via Pu-239 production with their associated signatures.⁽¹⁾ Products and by-products from these activities would include modified uranium isotope ratios in the case of uranium enrichment and numerous fission and neutron activation products in the case of plutonium production. A fraction of these signature radionuclides would enter the environment and would be concentrated by natural processes in the surface soils, sediments, and in terrestrial and aquatic bioaccumulators.

The signature radionuclides associated with reactor operations include those in both gaseous and liquid effluents. The fission process results in the production of several noble gas radionuclides, as well as halogen radionuclides which are relatively volatile and are more likely to be released. Spectra of relatively short-lived radionuclides such as Sr-89 ($t_{1/2} = 50$ d), Ba-140 ($t_{1/2} = 13$ d), Zr-95 ($t_{1/2} = 64$ d), Nb-95 ($t_{1/2} = 35$ d), I-131 ($t_{1/2} = 8$ d), and Ru-103 ($t_{1/2} = 40$ d) may be some of the first to be observed from plutonium production operation, and the longer-lived fission process radioisotopes Sr-90 ($t_{1/2} = 29$ yr), Ce-144 ($t_{1/2} = 284$ d), I-129 ($t_{1/2} = 10^6$ yr), Ru-106 ($t_{1/2} = 386$ d), and plutonium isotopes, may be more prevalent after longer periods.

In the case of the Hanford operations, reactor cooling water was discharged to the Columbia River and several of the radionuclides became attached to particulate material and were deposited in sediments behind dams. Collection and analyses of these sediments provided an excellent means of detecting reactor operations.

Fuel reprocessing involves the removal of the fuel cladding either by chemical or physical means followed by dissolution of the uranium fuel. During fuel dissolution, the volatile radionuclides are released from the dissolver tank along with oxides of nitrogen, and these gases pass through various types of filters and reactors to trap most of the fission and activation products. Those which are most readily emitted from reprocessing plants include Kr-85, H-3, I-131 (if present), I-129, Tc-99, C-14, He-3, and in some cases particulate radionuclides such as Ru-103, Ru-106, Ce-141, Ce-144, Cs-137, and Sr-90. A fraction of the radioiodine is released to the atmosphere during the dissolution process, and subsequent to this process it is eluted from sorption beds which are typically employed for its trapping. In the case where production of high enriched U-235 is the objective of the proliferator, the liquid and gaseous effluent may contain enriched and depleted uranium in chemical forms associated with the enrichment process. These signature materials may be detectable in air particulates, soils, groundwater, and biota.

3.0 DISCUSSION

Effluent signatures are observable through sample collection and subsequent laboratory analyses, and in some cases they might be observed by real-time measurements. The fission process results in the production of several noble gas

radionuclides, as well as halogen radionuclides, which are relatively volatile, and these may be released during reactor operations. The noble gas radionuclides will always be released to some degree and, depending on the reactor confinement system, varying amounts of the halogen radionuclides will also be released. While sampling for the noble gas radionuclides is rather complicated, the collection of their daughter radionuclides can easily be accomplished by passing air through particulate filters. In conducting a survey at a suspect production site, those radionuclides with half-lives of several hours or more could be collected for subsequent laboratory analysis; however, the very short-lived radionuclides may require in situ analysis. For example, a large amount of Ar-41 (1.82 hr) is produced from atmospheric argon (Ar-40) which may be dissolved in the cooling water or may simply be present as a component of the reactor cover gas. The plume of Ar-41, and perhaps other radioactive gases, may be detectable with a high efficiency ground-based or airborne radiation sensor.

The major reactor effluent water radionuclides, together with their release rates from the world's first plutonium production reactor, the Hanford B reactor, during May 1960 have been summarized.⁽²⁻⁴⁾ With eight such reactors in operation, very large amounts of radioactivity entered the river, which included up to 100 curies/day quantities of radionuclides such as Na-24, P-32, Ca-45, Sc-46, Mn-56, Cu-64, As-76, Cr-51, Co-60, Zn-65, Zn-69m, Ga-72, Sr-89, Sr-90, I-131, Ba-140, La-140, Eu-152m, Eu-152, Sm-153 and Np-239. This spectrum of radionuclides was typical of that from the original eight plutonium production reactors at Hanford; however, the operation of the newer N reactor involved recirculation of the cooling water and discharging a few percent to a trench which was located parallel

to and approximately 200 meters from the Columbia River. The radionuclide attenuation via soil adsorption which occurred during the approximately six-day transit time from the trench to the river ranged from 2 to 5 orders of magnitude. However, even with this approach, substantial quantities of several radionuclides did enter the Columbia River and could be observed throughout its entire downstream length.

When reactor effluent waters entered the Columbia River, several of the radionuclides became attached to particulate material and some were deposited in sediments behind the Columbia River dams. The physical forms of the reactor effluent water radionuclides and their concentrations throughout various reaches of the river over a one-year period have been summarized.⁽²⁾ These data illustrate that by separating radionuclides from a large volume of water, it is easy to detect reactor effluent discharges which have occurred at upstream locations.

Radionuclides which become associated with particulates within a river system may be deposited in the river bottom sediments and collection and analyses of these sediments provide an excellent means of detecting reactor effluent discharges at upstream locations. There are several bio-accumulators of radionuclides which concentrate those present in river water. These include terrestrial vegetation which is irrigated with river water and the associated food chain items, as well as aquatic biota within the river. Concentrations of radionuclides in river biota relative to those in river waters and a summary of some of the radionuclide concentrations in four types of fish have been documented.^(3,4) It is clear that sampling of river biota followed by laboratory analysis could provide an indication of upstream reactor operations.

Following the exposure of uranium fuel in a nuclear reactor, it is allowed to decay for a certain period of time prior to reprocessing for plutonium extraction. The decay interval depends on the period of time the country may be willing to wait for the extraction of plutonium. One of the major considerations in determining the decay period is the problem of release of volatile I-131 ($t_{1/2} = 8$ days). If decay periods of a year or more are permitted, then essentially all of the I-131 will have decayed. On the other hand, if decay periods of 3 months or less are used, there will be a considerable amount of I-131 present in the fuel and a substantial amount of this may be released to the environs.

As previously indicated, dissolution of nuclear fuels using nitric acid releases volatile radionuclides along with oxides of nitrogen. While these gases pass through various types of filters and traps, several radionuclides, including all of the Kr-85, some tritium, I-131 (if present), I-129, Tc-99, C-14, He-3, and in some cases particulate radionuclides such as Ru-103, Ru-106, Ce-141, Ce-144, Cs-137, Sr-90, etc., are released. A fraction of the radioiodine is released to the atmosphere during the dissolution process, and subsequent to this process additional release results from elution of the sorption beds which are employed for its trapping.

While I-129 is a naturally-occurring radionuclide formed by spontaneous fission of U-238 in the earth's crust, its concentration at the earth's surface in vegetation and in natural waters is very low. Therefore, its measurement in environmental matrices provides an excellent indication of reprocessing activities. It can be measured with very high sensitivity by various types of laboratory techniques.

During the operation of the Hanford (Richland, Washington USA) reprocessing plants, monitoring programs⁽⁵⁻¹⁰⁾ were carried out to measure the I-129 in the atmosphere and in other compartments of the environment. It is clear from these studies that the concentrations of this radionuclide are some 2 orders of magnitude higher in the environs of Richland, Washington than on the Olympic Peninsula (500 km upwind), which is in the extreme northwest corner of the State of Washington, USA. Concentrations in Spokane, Washington (200 km downwind) are intermediate.

The observed concentrations of I-129 in bovine thyroids collected from meat packing firms throughout southeastern Washington indicated that by far the highest concentrations were from area near the Hanford Site. The concentrations in air, rain, grass, and soil provided good indications of nuclear fuel reprocessing activities. Other types of vegetation, including perennial mosses, lichens, etc., are good indicators of nuclear fuel reprocessing activities.

Nuclear fuel reprocessing at Hanford required huge amounts of water which were used in the process itself for cleaning reprocessing equipment and washing down contaminated areas within the reprocessing cells. These waters, which contained relatively small amounts of fission and activation products, were discharged to the ground. The underground water plumes migrated down gradient with tritiated water in the lead.⁽¹¹⁾ Collection and analysis of well water samples for tritium indicate its presence and that of a wide range of fission and activation products, and could thus provide an indication of reprocessing activities at a suspect site.

Based on the properties and quantities of signature radionuclides which would be released to the environment as a result of reactor operations or fuel reprocessing, one can select sampling strategies which should permit the early detection of these activities. The detection of concealed nuclear reactor operations and reprocessing activities based on possible sample collections is summarized in Tables 1 and 2. These collections involve the sampling of air, water, sediments, biota, vegetation, and soil. Their analyses would involve returning the samples to the laboratory for the measurement of radionuclides of the types indicated. Most of these collections could be made in a relative straightforward manner with a minimum of special equipment so that costs could be minimal and the confidence could be high for detecting signature materials indicative of proliferation activities. Examples of the release, distribution, and accumulation of the radionuclides have been discussed and sampling scenarios are summarized below.

Air Sampling: In order to insure a high sensitivity for the measurement of airborne radionuclides, it is important to employ Large Volume Air Sampling (LVAS). Sampling at high rates, tens of cubic meters per minute, improves detection probability. However, sampling at lower rates could be satisfactory if one were near (within a few kilometers) the suspect proliferation site. Particulate radionuclides are readily captured on efficient air filters which have relatively low-flow resistance, and the iodine radionuclides can be trapped on charcoal-impregnated filters or other filter matrices. The subsequent analyses of these materials at the laboratory would indicate the presence of modified uranium isotope ratios

or radionuclides associated with reactor operations and fuel reprocessing as indicated in Tables 1 and 2.

Water Sampling: Aqueous effluents from nuclear activities are generally discharged to either surface or subsurface waters. They can be readily separated from the water using large volume water sampling techniques.⁽¹²⁾ Large volume water samplers have been used for the past three decades by Pacific Northwest Laboratory (PNL) for collection of radionuclides around the Hanford environs, through the length of the Columbia River, and for hundreds of miles at sea. With this system, the water is pumped at a rate of 30 to 40 liters/minute through filters for collection of particulate radionuclides and through ion exchange or sorption beds for collection of dissolved radionuclides (see Tables 1 and 2).

Sediments: As indicated in the body of this report, several of the radionuclides associated with uranium enrichment and reactor operations and reprocessing would be deposited in sediments of water bodies to which they are discharged. In order to provide a large amount of sediment for analysis, 15-cm diameter cores are collected from slack water reaches of rivers; however, most any kind of sediment collector would be satisfactory for collecting sediment materials for laboratory analysis.

Biota: Essentially all biota from fresh waters to which radionuclides are discharged will concentrate the radionuclides by a few orders of magnitude. Filter feeders such as oysters, mussels, and clams are particularly good bioconcentrators and may concentrate radionuclides or other trace constituents by 4 to 5 orders of magnitude. Their collection and subse-

quent laboratory analysis provides a good indication of the operation of nuclear processes.

Vegetation: Where radionuclides are released to the atmosphere, vegetation is a particularly good collector for detection of the processes which are responsible for these releases. Grass clippings are particularly good since they would contain material from recent releases. Other types of vegetation which require longer growing periods may also be desirable. Examples of vegetation which has been commonly used for measurement of deposited radionuclides are shown in the body of this report.

Soils: Airborne radionuclides, except for the noble gases, are eventually deposited on the earth's surface and the concentrations are highest near the points of release. To provide the highest sensitivity for detection of radionuclides which would be deposited from the atmosphere, samples should be collected from a minimal soil thickness over a wide area for subsequent laboratory analysis.

Detection of Radionuclides Based on Overflights: The operation of nuclear reactors and fuel reprocessing plants results in the release of radionuclides to the atmosphere. The most likely radionuclides to be released would be noble gas fission products and, in the case of reactor operations, Ar-41. An aircraft flight through areas downwind from suspected nuclear activities could possibly observe the increased radionuclide levels on a real-time basis. To maximize detection sensitivity, large areas and/or high-resolution sensors should be employed. While reconnaissance flights of this type would be a rather expensive approach, they

could be useful in surveying a number of sites in a relatively short period of time. Also, these flights could incorporate sampling procedures to collect both radioactive gases and particulates for laboratory analysis.

4.0 SUMMARY

The detection of uranium enrichment processes, nuclear reactor operations, and fuel reprocessing activities is possible based on environmental sampling and analysis. Those signatures which may be the best indicators of these processes and their collection techniques are summarized in Tables 1 and 2.

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TABLE 1

DETECTION OF A CONCEALED OPERATING NUCLEAR REACTOR
(Collection for Laboratory Analysis)

<u>SAMPLING</u>	<u>SIGNATURE</u>	<u>COLLECTION TECHNOLOGY</u>	<u>LIMITATIONS</u>
Air --Vehicle --Stationary --Aircraft	Short-lived noble gas daughters, radioiodines, and tritium	LVAS* using filter media and chemical sorption bed	Detection distances - or release rates (10s to 100s km possible)
Natural Waters --Rivers, lakes, and seawater	Activation/fission products (Na-24, As-76, P-32, Cu-64, Zn-65, I-131, Ba-140, La-140, Eu-152, Np-239, etc.)	LVWS** Pump water through an ion exchange media	Effluent must enter natural waters
Sediments	"	Sample river, lake, ocean sediments	"
Biota (natural concentrations)	"	Fish, oysters, etc.	"
Vegetation --Terrestrial	"	Cut grass	Vegetation must be adjacent to available facility
Soil Samples	"	Collect surface soils (top few millimeters)	Detection distance depends on source term

* Large Volume Air Sampler

** Large Volume Water Sampler

TABLE 2
DETECTION OF REPROCESSING ACTIVITIES
(Collection for Laboratory Analysis)

<u>SAMPLING</u>	<u>SIGNATURE</u>	<u>COLLECTION TECHNOLOGY</u>	<u>LIMITATIONS</u>
Air --Vehicle --Stationary	Kr-85, tritium, I-131, I-129, Tc-99, Ru-103/Ru-106, etc.	LVAS* using filter/sorption beds	Distance depends on release rates
Natural Waters --Rivers, lakes and seawater	Fission products, (tritium, Cs-137, Ru-103/Ru-106, Ce-141/Ce-144, etc.)	LVWS** using filters/sorption beds	Effluents must enter natural waters
Subsurface Waters	"	LVWS** using filters/sorption beds	Effluents must reach sampling wells
Sediments	"	Collect bottom sediments	"
Biota (plankton/ algae)	"	Plankton nets, algae growths	Biota must be available
Vegetation (terrestrial)	"	Grass, vegeta- tion clippings	Vegetation must be available
Soil Samples	"	Top millimeter over wide area	Distance depends on release rate

* Large Volume Air Sampler

** Large Volume Water Sampler

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