DETERMINATION OF TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIAL (TENORM) IN ASHES FROM COAL-FIRED THERMAL POWER PLANTS IN THE PHILIPPINES

by

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Dedicated to my husband, Manuel Juan and my sons, Juan Miguel and Gabriel Martin.

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ABSTRACT

DETERMINATION OF TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIAL (TENORM) IN ASHES FROM COAL-FIRED THERMAL POWER PLANTS IN THE PHILIPPINES

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The activity concentration (AC) of TENORM - ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K in feed coal, bottom ash and fly ash samples from four coal-fired thermal power plants C, M, P and S were determined using two techniques: inductively coupled plasma mass spectrometry (ICP-MS) and high purity germanium (HPGe) gamma spectrometry. For ^{232}Th and ^{238}U [determined at National Institute for Radiological Sciences (NIRS) by the ICP-MS)], Plant S feed coal (FC) sample that originated from China had the highest AC (15.77 ± 0.32 Bq/kg and 13.67 ± 0.82 Bq/kg, respectively), followed by Plant M FC sample also from China (8.31 ± 0.33 Bq/kg and 5.84 ± 0.12 Bq/kg, respectively), while Plants C and P FC samples that originated from the Philippines and Indonesia had the lowest ACs of ^{232}Th and ^{238}U. Plant S also had the highest bottom ash (BA) AC of 80.86 ± 3.23 Bq/kg and 100.20 ± 4.01 Bq/kg, respectively while Plant P had the highest fly ash (FA) AC of 155.96 ± 6.24 Bq/kg and 268.03 ± 10.72 Bq/kg, respectively.

For AC's of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K determined by NIRS HPGe, Plant C had the highest in the FC sample (11.70 ± 1.39 Bq/kg, 13.65 ± 4.99 Bq/kg, 11.35 ± 3.96 Bq/kg and 80.23 ± 10.91 Bq/kg, respectively). For AC's in the BA

samples, Plant M had the highest ^{226}Ra (106.73 ± 6.74 Bq/kg) and Plant S had the highest ^{228}Ra and ^{40}K (66.64 ± 8.16 Bq/kg and 400.93 ± 43.06 Bq/kg, respectively). For AC's in the FA samples, Plant S had the highest ^{226}Ra and ^{228}Ra AC's (131.13 ± 8.09 Bq/kg and 87.70 ± 10.45 Bq/kg, respectively) while Plant C had the highest ^{40}K AC (369.08 ± 40.87 Bq/kg).

The highest AC enhancement of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K relative to feed coal occurred in Plant P FA sample, with ^{238}U showing the highest enhancement of 93.72 among the radionuclides. When normalized with ^{40}K, ^{238}U in Plant P FA sample also had the highest enrichment factor (EF). Except for Plant C samples, ^{228}Ra, ^{228}Th and ^{40}K were about equally partitioned between BA and FA samples; ^{238}U had consistently higher partitioning in all FA samples than BA samples; ^{226}Ra and ^{232}Th had varied partitioning behavior among the Plants' BA and FA samples. The behavior of the radionuclides during combustion was explained to be influenced by their physical and chemical characteristics and their association with the alumino-silicate minerals in the coal.

For most samples, positive correlations between NIRS ICP-MS and NIRS HPGe were very high for ^{226}Ra with ^{238}U (R^2=0.98), and ^{228}Ra with ^{232}Th (R^2=0.94). Correspondence between ICP-MS and HPGe results were generally high with slopes of 0.90 and zero intercept for both ^{226}Ra vs ^{238}U and ^{228}Ra vs ^{232}Th. Correlations between NIRS HPGe and PNRI HPGe were also very high for ^{226}Ra (R^2=0.93) and ^{228}Ra (R^2=0.91), and high for ^{40}K (R^2=0.86). However, the slopes of the correlation lines gave only 0.65 to 0.68 correspondence of NIRS

HPGe relative to PNRI HPGe. This could be attributed to the slight difference in sample and standard geometry used in PNRI HPGe experiment and different multi-channel analyzer emulation software used by NIRS and PNRI HPGe's.

The results of more detailed study in Plant C showed that the ACs of ^{226}Ra, ^{228}Ra, and ^{40}K were similar between two sampling periods in 2005 and 2006; the ACs in the ash pond were generally slightly lower than that in the BA and FA samples; and the ACs showed a slight decreasing trend with ash pond depth.

The ACs in both BA and FA samples from Plants C, M, P and S were all below the International Atomic Energy Agency (IAEA) and European Commission (EC) recommended AC levels for regulatory control.

The absorbed gamma dose rates in air inside Plant C ranged from 29-36 nGy/h; in its vicinity (adjacent agricultural, public and residential areas) 27-41 nGy/h; and in the ash pond, 44-56 Gy/h. These were within the reported dose rates in Marinduque, Batan Island, and worldwide average in UNSCEAR.

Based on the AC values in FA samples from Plant C, the estimated discharges of radionuclides from the stacks were lower compared to that of the European Commission screening levels, thus detailed site-specific dose assessment may not be necessary.

Using the highest AC results of ^{232}Th, ^{226}Ra, and ^{40}K in FA samples from Plants C, M, P and S in calculating radium equivalent (Ra eq) classification (used for the purpose of controlling radiation dose from building materials), the fly ash from all Plants could be recommended for use in building residential houses.

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INTRODUCTION

1.1 Background

Elevated concentrations of *naturally occurring radioactive materials* (NORM) are often found in certain geological materials such as igneous rocks, ores and in fossil fuels. Extraction and subsequent processing of these materials may expose or concentrate the naturally-occurring radionuclides in the products, by-products, residues and wastes to levels well above natural background. NORM that becomes concentrated by any human activity is often referred to as *technologically enhanced NORM* or *TENORM*.

The terms TENORM and "technologically enhanced" as defined by the Health Physics Society NORM Working Group (Tsurikov, 1999) are as follows:

"TENORM" – means naturally occurring radioactive material, not subject to regulation under the Atomic Energy Act, disturbed or altered from natural settings, or present in technologically enhanced state due to human activities, which may result in a relative increase in radiation exposures and risks to the public above background radiation levels.

"Technologically enhanced" means that the physical, chemical, radiological properties and concentrations (of NORM) have been altered such that there is a potential for:

- Redistribution and contamination of environmental media (soil, water, and air);

- Increased environmental mobility in soils and ground water;
- Incorporation of elevated levels of radioactivity in products and construction materials; and
- Improper disposal or use of disposal methods that could result in unnecessary and relatively high exposures to individuals and populations in any environmental pathway and medium."

However, the term *NORM is preferred instead of TENORM* by the European Commission which is defined as "all naturally occurring radioactive material where human activities have increased the potential for exposure in comparison to the unaltered situation; the activity concentrations may or may not be increased" (European Commission, 2003). The activity concentration (AC) is the activity (in becquerel, Bq) per unit mass (kg) of the material in which the radionuclides are essentially uniformly distributed (IAEA, 2007).

The mining of ores and minerals, oil and gas extraction, as well as the cement, fertilizer, and fossil fuel-powered industries have the potential to produce very large amounts of residues or wastes that result in TENORM. If these residues and wastes are not properly and safely managed, the occurrence of TENORM over large areas becomes possible causing unnecessary natural radiation exposure to the members of the public. Thus, the issue on TENORM in residues or wastes outside of the nuclear fuel cycle has recently received considerable global attention.

From these recent developments, the IAEA (2003) emphasizes the importance, as a first step, for industry and regulatory bodies in Member States

to understand when and where TENORM can occur and also to identify the locations where concentrations of TENORM can be greatest within a given process. In many countries, the determination as to what concentration for a given exposure situation TENORM becomes a potential radiological concern is given high priority. Many developed countries have conducted inventories and are selectively regulating levels of NORM and TENORM of radiological concern. For example, in the United States, the identification of TENORM sources and the determination of their potential risks remain a major focus of work of the US Environmental Protection Agency (USEPA). The highest concentration of TENORM in the USA comes from the scales of pipes and tanks in oil and gas industries (http://www.epa.gov/radiation/tenorm).

The industries operating within the European Union which process materials that contain NORM and are considered to be of potential significance with regard to public exposure have been identified and the quantities of NORM wastes discharged into the air, rivers and seas or disposed of in the European Union have been reviewed (European Commision, 2003). In Germany, the rare earth elements processing industry involving monazite and oil and gas industry ranks number one in terms of maximum activity concentration and maximum effective dose rates to workers, respectively (http://www.uni-essen.de).

In Hungary, the survey of TENORM was first based on the amount of residues and the activity concentrations in the residues were compared with the average activity concentration of typical Hungarian soil. The radioactivity in coal mined in Hungary is higher than the average world value such that the radiation

levels of ash and slags arising from coal-fired power plants are elevated, too (Juhasz, et.al., 2005). For non-nuclear industries in the Netherlands, the highest human induced radiation doses were found in the cement industry, elemental phosphorous production, phosphoric steel production and iron and steel production. Consequently, the maximum doses to the public due to non-nuclear industries exceeded by more than three orders of magnitude compared with those of the nuclear industry (Jannsen, et al., 1998).

The United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR) has accumulated a large amount of data on NORM/TENORM. The main industries that use or process raw materials that contain NORM and consequently emit radionuclides to air and water that lead to eventual exposure to humans along with the by-products or wastes they generate have been identified by UNSCEAR. These include phosphate processing, metal ore processing, uranium mining, oil and gas extraction, scrap metal industry, and industries processing zircon sands, fossil fuels, building materials, and thorium compounds (UNSCEAR, 2000).

Meanwhile in Asia, the Task Group of Radioactive Waste Management (RWM) Project under the Forum for Nuclear Cooperation in Asia (FNCA) came out with a status report on inventory and management of NORM/TENORM of each volunteer country as a result of discussions and survey meetings held in Australia in February 2003, Malaysia and Vietnam in August 2003 and in China and Thailand in August 2004 (FNCA RWM-R003, 2005). Survey meetings held in Indonesia and the Philippines were concluded in August 2005, hence the

information on TENORM in these countries was not included yet in the report. As mentioned in the report on status of TENORM, Japan performed on-site dose rate and activity concentration analyses of monazite, phosphate ore, titanium ores, zircon, etc. as these are the materials that may contain relatively high concentration of NORM, and coal, as this material is imported in large amounts. The results form the basic information for developing regulatory policies in Japan. Yonehara (2005) reported that there has been on-going discussion by the Radiation Council of Japan on the principle for regulation of NORM/TENORM.

The industries in Australia where NORM is involved, the scale of production, typical radionuclide concentrations, and how wastes are managed have been identified. These include mineral sand and mining processing, titanium pigment production, zircon and ceramics industry, alumina production, copper mining and processing, phosphate industry, tantalum mining and processing, iron smelting, oil and gas production, coal-fired power generation, water treatment, and building materials industry. There are nine separate jurisdictions in Australia responsible for radiation protection that lack uniformity in areas such as licensing, exemption limits and definition although radiation protection regulations are applied so that safety is not compromised. A National Directory for Radiation Protection, a uniform national framework for radiation protection has been developed for future incorporation by nine (9) separate jurisdictions (State, Territory, and Commonwealth) in Australia.

In the case of China, limited inventory has been done. Coal slag in some areas was reported to have activity concentration of more than twice the IAEA

recommendation for ^{238}U and ^{232}Th. China also has no specific regulation that directly controls NORM/TENORM. Thailand and Vietnam reported that no inventories and studies on the locations and extent of TENORM have been done and that both countries have no regulation that directly controls NORM and TENORM. There is a need for guidance that contain a listing of various types of minerals and sites with TENORM, advice for health and safety precaution, and on how to conduct radiation site surveys, field sampling, clean up and final survey for site clearance.

In Malaysia, the wastes associated with TENORM are generated mostly in the tin mining and smelting, processing of minerals, and oil and gas industries. Since Malaysia has existing policy for radioactive waste management that includes activities related to TENORM, these industries are under regulatory control (Omar, et al, 2004; FNCA RWM-R003, 2005). While many countries selectively regulate NORM/TENORM, there has not been any international consensus on the regulation of NORM/TENORM (Tsurikov, 1999; IAEA, 2003).

As a result of TENORM regulation in most developed countries, the occurrence of TENORM in industrial residues or wastes has also become a growing issue because of increased waste management costs. Many developed countries have established concentration levels at which TENORM is considered "radioactive" and must be controlled or regulated. However, in the United States, TENORM is not subject to regulatory control by the U.S. Nuclear Regulatory Commission (USNRC) under the Atomic Energy Act (AEA) because it does not meet the definition of source material, such as high grade uranium and thorium

ore, special nuclear material, or byproduct material. The USNRC has not classified NORM as low-level radioactive waste (LLW) (Smith, et. al., 2003; http://www.epa.gov/radiation/tenorm/regs).

USEPA has used its authority under a number of existing environmental laws to regulate some sources of TENORM. USEPA has the authority to set standards involving exposure to NORM, but USEPA has not implemented regulations specific to NORM. As a result, NORM is left up to the individual States for regulation, hence a patchwork of non-uniform rules for NORM exist. A model regulation for NORM has been proposed by the Conference of Radiation Control Program Directors, Inc. (CRCPD) to provide a uniform basis for exemption of NORM, disposal and recycling of residues and wastes containing TENORM from industrial processes (McBurney, 2004).

The European Council Directive 6/29/EURATOM of 13 May 1996 on "laying down the basic safety standards for the protection of the health of the workers and the general public against the danger arising from ionizing radiation" has provisions for NORM under Title VII on "Significant increase in exposure due to natural radiation sources". The Directive introduces *work activities* to refer to the presence of natural radiation sources that lead to *a significant increase* in the exposure of workers or members of the public (and the material or source is not used because of its radioactive, fissile and fertile properties). Where natural radionuclides which are or have been processed because of their radioactive, fissile or fertile properties are utilized, such cases are considered *practices.*

The European Commission has issued guidance to its Member States on the practical use of the concepts of clearance and exemption to natural radiation sources (European Commission, 2001), and a proposal for harmonized approach for effluent and dose control (European Commission, 2003). Among fifteen Member States of the European Community, fourteen have enacted Title VII of the said Directive (except for Portugal as of 2002); eleven Members States have completed the initial identification of work activities; and nine Member States have applied the concept of exemption and clearance to NORM (European Commission, 2003).

The International Commission on Radiological Protection (ICRP) was expected to release the basis for the next generation of radiation protection regulations around the world that addresses stakeholders' involvement in decision-making processes regarding human and environmental risks that would better reflect the modern societal needs. The new ICRP recommendations have been completed and were finally adopted by the ICRP Main Commission in March 2007 (Pinak, et.al., 2007). According to ICRP Publication 91 (2003) the current system of radiation protection is not generally applicable to the environment, nor does it correspond to managerial needs or society's demands. The ICRP's current policy statement is increasingly being challenged because of its lack of supporting scientific evidence, transparency, and its lack of connection with society's environmental protection objectives; and that there is a necessity to formulate a more comprehensive approach to embrace the protection of both humans and other living organisms. The ICRP will include recommendations for

exclusion levels of NORM or TENORM in order to effectively define what is to be treated as radioactive and to avoid excessive regulation of radiation sources (Andersen, 2004; Clarke, 2004). While for human beings the *Reference Man* is the primary reference for dose assessments, a set of primary *reference fauna and flora* or *reference organisms* will be proposed as representatives of the biotic component of the environment for environmental protection (Clarke, 2000; Larsson and Holm, 2002; ICRP, 2003). This development will entail future revision of the International Basic Safety Standards (IBSS) (IAEA, 1996) and consequently, the relevant Parts of the Code of PNRI Regulations (CPR).

Meanwhile, the IAEA published a safety guide document entitled "Application of the concepts of exclusion, exemption and clearance" which provides values of activity concentration of natural origin in bulk amounts (>1 ton) that can be excluded from regulation (IAEA, 2005).

The Philippine Nuclear Research Institute (PNRI), formerly the Philippine Atomic Energy Commission, is mandated by the Science Act of 1958 (Republic Act 2067), an Act to Integrate, Coordinate, and Intensify Scientific and Technological Research and Development and to Foster Invention; To Provide Funds Therefore; and for Other Purposes, and Republic Act 5207 of 1968 - An Act Providing for the Licensing of Atomic Energy Facilities and Materials, Establishing the Rules on Liability for Nuclear Damage, and for Other Purposes, to regulate atomic energy facilities and radioactive materials in the Phillipines. All sets of regulations that have been issued by the PNRI according to these Acts are codified in the Code of PNRI Regulations (CPR). Part 2 of the CPR entitled

"Licensing of radioactive material" provides the definition of radioactive material as "any material which spontaneously gives off electromagnetic and/or ionizing radiation having a specific activity greater than 70 kBq/kg (0.002 uCi/g). This includes source material, special fissionable material, and atomic energy material as defined herein and (any) elsewhere in the act and code" (PNRI, 1990). The definition of radioactive material does not cover NORM. Part 3 of the CPR entitled "Standards for protection against radiation" (PNRI, 2004), which is based on the International Basic Safety Standards (IAEA, 1996) provides among others, values of annual dose limits for workers and general public, exempt quantities and clearance levels of artificial or man-made radionuclides. The concept of *work activities* has not been used yet in the International Basic Safety Standards. Thus, CPR Part 3 does not include provisions for the protection of workers and the general public from exposures to radiation emanating from NORM or TENORM.

The Philippines has various industries with raw materials, by-products and residues or wastes that may contain elevated amounts of TENORM such as in mining, fertilizer production, iron and steel production, cement production, coal-fired power plants, oil and gas extraction, and oil refining. However, there has been no comprehensive effort yet to conduct a nationwide inventory of TENORM. Like most countries in Asia, the Philippines has no specific set of regulations yet for the control of NORM/TENORM. The evaluation and inventory of NORM/TENORM in the Philippines are conducted by the PNRI on a case by case basis through specific research projects. So far, there were studies

conducted by the Philippine Nuclear Research Institute (PNRI) of NORM in coal mining, rare earth minerals and other ores, and in soils in some parts of the country. In the case of TENORM, there is an on going collaboration between PNRI and a fertilizer company to conduct measurements and assessments of TENORM in the plant, in phosphogypsum waste piles and ponds, and ground water. Radon has been measured in several coal mines in the country

In coal-fired thermal power plants where large amount of ashes are produced and utilized for various purposes, no detailed study yet on TENORM has been conducted in the Philippines. It becomes important to determine the levels of TENORM, as an initial approach, since there are now at least twelve (12) coal-fired thermal power plants operating in Luzon and the Visayas, some of which are utilizing imported coal from Australia, China, and Indonesia.

1.2 Objectives of the study

1.2.1 General objectives

The general objectives of the study are the following:

- To gather data on TENORM in ashes from coal-fired thermal power plants in the Philippines;
- To provide data for use as bases in the establishment of a national policy on the management of NORM/TENORM for the protection of the workers, general public, and the environment;
- To recommend the use of ashes based on TENORM data; and
- To help increase awareness on NORM/TENORM and their potential radiation hazards.

1.2.2 Specific objectives

The specific objectives are the following:

- To determine the activity concentration (Bq/kg) in feed coal, fly ash, bottom ash and ash pond samples from four coal-fired thermal power plants codified as Plants C, M, P, and S of the following radionuclides:
  - ^{238}U and ^{232}Th, directly using inductively coupled plasma mass spectrometry (ICP-MS);
  - ^{226}Ra, ^{228}Ra, and ^{228}Th, indirectly through their gamma emitting decay products using high purity germanium gamma spectrometer (HPGe GS) and gamma-emitting ^{40}K, directly also by HPGe GS;
- In Plant C, to do a more detailed study on the activity concentration of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K in ashes and ash pond samples in terms of the following:
  - The temporal variation (wet and dry) of activity concentration of ^{226}Ra in the ash pond;
  - The variation of activity concentration of ^{226}Ra with depth in an excavated area of the ash pond;
  - The absorbed gamma dose rate in air (nGy/h) inside and in the vicinity of a coal-fired thermal power plant; and
  - An assessment of the dose to the workers and members of the public from TENORM in the fly ash and ash pond considering the present use, and if feasible, including the future-use scenario of the ash pond after plant phase-out.

CHAPTER 2

LITERATURE SURVEY

2.1 Naturally-occurring radioactive material (NORM)

Naturally radioactive elements have been present in our environment since the earth's creation. They are ubiquitous and are found in all living organisms including man and in every environmental material. Uranium, thorium and potassium are the main elements contributing to natural radioactivity. Uranium has two primary isotopes: ^{238}U and ^{235}U. Both are radioactive and occur in nature in fixed proportion (see Table 2.1). Considering the very small proportion of natural occurrence of ^{235}U with respect to ^{238}U, it is seldom of radiological significance (EU 2003). Thorium on the other hand has only one isotope, ^{232}Th with natural abundance of 100% and has a specific activity of 4060 Bq/g. All three parent isotopes, ^{238}U, ^{235}U, ^{232}Th have very long half-lives and their decay series all terminate in stable isotopes of lead, (see Tables 2.2 and 2.3 for ^{238}U and ^{232}Th decay series, respectively).

Among the three isotopes of potassium, ^{39}K, ^{40}K and ^{41}K, only ^{40}K is radioactive that decays to ^{40}Ar, a stable isotope. ^{40}K has an isotopic abundance of 0.0117 %, has also a very long half-life of 1.277×10^9 y (Firestone, 1996), and has a specific activity of 30.3 Bq/g. It emits a beta particle with energy of 1.314 MeV (89.3%) and a gamma with energy of 1.46 MeV (10.7%). Potassium is present in most terrestrial and biological substances, e.g., it is a macronutrient for plants. The body of a 70 kg person contains about 140 g of potassium and thus

an activity of about 4000 Bq of ^{40}K (http://www.orau.org). The level of ^{40}K in man is homeostatically controlled (Lalit and Mishra, 1986, EC, 2003). Thus, when the level necessary for the person is reached, no more ^{40}K can be taken up. Because of the relatively low dose coefficient of ^{40}K, inhalation dose to the lungs can be neglected so that dose calculation for ^{40}K is limited to external exposure (European Commission, 2001). Practically, everything we eat and drink are slightly radioactive, consequently, our bodies always contain a small amount of natural radioactivity - enough to give each of us a radiation dose of between 0.2 and 0.4 mSv/y (Mitchell and Vintró, 2002).

NORM consists of ^{238}U, ^{235}U, ^{232}Th, their decay products, and ^{40}K in varying proportions. Most of these radionuclides undergo a series of transformation by spontaneously emitting energy in the form of alpha, beta and gamma with each transformation and become another radionuclide until reaching the last step. Understanding the ^{238}U, ^{235}U, and ^{232}Th decay series is important when considering exemption and clearance of wastes containing TENORM for disposal or reuse. This is because of the fact that as radioactive decay progresses, the concentration of the original radionuclide decreases while the concentration of their decay products increase, which in turn decrease as these undergo respective transformations. During exposure assessments, close attention should be given to long-lived decay products, e.g., ^{226}Ra, rather than ^{222}Rn alone, because it decays to ^{222}Rn. ^{226}Ra continues to generate ^{222}Rn during its much longer half-life.

Table 2.1 Isotopic composition of natural uranium

	^{238}U	^{235}U	^{234}U	Total
Atom (%)	99.275	0.72	0.0054	100
Weight (%)	99.284	0.711	0.0053	100
Activity (%)	48.9	2.2	48.9	100
Activity in 1g U_{nat} (Bq)	12,356	568	12,356	25,280

http://www.health.state.ny.us/nysdoh/radon/chain.htm; http://www.antenna.nl/wise/uranium/rdfi60.html

Table 2.2 Uranium series

Nuclide	Half-life [1,2]	Energy (MeV)		
		Alpha[1,2]	Beta[1,2]	Gamma[3] (No. of photons/transformation)
U-238	4.51 x 10 9 y	4.18		
Th-234	24.10 days		0.193, 0.103	0.092(0.04), 0.063(0.03)
Pa-234	1.175 min		2.31	1.0(0.015), 0.76(0.0063)
U-234	2.48 x 10^5 y	4.763		
Th-230	8.0x 10^4 y	4.685		
Ra-226	1,622 y	4.777		0.186(0.035)
Rn-222	3.825 d	5.486		
Po-218	3.05 m	5.998		
Pb-214	26.8 m		0.65	0.352(0.367), 0.295(0.189)
Bi-214	19.7 m	5.505	1.65, 3.37	0.609(0.461), 1.120(0.15), 1.765(0.158)
Po-214	1.64 x 10^{-4} s	7.680		
Tl-210	1.32 m		1.96	2.36(1), 0.783(1)0.297(1)
Pb-210	22.3 y		0.017	0.0467(0.045)
Bi-210	5.00 d		1.17	
Po-210	138.40 d	5.298		0.802(0.000012
Pb-206	Stable			

Source: [1]http://www.health.state.ny.us/nysdoh/radon/chain.htm;
[2]Cember, 1988; [3]Firestone, 1996

Table 2.3 Thorium series

Nuclide	Half-life[1,2]	Energy (MeV)		
		Alpha[1,2]	Beta[1,2]	Gamma [1,2,3] (No. of photons/transformation)
Th-232	1.39 x 109 y	3.98		
Ra-228	6.67 y		0.01	
Ac-228	6.13 h		1.11	1.59(n.v), 0.966(0.2), 0.908(0.25)
Th-228	1.91 y	5.421		0.084(0.016)
Ra-224	3.64 d	5.681		0.241(0.038)
Em-220	52 s	6.278		0.542(0.0002)
Po-216	0.158 s	6.774		
Pb-212	10.64 h		0.35, 0.59	0.239(0.43)
Bi-212	60.5 m	6.086 (35.7%)[4]	2.25 (64.1%)[4]	0.04(0.034 branch)
Tl-208	3.1 m		1.80,1.29, 1.52	0.511(0.22), 0.583(0.86), 2.615(0.997)
Pb-208	Stable			

Source: [1]http://www.nuenergy.org; [2]Cember, 1988; [3]Firestone, 1996;
[4]**European Commission, 2003**

2.2 TENORM activity concentration in typical industrial processes

T. F. Gesell and H.M. Prichard in 1974 first introduced the term technologically enhanced natural radiation (TENR) as another source of radiation exposure in addition to natural, medical, and man-made non-medical sources. They defined TENR exposures as exposures to natural sources of radiation (i.e. naturally occurring radioisotopes and cosmic radiation) which would not occur without, or would be increased by some technological activity not expressly designed to produce radiation. Included as among the TENR sources were coal, natural gas, liquefied petroleum gas, building materials, water, fertilizer, and air travel. The term TENORM apparently originates from the term TENR coined by Gesell and Prichard.

The following are examples of identified industrial processes and by-products or wastes that contain TENORM considered to be of potential radiological significance (UNSCEAR, 2000; EC, 2003):

2.2.1 Fossil fuel combustion

For electric power production the most important fossil fuels are coal, natural gas and oil. Large amounts of fly ash and bottom ash result from coal combustion that may contain TENORM.

2.2.2 Oil and gas extraction

The large volumes of production water needed for the extraction of oil and gas may contain natural radionuclides, mainly ^{226}Ra and its decay products. Scales may form as a result of precipitation at the oil/water interface. Radon decay products (^{210}Pb and ^{210}Po) may be deposited.

2.2.3 Metal ore processing

Important metal ores are tin, tantalite, and pyrochlore (e.g., niobium, iron and manganese). Most of the metals are separated using charcoal or coke. By products are furnace slag that is often used in cement production and tar coal that is used to produce electrode pitch, creosote oil, soot oil, and road tar mix.

2.2.4 Phosphate processing

This industry may be sub-divided into a) wet processing, b) thermal processing, and c) fertilizer production. The primary product is phosphoric acid. In the thermal process, the product may be

phosphorous or using nitric acid, phosphoric acid. Phosphoric acid is used in the manufacture of fertilizers. Phosphogypsum is produced as a by-product in wet phosphate processing industry, and in thermal process using cokes and silica, slag as a waste product is produced.

2.2.5 Titanium oxide pigment production

Titanium pigments include titanium dioxide and synthetic rutile. Processing wastes include cokes, ores, and SiO_2 particles and filter cake.

2.2.6 Zircon sands and rare earth processing

The processing involves sieving, washing, drying and grinding. No specific waste products are produced.

2.2.7 Building materials

Materials used in building industry that include marl, blast furnace slag, fly ash, clay for the ceramic industry, and silex for the cement industry that may contain radionuclides of radiological significance.

2.2.8 Thorium and thorium compounds

Thorium is used mainly as an additive in other products such as welding electrodes, gas mantles. It is retrieved from monazite and thorite. The enhanced activity concentration is present mainly in the primary product, metallic thorium.

2.2.9 Scrap metal

Scrap metal such as tubing, valves, and heat exchangers from various process industries may contain scales with TENORM. Since materials from nuclear industries and the uncontrolled releases of radioactive sources may add to this material, which may be recycled, the scrap metal industry is a source of radionuclide releases into the environment.

The concentrations of NORM in raw materials or ores vary worldwide depending on the locations where these materials are found and consequently the associated TENORM when the raw materials are processed. Table 2.4 presents a comparison of some worldwide typical concentrations of natural radionuclides in raw materials, products or wastes of processing industries (UNSCEAR, 2000). For comparison, the summary of the levels of NORM/TENORM in Philippine soils and volcanic ash are presented in Table 2.5.

Table 2.4 Examples of activity concentrations of NORM/TENORM in raw, produced material and in residues or wastes of processing industries (UNSCEAR, 2000)

Material	Typical concentration in ore/raw material (Bq/kg)		Typical concentration in product or wastes (Bq/kg)	
	^{238}U-series	^{232}Th-series	^{238}U-series	^{232}Th-series
Natural gas Oil	340 kBq/m^3 (^{222}Rn)		1,000-1,000,000 (pipe scale) 8,000-42,000 Bq/m^3 (production water) 33600-65500 (pipe scale)[1] 434,000 (max in well head scale, Malaysia)[2]	479,000 ((max in well head scale)[2]
Coal	10-250; 2 (Philippines)[3] 15-67 (China)[4] 10-50 (Australia)[5]	10-250 5-50 (Australia)[5]	20-40 (cokes) 100-300 (coal tar) 200 fly and bottom ash; 400 (fly dust) 50-200 (Australia)[5]	200 (fly dust) 50-190 (Australia)[5]
Monazite (rare earth)	6000-40000	8000-300000	450,000 (^{226}Ra in sulfate precipitate)	3,000,000 ^{228}Ra in sulfate precipitate
Artificial fertilizer			300-3000	8-40
Phosphate	200-1500	20 (Florida ore)	Phosphogypsum: 900-1300 (Central Florida ore); 250-420 (Philippines)[6] 22-695 (Brazil)[7]	20 (phosphorous slag) 7-175 (Brazil)[7]
Zirconium sand	200-74000	400-40000		
Ilmenite	2300	1200		
Cement Industry:				
Marl	22	3	50-110 (cement) 20 (silex)	30-100 (cement) 3 (silex)
Schist	40	56		
Portland clinker	80	50		
Rutile	3800	560		
Cement[8]	35-68	20-50	50 (cement brick); 60 (cement plaster)	30 (cement brick); 50 (cement plaster)

[1]Hamilton, et. al. (2004); [2]Omar, et. al., (2004); [3]Dela Rosa, et. al. (1984); [4]Yang (2007); [5]FNCA RWM-R003; [6]Nazarea, et.al.,2004; [7]Mazilli, et.al,(1999); [8]Xinwei (2005)

Table 2.5 NORM levels in Philippine soil and volcanic ash

Sampling locations	Concentration (Bq/kg wet weight)		
	^{238}U series	^{232}Th series	^{40}K
Soil			
Nasugbu, Batangas	23.4	24.4	385.8
Pagsanjan, Laguna	27.3	49.2	484.8
Bagiuo City	37.2	15.7	224.6
Linapacan Island, Palawan	30.1	24.1	246.0
Volcanic ash (Mt. Pinatubo eruption) Pampanga, Zambales and Tarlac	12.6	14.0	330.2

Duran, et al. (1992)

2.3 Coal-fired thermal power plants in the Philippines and coal consumption

The Philippines is largely a coal consuming country with coal having the highest contribution to the power generation mix at 27% in 2005. Local demand for coal is not limited to power generation. The cement industry utilized 20% of the country's coal supply in 2005 and 1% went to other industries such as alcohol, sinter, rubber boots, paper and chemical manufacturing, fertilizer production and smelting. The local coal production industry has been robust in the past three years, from a historical yearly average production of 1.5 million metric tons (MMT) to 3 MMT. Increased production is expected in the near future as new contracts get to full blown production, and exploration contracts convert to production agreements. To date, there are thirty six coal operating contracts,

sixteen of which are under exploration stage to verify the potential of the coal fields, and forty three small-scale coal mining operators (http://www.doe.gov.ph).

The 2004-2013 Philippine Energy Plan (PEP) Update provides some perspective of indigenous coal production. In Luzon, it is projected to reach 0.57 MMT in 2008 and 1.19 MMT in 2013 from the 2004 level of 0.19 MMT. Albay will be the sole producer from 2004 to 2005 while Isabela and Cagayan will start producing in 2006 and 2008, respectively. In the Visayas, coal production will increase from 1.87 MMT in 2004 to 2.33 MMT in 2008 and 3.54 MMT in 2013 with Semirara contributing the biggest share. On the other hand, Mindanao coal output is foreseen to jump from 0.14 MMT in 2004 to 0.45 MMT in 2008 and 2.31 MMT in 2013 as supported by additional exploration and development activities of PNOC- Exploration Corporation (EC) in Marihatag and Surigao del Sur (http://www.doe.gov.ph). This provides us a picture on the future use of coal for power generation – it is going to stay and will continue to increase.

About two-thirds of the country's coal supply is imported mainly from Indonesia, China, and Australia and the remaining one-third is produced by the coal-mining subsidiary of the Philippine National Oil Company (PNOC) (http://www.eia.doe.gov). Based on the total consumption of fossil fuels for energy production in 1999 of 21.58 MMT, coal and coal products was only 3.7 MMT, which constituted only about 18 % of the total fossil fuel consumption (http://earthtrends.wri.org). About 82% of the fossil fuel consumption was on crude oil and natural gas. Based on the Philippine Energy Plan (PEP) for 2004-2013, it is aimed to have an average 50% self-sufficiency level for primary energy

supply in the next ten years to reach about 58% by 2013, the details of which are presented in Table 2.6.

Table 2.6 Primary energy supply (%) according to Philippine Energy Plan (PEP)

Energy supply	2004	2013
Imported oil	36	30
Imported coal	8	8
Local coal	3	6
Local oil	2	3
Natural gas	7	11
Hydro	5	5
Geothermal	8	8
Biomass, solar and wind	31	25
Self-sufficiency	55.5	58.2

The consumption of coal in the Philippines for electrical generation is mainly shared by twelve (12) coal-fired power plants: nine (9) are located in Luzon and the remaining three (3) are located in the Visayas. Table 2.7 shows the profile of coal-fired thermal power plants in the Philippines.

Table 2.7 Coal-fired thermal power plants in the Philippines

PLANT	POWER (MW)	LOCATION	PROPONENT	OWNER	YEAR COMMISSIONED
Pagbilao Unit 1	367.5	Pagbilao, Quezon)	Mirant (Pagbilao)	NPC-IPP	3/7/96
Pagbilao Unit 2	367.5	Pagbilao, Quezon	Mirant) (Pagbilao	NPC-IPP	5/26/96
Calaca 1	300.00	Calaca, Batangas	Far East Livingston (Singapore)	NPC	9/5/84
Calaca 2	350.00	Calaca, Batangas	Far East Livingston (Singapore	NPC	6/5/95
Masinloc I	300.00	Masinloc, Zambales	NPC	NPC	6/18/98
Masinloc II	300.00	Masinloc, Zambales	NPC	NPC	12/1/98
Sual 1	609.00	Sual, Pangasinan	Mirant (Sual)	NPC-IPP	10/23/99
Sual 11	609.00	Sual, Pangasinan	Mirant, Sual	NPC-IPP	10/5/99
Quezon Power	511.00	Mauban, Quezon	Quezon Power Phils.	Non-NPC	5/1/00
ACMDC (Toledo Power)	80.00	Toledo City, Cebu	Atlas Consolidated Mining	NPC-IPP	2/1/93
Cebu TPP1 (Salcon)	52.50	Naga, Cebu	Salcon Phils.	NPC-IPP	4/1/94
Cebu TPP2 (Salcon)	56.80	Naga, Cebu	Salcon Phils.	NPC-IPP	4/1/94

Source: http://www.doe.gov.ph

In 2002, the production of coal in the Philippines is 1.7 MMT (bituminous-1.68MMT; lignite - 0.02 MMT) and consumption at 5.2 MMT. The consumption of coal is not by power plants alone but includes cement factories and other coal-powered industries.

Tables 2.8 and 2.9 present the top five countries and world total consumption and production, respectively (http://www.eia.doe.gov).

Table 2.8 Top five countries based on coal consumption (MMT), 2002

	Production	Consumption
China	1,380	1,290
USA	992	997
India	356	382
Germany	210	248
Russia	235	208

Table 2.9 World coal production and consumption (MMT), 2002

	Production	Consumption
North America	1,070	1,045
Central and South America	58	33
Western Europe	445	646
Eastern Europe and Former USSR	693	639
Africa	229	169
Asia and Oceania	2,268	2,231
World total	**4,464**	**4,763**

The above data provide us some basis as to which country contributes the highest discharges of radioactivity (TENORM), toxic trace elements, SO_2, NO_x, and CO_2 into the environment. Many people are not aware that coal burning releases radioactivity and toxic metals. W. Cunningham (2001) predicts that the ultimate limit to the use of coal as a fuel may not be the amount of radioactivity or toxic elements released into the environment, but the amount of CO_2 released into the atmosphere that is a major contributor to global warming.

2.4 *Characteristics of coal and coal combustion by-products*

Coal is a fossilized plant material preserved by burial in sediments and altered by geological forces that compact and condense it into carbon-rich fuel. Most coal was laid down during the Carboniferous period (286 million to 360 million years ago) when the earth's climate was warmer and wetter than it is now

(Cunningham, W. P., 2001). Because coal takes a long time to form, it is essentially a nonrenewable resource. The formation of coal is in stages. When the plants died and decayed in swamps, they became layers of peat. Then as sediment covered the layers of peat and built up, it put pressure upon the peat. As temperature and pressure increased, peat was transformed into lignite - lowest ranked coal, soft, with color of dark black to various shades of brown. Then came sub-bituminous coal - lower ranked and softer than bituminous coal and with higher moisture content. Higher ranked is bituminous coal - generally low in moisture and has small amount of hydrogen and oxygen, ideal for metallurgical or coking and thermal uses. Finally anthracite - the top-ranked coal because it has the highest carbon content , therefore, the most heat value and the hardest of all coals (http://www.coal.ca). Lignite and sub-bituminous coals may have been formed less than 100 million years ago. The coals in Turkey which are generally low rank (lignite and sub-bituminous) have ages that range from 1.7-55 million years (Palmer, et al, 2004).

Coal is composed of such a complex mixture of materials, that it can be quite different from one deposit to another. Differences in coal deposits came from variations in the original plant materials that formed the deposit and in the process that created it. Different kinds of vegetation and variations in the amount of minerals influenced the composition of coal. Higher pressures and temperatures and the length of time of its formation also affect the quality of coal deposit. Coal is generally characterized by its contents (weight percent) of moisture, ash yield (non-combustible inorganic matter), volatile matter, fixed

carbon, total sulfur, sulfur in the ash, combustible sulfur, and gross calorific values (in calories/g or joule/kg) on as-received moisture basis. The as-received moisture values can be used to estimate the rank of coal (Palmer, et al., 2004). So, coal is chemically a very complex material and by no means pure carbon. As an example, a chemical formula for Illinois No.6 coal, a type of bituminous coal, is $C_{100}H_{85}S_{2.1}N_{1.5}O_{9.5}$ (Manahan, S. E., 1994).

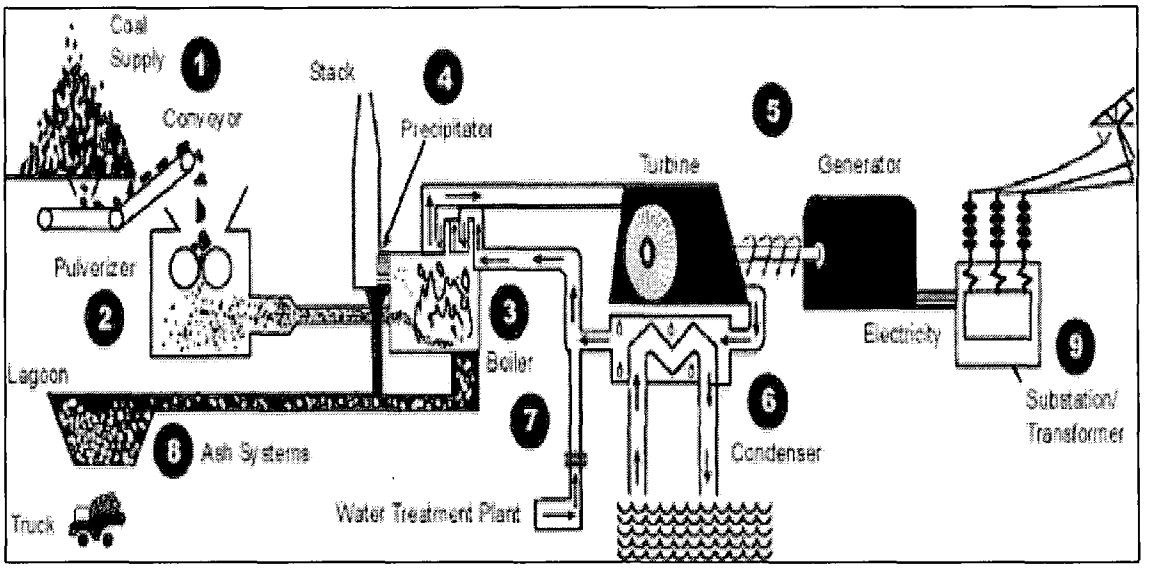
Among the fossil fuels (coal, natural gas, and petroleum) coal is the most impure. Coal consists of major elements other than (C, H, S, N, and O) such as Na, Mg, Al, Si, K, Ca, Ti, Fe and trace elements such as As, B, Be, Bi, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Ga, Gd, Ge, Hf, Hg, Ho, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, P, Pb, Rb, Sb, Sc, V, Cr, Sc, Se, Sm, Sr, Tb, Th, Tm, U, V, W, Y, Zn, and Zr (Pires and Querol, 2004). The major elements of coal can be responsible for the adverse coal utilization potential in power plants such as slagging (refers to ash that melts and fuses to boiler walls), abrasion (erosion or wearing away), and fouling (accumulation of sintered ash on boiler tubes in the convective passes of coal boilers), while trace elements are important in terms of environmental, economic, and technological behavior of coals and combustion by-products and their effects on human health (Palmer, et al., 2004). While coal consists largely of organic matter, it is the inorganic matter in coal—minerals and trace elements—that have been cited as possible causes of health, environmental, and technological problems associated with its use (IAEA, 2003). Lately, the CO_2 emitted from the burning coal has been tagged to cause global warming.

Humans however, have benefited from the use of coal for over 4,000 years now (http://www.coal.ca). The Chinese were the first to use coal as a fuel in about 1100 BC (Kruszelnicki, 2006). The use of coal, in all likelihood will continue for as long as there is need for electricity, steel and for other industrial and domestic purposes. In the Philippines, about 27% of electricity generation is fueled with coal. When coal is burned to generate electricity, it leaves behind residues or wastes, i.e., bottom and fly ash that can be utilized as products or raw materials primarily in the construction industry.

A simplified schematic diagram of how a coal-fired thermal power plant works is shown Figure 2.1.

1 Coal supply - Coal is unloaded from barges to coal storage yard. The coal is delivered by a conveyor belt to the crusher, then to the coal silos in the power plant building.

2 Pulverizer -The coal is then fed to the pulverizers where it is crushed to a fine (talcum-like) powder, mixed with air and blown into the boiler (3) or furnace for combustion.



Source: http://www.canadiancleanpowercoalition.com

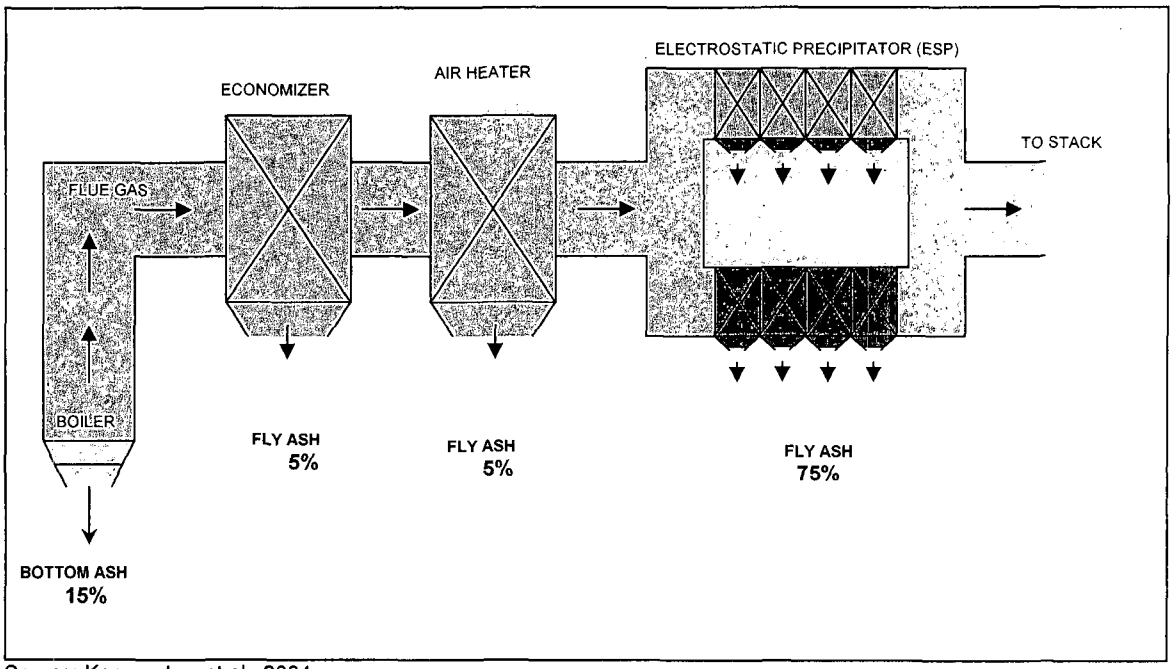
Figure 2.1 Schematic diagram of how coal-fired thermal power plant works

3 Boiler - The coal-air mixture ignites instantly in the boiler. Millions of liters of purified water are pumped through tubes inside the boiler. Intense heat from the burning coal turns the purified water in the boiler tubes into steam, which spins the turbine (5) to generate electricity.

4 Electrostatic precipitator (ESP), stack – As coal is burned, heavy and light ash particles (the noncombustible mineral content of coal) with radioactive and toxic trace elements are produced as by-products. About 15% of coal remained as ash. The heavy ash particles go down to the bottom of the boiler and are called bottom ash (or slag), while the light particles rise with the flue gas as fly ash (about 75% of ash) as shown in Figure 2.2. The degree of partitioning of the trace elements between the bottom and fly ashes depends mostly on their geochemical association and volatility. The ESP removes fly ash particulates by transferring charges to the particulates and then collecting them. Modern ESP

collect about 99% of the fly ash while the uncollected very fine fly ash together with the gaseous by-products such as radon, carbon dioxide, sulfur dioxide, and nitrogen oxides, volatile trace elements such as mercury and lead, are finally released and dispersed into the atmosphere via high smoke stacks. Some power plants employ flue-gas desulfurization (FGD) to further reduce the release of sulfur into the atmosphere with gypsum as by-product.

5 Ash system, ash lagoon or pond. The bottom ash is collected during cleaning of the boiler and transferred through slurry pipes to the ash lagoon or pond. The collected fly ash is purchased by cement and construction companies for various purposes and the remainder is also brought to the ash pond with the bottom ash (http://www.canadiancleanpowercoalition.com; Daniels W. L, et al, 2000; Cunningham, W. P., 2001).



Source: Karangelos, et al., 2004

Figure 2.2 Example of ash discharges from a coal-fired power plant

Fly and bottom ashes are characterized by relatively high contents of SiO_2 and Al_2O_3, and low content of alkaline oxides as in the case of Brazilian and European coals. These characteristics influence leaching processes and the potential uses of these ashes. The main components of the fly ash are the glassy aluminum-silicate matrix, mullite, quartz and magnetite. Bottom ash has similar composition with a higher content of magnetite (Pires and Querol, 2004). Fly ash generally has a silt loam texture with 65-90% of the particles having diameters of less than 10 μm. Ash from bituminous coal is usually finer than that produced by the burning of lignite. In general, fly ash has low hydraulic conductivity, bulk density (1.01-1.43 g/cm^3), and specific gravity (1.6-3.1 g/cm^3). Some fly ash materials, particularly those from sub-bituminous coals, can have a cementing effect (pozzolonic activity) when added to moist soils which is controlled primarily by the CaO content of the ash. The American Society for Testing Materials (ASTM) defines two classes of pozzolanic fly ash based mainly on CaO content, Class C (> 20% CaO) and Class F (< 20% CaO). Both classes of fly ash are pozzolonic, meaning they form cements when exposed to water and an activator. For Class F ashes, the activator is usually added as CaO from Portland cement. Class C fly ash contains enough CaO that it is self-cementing. Class C ashes are generated from burning lignite and sub-bituminous coal whereas ash generated from bituminous and anthracite coals may meet Class F standards (Daniels, et al, 2000).

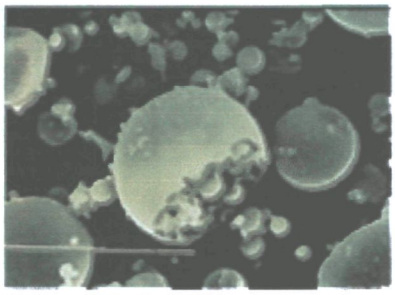
In a study of 11 fly ashes from various U.S. power plants, Daniels, et al (2000) reported that the major components of ash are Al, Fe and Si, with smaller

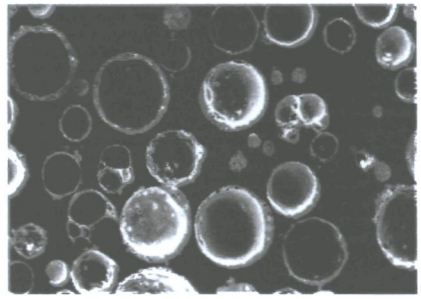
concentrations of Ca, K, Na, Ti, and S. Several ashes have high Ca concentrations because of surface CaO deposits. Ash from bituminous coals is generally higher in Fe, K and S, and lower in Mg and Ca compared with ash from sub-bituminous and lignite. Fly ashes contain varying amounts of numerous trace elements. Many of the trace elements present in fly ash show a definite concentration trend with decreasing particle size. The relative distribution of trace elements on the surface and in the internal matrix of fly ash particles has important environmental implications. Surface deposited metals may be easily mobilized in leaching waters, while metals in the silica matrix are released only after periods of extended weathering (Daniels WL, et al, 2000).

In fly ash, uranium is reported to be more concentrated in the finer sized particles with preferential location within the glassy component of fly ash particles. If during coal combustion some uranium is concentrated on ash surfaces as a condensate, then this surface-bound uranium is potentially more susceptible to leaching. However, there was no obvious evidence of surface enrichment of uranium found in the hundreds of fly ash particles examined by the United States Geological Survey (USGS) researchers based on the use of fission-track radiography. This is a sophisticated technique for observing the distribution of uranium in particles of about 1 μm diameter (http://greenwood.cr.usgs.gov).

Figure 2.3 (a) and (b) show the scanning electron micrographs of fly ash particles that are spherical, silt-sized, amorphous mineral structures comprised primarily of aluminum and silica oxides, and cenospheres (hollow glassy

spheres), respectively. Figure 2.4 is a photograph of a hollow glassy sphere of fly ash and its corresponding fission track image. The diameter of this relatively large glassy sphere is approximately 100 μm. The distribution and concentration of uranium are indicated by fission tracks, which appear as dark linear features in the radiograph.

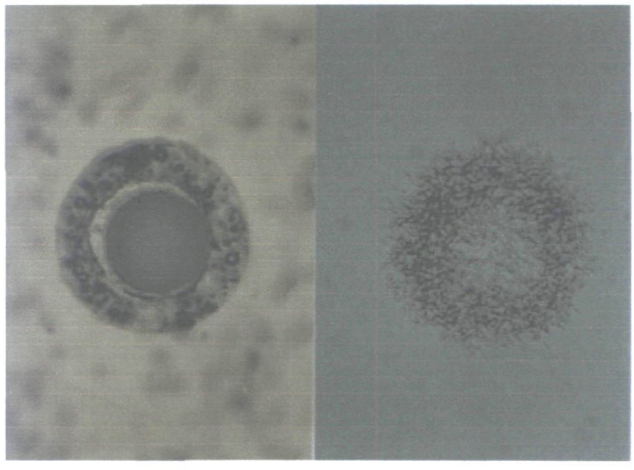




Sources: http://geocities.com;
http://www.we-energies.com/environment/

(a) (b)

Figure 2.3 (a) Scanning electron micrograph of fly ash particles (b) cenospheres (hollow spheres)



Source: http://greenwood.cr.usgs.gov/energy

Figure 2. 4 Photograph (left) of a hollow glassy fly ash particle and (right) ^{238}U fission track radiograph

2.5 Post-combustion partitioning of major and trace elements

Klien, et al. (1975) reported three classes of partitioning of thirty-seven major and trace elements in bottom and fly ashes from large cyclone-fed power plant installed with high efficiency ESP located in the U.S.A. U and Th that are the object of this study are among the trace elements that are classified.

Class1 (Twenty elements): Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, *Th*, and Ti – are readily incorporated into the slag or bottom ash. These elements are not volatilized and are partitioned about equally between the inlet fly ash and slag.

Class II (Nine elements): As, Cd, Cu, Ga, Pb, Sb, Se, W, and Zn – are poorly incorporated into the slag. These elements are concentrated in the inlet fly ash compared to the slag. These elements volatilized on combustion and are preferentially depleted from the slag (volatility effect) and concentrated on the outlet fly ash compared to the inlet fly ash (particle size effect).

Class III: Hg, Cl, and Br remain essentially in the gas phase.

The other elements – Cr, Cs, Na, Ni, *U*, and V – cannot be definitely assigned to a class but appear to be intermediate between Class I and II. The ESP is less efficient in removing the elements that concentrate on the very fine particulates and are essentially without effect on such volatiles as Hg and the gaseous by-products, thus discharged into the atmosphere through the stack (Klein, et.al. 1975).

According to Klein, et al. (1975), it was Natusch, *et al.* (1974) who proposed volatilization-condensation or adsorption mechanism to account for the

size- concentration behavior. Those elements that accumulate on the smaller fly ash particles are assumed to be volatile at the temperature of combustion (1300-1600 ^{0}C); as the flue gas cools, the volatile elements condense or adsorb on the fly ash. Those elements that are not volatile in the combustion zone form the fly ash particles upon which the volatile elements condense. The elements that are enriched on the smaller particles usually have boiling points comparable to or less than the temperature of the combustion zone.

Coles, et al. (1979) reported the concentrations of 42 major and trace elements in four size fractions (with mass median diameters of 2.4, 3.7, 6.0 and 4.5 μm) of stack fly ash from a large US western coal-fired power plant. Based on the enrichments relative to coal as a function of fly-ash particle size, the elements are grouped into three classes:

Group 1: Elements that show little or no enrichment in the small particle fraction (Al. Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, *Th*, Ti, and the rare earth elements: Ce, Dy, Eu, La, Sm, Tb, and Yb). Group I elements are classified as lithophiles that are associated with aluminosilicate minerals and are expected to be distributed in the aluminosilicate ash matrix of the fly ash.

Group II: Elements whose enrichments increase with decreasing particle size (As, Cd, Ga, Mo, Pb, Sb, Se, W, and Sn). Group II elements are classified as chalcophiles and are associated with sulfide minerals, thus they are mostly volatilized during combustion and later condense onto the smaller fly ash particles.

Group III: Elements whose behavior is intermediate to that of elements in Groups I and II (Ba, Be, Co, Cr, Cu, Ni, Sr, *U*, and V). All Group III elements show enrichment on smaller particles but the behavior of these elements is not easily understood as those of Group II elements. Among the Group III elements, U was reported to show the greatest small particle enrichment. *Coles, et al* (1978) suggest that the small particle enrichment of U is the result of its bimodal residence in coal, as uraninite (UO_2,) – organic association, and coffinite [$U(SIO_4)_{1-x}(OH)_{4x}$] – inorganic association. The characteristics of U during combustion process are determined by the conditions of the boiler as well as its physical and chemical form in the feed coal. In an oxidizing combustion environment of power plant boilers with a temperature range of 1500-1600 ^{0}C, volatile species of UO_3 are expected to be formed. U that is originally incorporated with a silicate, i.e. coffinite, may be incorporated into a silica melt. Thus, the bimodal existence of U in coal can simultaneously give rise to both volatile and nonvolatile species.

Coles, et al. (1978) provide the following scenario to describe the behavior of NORM/TENORM throughout coal deposition, combustion, and emission;

- Associated with the accumulation of organic matter is a significant fraction of clay minerals, silt, and other inorganic sedimentary material containing alumino-silicate minerals containing ^{40}K, ^{232}Th and a portion of the silicate-associated U that will later comprise the coal fly ash and bottom ash.

- The organic accumulation environment ends and a deposition environment prevails which buries the organic matter. Coal metamorphism then occurs.
- Ground and surface waters containing U as soluble uranyl carbonate salts and varying amounts of soluble silica, penetrate down through the overburden coal.
- U is absorbed by coal and, depending on the silica content of water, is reduced to uraninite or coffinite.
- Coal is mined, cleaned, pulverized, and fed into the furnace for power production. Much of the alumino-silicate minerals (mostly clay) form a melt and drop at the bottom of the boiler as bottom ash or slag. Radioactive gases (^{222}Rn and ^{220}Rn) and highly volatile radionuclides (^{210}Pb and ^{210}Po) continue along with the flue gases and fly ash to the ESP. Much of the U that was mineralized as coffinite remains with the bottom ash while the U that is dispersed in the coal as uraninite becomes volatile as UO_3 species and continues along with the gases and fly ash.
- As the flue line becomes cooler, U preferentially condenses first then followed by Pb and Po on the finer fly ash particles because of their high surface to mass ratio.
- The ESP collects most of the particulate mass. The uncollected finer particles enriched in ^{210}Pb and ^{210}Pb, moderately enriched with ^{238}U

and slightly enriched with ^{226}Ra, ^{228}Ra, and ^{228}Th continue up the stack with the gases and discharged into the atmosphere.

- The mineralogical or chemical form in which the radionuclides or trace elements exist in the coal has important effect on their subsequent combustion chemistry and emission characteristics.

Th, and to some extent U, is normally associated with the very chemically resistant mineral zircon. Zircon is an ubiquitous mineral in many common rocks, does not weather easily and is common in sedimentary environments. Th in the coal may be deposited as zircon along with the other silicate-based minerals which make up the ash after the coal is burned. Submicron mineral grains incorporated with Th may be carried by the gases after combustion and follow the course of the fly ash. Thus, Th can also be found in the fly ash if it exists in the coal as submicron particles (Coles, et al. 1978).

The results of the work by Pires and Querol (2004) on the characterization of Candiota (South Brazil) coal and combustion by-products include classification of elements into three groups based on the analysis of their concentrations in fly and bottom ashes, and enrichment or depletions of these concentrations compared to that in coal.

Group 1 (volatile elements with subsequent condensation): As. B, Bi, Cd, Ga, Ge, Mo, Pb, S, Sb, Sn, Tl, and Zn;

Group II (elements enriched in bottom ash): Ca, Fe, Mn, P, Ti, and Zr;

Group III (low volatile elements with similar concentration in fly ash and bottom ashes): Al , Ba, Be, Co, Cr, Cs, Hf, K, Li, Mg, Na, Ni, Rb, Sr, Th, U, W, Y

and most rare earth elements (REE). They observed that the partitioning of the trace elements in the fly and bottom ashes is not very strong in Brazilian power plants (Presidente Medici Power Plant or UTPM-446 MW). They attributed this to the low combustion efficiency of the plant due to the high mineral matter contents of Candiota coal (~50%). U belongs to the intermediate elements based on the classification of Klein, et al. (1975) but falls under a different classification by Pires and Querol (2004), while the classification of K and Th is consistent (similar concentration in fly and bottom ashes) in both studies.

2.6 Potential risks of NORM/TENORM from coal-fired thermal power plants and recommendations to regulate for radiation protection

Ambient radiation levels in some geographical regions where many people live are much higher than the world average natural radiation dose of 2.4 mSv/y, e.g. Guarapari Beach, Brazil up to 790 mSv/y; Ramsar, Iran, up to 700 mSv/y; Southwest France, up to 88 mSv/y; Kerala Beach, India, up to 35 mSv/y (Cuttler, 2004). Only about 15% of the human exposure to ionizing radiation comes from artificial sources. The remaining 85% of the annual dose is the result of exposure to natural radiation-cosmic rays, natural radioactivity in the food we eat, air we breathe, water we drink, and soil we live on, and due to technologically enhancement of natural radioactivity (Tsurikov, 1999). Radiation from NORM/TENORM or artificial sources affect the living cells in the same way, so health effects are not expected to be any different for the same dose from either source, both short term or long term.

According to ICRP (1990), the significance of an exposure (the process of being exposed to radiation or radioactive material) is determined by the resulting doses. Ionizing radiation causes both *deterministic and stochastic effects* in irradiated tissue. *Stochastic effects,* which are random or statistical in nature, are believed to occur even at lowest doses and therefore must be taken into account at all doses. *Deterministic effects* result from the killing of cells above some level of dose or threshold for clinical effect. Stochastic effects may result when an irradiated cell is modified rather than killed. Modified somatic cells may subsequently, after long delay, develop into a cancer. Stochastic effects have no threshold dose and the severity of the cancer is not affected by the dose. The ICRP (1990) uses the term *detriment* (instead of risk) to represent the combination of the probability of occurrence of a harmful health effect and a judgment of the severity of the effect. The principal components of detriment are the following stochastic quantities: (1) the probability of attributable fatal cancer (leukemia, breast, colon, lung, stomach, etc); (2) the weighted probability of attributable non-fatal cancer; (3) the weighted probability of severe hereditary effects; and (4) the length of time lost if the harm occurs. Table 2.10 presents the nominal probability coefficients for stochastic effects.

Table 2.10 Nominal probability coefficients for stochastic effects

	Detriment (10^{-2}/Sv)			
Exposed population	**Fatal cancer**	**Non-fatal cancer**	**Severe hereditary effects**	**Total**
Adult workers	4.0	0.8	0.8	5.6
Whole population	5.0	1.0	1.3	7.3

The values of committed effective dose coefficient of the radionuclides in ^{238}U series (IBSS, 1996) that are useful in calculating the dose received by the organs of interest in Sv from the inhalation and ingestion of 1 Bq of the radionuclide are presented in Table 2.11. The table shows that the higher the values of dose coefficients for inhalation and ingestion of the radionuclide, the higher the dose, hence, the risk to the exposed individual. The values of the committed effective dose coefficients also indicate the relative hazard of the radionuclide.

Table 2.11 *Committed effective dose coefficient per unit intake of radionuclide in the ^{238}U series via inhalation and ingestion for members of the public, age > 17 years old (Sv/Bq)*

Radionuclide	Inhalation			Ingestion
	Fast	Moderate	Slow	
^{238}U	5.0×10^{-7}	2.9×10^{-6}	8.0×10^{-6}	4.5×10^{-8}
^{234}Th	2.5×10^{-9}	6.6×10^{-9}	7.7×10^{-9}	3.4×10^{-9}
^{234}Pa	-	-	-	5.1×10^{-10}
^{234}U	2.53×10^{-7}	1.99×10^{-6}	3.58×10^{-5}	4.9×10^{-8}
^{230}Th	1.0×10^{-4}	4.3×10^{-5}	1.4×10^{-5}	2.1×10^{-7}
^{226}Ra	3.6×10^{-7}	3.5×10^{-6}	9.5×10^{-6}	2.8×10^{-7}
^{218}Po				
^{214}Pb	2.8×10^{-9}	1.4×10^{-8}	1.5×10^{-8}	1.4×10^{-10}
^{214}Bi	7.1×10^{-9}	1.4×10^{-9}		1.1×10^{-10}
^{210}Pb	9.0×10^{-7}	1.1×10^{-6}	5.6×10^{-6}	6.9×10^{-7}
^{210}Bi	1.1×10^{-9}	9.3×10^{-8}		1.3×10^{-9}
^{210}Po	6.1×10^{-7}	3.30×10^{-6}	4.3×10^{-6}	1.2×10^{-6}

For the detailed discussion, refer to IBSS (IAEA, 1996)
The period for calculating the committed dose for intakes is 50 years for adults.

The important routes of TENORM exposures of workers in coal-fired thermal power plants are normally external gamma radiation and inhalation of fine ash during periodic cleaning and maintenance of boilers and ESP systems, working near fly ash silos or storage buildings, working in ash ponds or landfills,

and during transport of ash to landfills, construction sites, and mills where the ash is processed for the preparation of concrete. Exposures to the members of the public may arise from the use of ash by-products, from atmospheric discharges of ash via stacks, from disposal of ash, living in residences near ash ponds, or living in houses with building materials mixed with fly ash. The important routes of radiation exposure from TENORM of the public are external gamma radiation, inhalation and ingestion.

Recognition that some raw materials inherently have high natural radionuclide contents, and that the processing of these raw materials modify their chemical or physical forms which results in the enhancement of the radionuclide contents rendering them as TENORM, which may lead to enhanced exposures of workers and the public, the IAEA published in 2004 Safety Guide No.RS-G-1.7 on "Applications of the concepts of exclusion, exemption, and clearance". The objective of the this safety guide publication is to provide guidance to national authorities, including regulatory bodies, and operating organizations on the application of the concepts of exclusion, exemption and clearance as recommended in the International Basic Safety Standards (IAEA, 1996). The Safety Guide is important to this study because it includes specific values of activity concentration not only for radionuclides of artificial origin but also for radionuclides of natural origin. The derived values of activity concentration are for bulk amounts (more than 1 ton) of material that can be used as basis by regulatory bodies to exempt material with NORM/TENORM from regulatory control. As a first step, the activity concentration of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, and

^{40}K determined in this study will be compared with the values as published in the IAEA Safety Guide No. RS-G-1.7. If the results of the determination of activity concentration of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, and ^{40}K in the ash samples from coal-fired thermal power plants are below the values as published in the said Safety Guide, the last specific objective of this dissertation to perform dose assessments becomes unwarranted.

The values of activity concentration for radionuclides of natural origin as provided in IAEA Safety Guide No.RS-G-1.7 (IAEA, 2004) were determined on the basis of consideration of the upper end of the worldwide distribution of activity concentrations in soil with the intention to exclude from regulation virtually all soils but not to exclude from regulations ores, mineral sands, industrial residues and wastes which are recognized as having significant activity concentrations. The activity concentration values were chosen as the optimum boundary between, on the one hand, the ubiquitous unmodified soil concentrations and, on the other hand, activity concentrations in ores, mineral sands, industrial residues and wastes. The derivation of activity concentration levels for naturally occurring radionuclides was based on a methodology that placed greater emphasis on optimization of protection and regulatory resources.

The values of activity concentration for radionuclides of natural origin are given in Table 2.12.

Table 2.12 Values of activity concentration for radionuclides of natural origin that may be used for exclusion, exemption and clearance

Radionuclide	Activity concentration (Bq/kg)
^{40}K	10,000
All other radionuclides of natural origin	1,000

The above values are valid for the natural decay chains in secular equilibrium, i.e. those decay chains headed by ^{238}U, ^{235}U or ^{232}Th, with the value to be applied to the parent of the decay chain, The values can also be used individually for each decay product in the chains or for the head of subsets of the chains, such as the subset with ^{226}Ra as its parent.

The doses to individuals as a consequence of the above activity concentrations are unlikely to exceed 1 mSv in a year, excluding the doses incurred from exposures to radon. These levels are around a factor of 20 higher than the population weighted average activity concentrations of natural radionuclides in soil and are therefore unlikely to incur unwarranted regulatory burden (IAEA, 2005).

The values of activity concentration (for radionuclides of artificial and natural origin) provided in the Safety Guide do not apply to

- Foodstuffs, drinking water, and animal feed. The World Health Organization provides the relevant guidelines. (Guidelines for drinking water quality, Vol. 1: Recommendations, WHO, Geneva, 1993 and addendum to Vol. 1, 1998 and Joint Food and Agriculture organization of the United Nations/World Health Organization Food Standards

Programme, Codex Alimentarius Commission, Codex Alimentarius, Vol.1, Section 6.1 (1991)

- Radon in air, as action levels for the concentration of radon in air are provided for in the IBSS (1996);
- ^{40}K in the body, which is excluded from the BSS; and
- Material in transport in accordance with the IAEA Transport Regulations (2004).

The European Commission (EC) was three years ahead of IAEA in publishing its guidance document to its fifteen Member States on the application of the concepts of exemption and clearance to sources of natural radiation, Radiation Protection (RP) 122, Practical use of the concepts of clearance and exemption, Part II – Application of the concepts of exemption and clearance to natural radiation sources (EC, 2001). RP 122 provides general clearance and exemption levels that are valid for large classes of materials and for all possible destinations. The radiological model used to establish the general clearance and exemption levels account for all pathways of radiation exposure. The enveloping scenarios and parameter values are developed based on expert opinion for the combined exposure paths: ingestion, inhalation, and external gamma radiation. In each case, the most restrictive of the enveloping scenarios is adopted and the activity concentration that gives a dose of 300 μSv/y is used to define the radionuclide-specific clearance and exemption level. According to RP 122, below the exemption and clearance levels there are no more constraints.

This publication focuses on radiation protection. In the case of very low level radioactive materials, health aspects other than radiation may be prominent, e.g., chemical toxicity of industrial waste. Management of the materials should comply with specific relevant regulations. Chemical risk may well be above the radiological risk. In cases, where other kinds of health risk are present, the choice of appropriate option of waste management should be made by balancing the severity of the different types of risks, radioactive or chemical, that are involved.

The scope of the radiological assessment in RP 122 covers the following:

- Workers and members of the general public coming into contact with NORM or TENORM (TENORM is also referred as NORM in RP 122);
- Development of exemption/clearance levels based on the radiological assessment of relevant exposure pathways of NORM;
- Calculations based on the dose criterion for the workers and members of the general public of 0.3 mSv/y (about 3 times lower than the dose criterion of BSS of 1 mSv/y);
- Scenarios based on common recycling and disposal options for industrial NORM residues or wastes; and
- Distinction between the following material types: waste rock, ash, sand, slag, and slag from the oil/gas industry;

The scenarios do not apply to the discharge of radioactive substances with air or water, nor to intervention cases and the remediation of former mining sites. RP 122 includes description of enveloping scenarios that correspond to

typical recycling and disposal options for residues or wastes and the reference group of persons such as workers and/or members of the general public) exposed in the scenarios.

Recycling scenarios are as follows:

- transport over long/short distances (workers)
- Storage of moderate quantities indoors, (workers)
- Road construction with TENORM building materials (workers)
- Building construction with TENORM containing building material (workers)
- Building construction using undiluted TENORM as unshielded surface cover (workers)
- Persons living in a house with TENORM containing building materials (members of the public)
- Persons living in a house where undiluted TENORM as unshielded surface cover is used (members of the general public)

Disposal scenarios are as follows:

- Transport over short/long distances (workers)
- Disposal on a heap or a landfill (workers)
- Persons living in a house near a heap or landfill (workers)

RP 122 also defines the radionuclides and the decay chains considered in the modeling. It discusses the concept of background reduction, multiple exposure of reference persons, and the scenario independent parameters such as: for workers -annual working time, breathing rate, and direct ingestion rate; for

the members of the public, the parameters dependent on the age group of the reference persons as defined in the European Directive (1996). RP 122 also considers the dilution factor which depends on the TENORM material and dust concentrations which depends on the type of scenarios. The recommended general exemption and clearance levels for all types of material based on the above considerations are presented in Table 2.13.

Table 2.13 General clearance and exemption levels in Bq/g for all types of materials based on RP 122 (European Commission, 2001)

Radionuclides	All materials	Wet sludge from oil and industry
^{238}U sec*	0.5	5
Unat**	5	100
^{230}Th	10	100
^{226}Ra+	0.5	5
^{210}Pb+	5	100
^{210}Po	5	100
^{232}Th sec***	0.5	100
^{232}Th	5	100
^{228}Ra+	1	10
^{228}Th	0.5	5
^{40}K	5	100

* 238U sec consists of 238U decay chain
** 238U sec and 235U sec are in their fixed natural ratio (99.3% and 0.73% atomic fraction)
*** 232Th consists of 232Th decay chain

It should be noted that the above values of activity concentration for exemption and clearance derived in RP122 are more stringent than the values in IAEA Safety Guide No.RS-G-1.7.

The EC also published RP 135 entitled "Effluent and dose control from European Union NORM industries: Assessment of current situation and proposal for a harmonized community approach" (EC, 2003), that provides guidance to EU

Member States on realistic approaches for assessing doses to members of the public from NORM discharges covering all stages, in terms of individual dose, due to discharges from NORM industries. The exposure pathways, the characteristics of the exposed groups, and the methods for determining doses have been addressed for two types of discharge to the environment: discharge to atmosphere and to bodies of water.

RP 135 provides the values for screening levels of discharges into the atmosphere and bodies of water. For discharges below these screening levels there is unlikely to be a reason for a more detailed and site-specific radiological assessment of the discharge. For those above the levels, a detailed analysis is advised. The derived NORM discharge screening levels in GBq/y are estimates of the amount of activity discharged to the environment from a NORM plant, which, if not exceeded, mean that it is very unlikely that the members of the public would receive an effective dose above a defined dose criterion of 300μSv/y. If discharge screening levels are exceeded it is recommended that the Regulatory Bodies in the European Community:

- verify the actual level of discharges;
- check stack height;
- check the existence of assumed exposure pathways; and
- decide on the need for site-specific assessment

Excerpts of the screening levels from RP 135 are presented in Appendix I.

According to the sensitivity analysis conducted by Tadmor (1986), the following parameters influence the radiological risks from a coal-fired power plant:

- Radioactivity content of coal – the radionuclide risk is dependent on the radioactive content of coal; therefore a strong relationship exists between radioactivity content and individual risk. It is important to avoid using coal of a high radioactive content. Papastefanou and Charalambous (1984) suggested that coal containing 0.37 Bq/g (10 pCi/g) of ^{226}Ra should not be burned.
- Fusibility temperature of ash – a lower fusibility (initial deformation) temperature of ash, below the combustion temperature, implies a higher percentage of ash separated as bottom ash and a lower ash percentage within the flue gases correspondingly released in to the atmosphere. This would result in a lower radionuclide release rate and consequently in a lower risk level.
- Combustion conditions – Combustion temperature may vary from 1200 ^{0}C in pulverized coal-type furnaces to temperatures higher than 1600 ^{0}C in cyclone- type furnaces. Such a difference influences the type and amount of radionuclides volatilized during the combustion process and subsequently released from the plant and thus the risk levels. This influence stems not only from the higher volatility of certain radionuclide compounds at higher temperatures, but also from a higher chemical reactivity of some constituents at higher temperatures, and

possible formation of new radionuclide compounds of high volatility. Therefore, a coal fired power plant with a lower combustion temperature should be preferred from the point of view of radionuclides release into the atmosphere.

- Distribution of ash and radionuclides – The ash content within the flue gases varies significantly with the furnace type. Thus, about 80% of the ash is carried by the flue gases in a pulverized coal furnace, 20-30% in a cyclone furnace, and only 10-20% in an underfed or traveling-grate stoker furnace, the remainder being separated as bottom ash. Furthermore, the percentage of particles finer than 10 μm in the flue gas ash of an underfed or traveling-grate stoker is the smallest (5%) among the different furnace types; in a pulverized coal furnace, the percentage of particles finer than 10 μm is 65 % and in a cyclone furnace it is 90%. It should be recalled that the efficiency of any dust control is lower for smaller size particles.
- Influence of the filtration system – The radionuclides may persist in a phase separate from the ash, and these radionuclides may be released from the stack in such a phase, and possibly in a volatile (gaseous) form. For these radionuclides, conventional dust control systems such as mechanical collectors, electrostatic precipitaors and fabric filters, would not prevent the atmospheric release. The only filtration system which may be efficient for these radionuclides is the wet scrubber system, which would absorb the radionuclides persisting

in a separate phase from the fly ash, including those in a volatile gaseous form. Therefore, a proper choice of filtration may help in reducing radionuclide release and consequently the radiological risk.

- Influence of release height – while the types of coal, furnace and filtration system influence the levels of environmental risks by actually changing the amount of radionuclides released from the plant, the release height does not change the amount of radionuclide released. However, a change in release height does alter the diffusion pattern of the radionuclides during their atmospheric transport. Thus, changes occur in the ground level concentration of the radionuclides as a function of distance and in the contribution of the different exposure modes to the risk and consequently in the risk levels.
- Influence of site characteristics – Site characteristics such as population distribution, land use and meteorology influence the radiological risk of a given plant with a given radionuclide release. Proper site selection for a coal-fired power plant plays an important role in diminishing its radiological risk.

From the sensitivity analysis, Tadmor concluded that the release rate of radionuclides, mainly that of the ^{238}U series, and the effective release height most significantly influence the individual and collective radiological risks. The data related to these parameters should be accurately known to perform a sound evaluation of the radiological impact of a coal-fired thermal power plant.

2.7 Studies on discharges of TENORM into the environment and estimates of radiological impacts

As early as 1956, Anderson and Turner reported elevated levels of atmospheric radon during smoky and fog conditions and pointed out that radon was released into the atmosphere during normal burning of coal. The results of their analysis then of radium contents in various representative samples of coals as used in Great Britain were said to be of narrow range and the absence of levels of a higher order suggested that burning coal did not represent a significant addition to the total atmospheric level. On the other hand, in 1955 Suess reported a decrease in ^{14}C activity in wood of trees from east coast of the United States which he attributed partly to the introduction of ^{14}C-free CO_2 into the atmosphere by coal and oil combustion and to the rate of isotopic exchange by atmospheric CO_2 and the bicarbonate dissolved in the ocean (Suess, 1955), later referred to as "Suess effect".

In 1964, Eisenbud and Petrow analyzed samples of ash from coal and oil power plants and showed that a 1000 MW coal-burning power plant will discharge into the atmosphere from about 1.04 GBq (28 mCi) to 37 GBq (1 Ci) per year of ^{226}Ra and ^{228}Ra. A similar size oil-burning plant will discharge 185 MBq (0.5 mCi) of Ra per year. Based on their measurements of natural radioactivity of fossil fuels, they concluded that conventional fossil-fueled plants discharged relatively greater quantities of radioactive materials into the atmosphere than nuclear power plants of comparable size that released fission products, when the physical and biological properties of the radionuclides were taken into consideration.

Jaworowski, et al. (1971) reported that the concentration of ^{226}Ra in samples of freshly fallen snow increased with decrease in distance from a power station in Warsaw. Their study on the temporal variation of ^{226}Ra in glacier ice samples showed that the concentration of ^{226}Ra had increased about a hundred times from 1888 to 1970 [1.6 $x10^{-4}$ Bq/kg (0.004 pCi/kg)] in 1988 to [7.6 $x10^{-3}$ (0.206 pCi/kg)] in 1970. They also considered burning of fossil fuel as the main source of ^{226}Ra in the atmosphere.

Fossil and nuclear fueled power plants were considered the principal means for meeting immediate power needs. However, the use of nuclear fueled plants was being restricted because reactor-related hazards were exaggerated. Comparison of routine discharges of hazardous agents from different types of steam power plants showed that nuclear-fueled plants produced the lowest concentrations of such agents relative to protection standards (Hull, 1971).

Coles, et al (1978) concentrated their study on chemical fractionation of the naturally occurring radionuclides during coal combustion from two US Western coal-fired power plants as they considered the information as necessary to make valid comparison between fossil and nuclear fuel plants. The chemical behavior of ^{40}K, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{235}U and ^{238}U were described in terms of enrichment factor (EF) in the finer stack fly ash particles. The EF values ranged from 5.0 for ^{210}Pb to 1.2 for ^{228}Th. ^{235}U and ^{238}U EF values were both 2.8; ^{226}Ra and ^{228}Ra were 1.9 and 1.6, respectively. Th- series nuclides and ^{40}K showed little fractionation. ^{210}Pb and ^{238}U tended to be depleted in the bottom and fly ash.

W. C. Camplin (1980) conducted an assessment of the radiological impact of atmospheric discharges from a hypothetical 2000 MWe power station located in Great Britain. Five pathways of exposure were considered: 1) external irradiation from the plume activity in the atmosphere; 2) inhalation of the plume; 3) external irradiation from activity deposited on the ground; 4) inhalation of activity resuspended from the ground; and 5) ingestion of contaminated foodstuffs. The reduction in radiation exposure due to naturally occurring ^{14}C by releases of stable carbon from the power station was also considered. The ingestion pathway was found to result in the highest individual doses, whereas the inhalation pathway made the dominant contribution to collective dose. The most important radionuclides were ^{230}Th, ^{210}Pb and ^{210}Po of the uranium series, ^{232}Th and ^{228}Th of the thorium series. During the 30 years operation of the power station, the collective effective dose equivalent commitment truncated to 500 years was estimated to be 340 man-Sv or 0.68 man-Sv/y. The maximum annual committed individual effective dose equivalent to an individual was estimated as 230 μSv, although it was considered improbable that this level of dose will be received in practice. Camplin identified related areas of research to increase the accuracy of the assessment. These were (a) measurement of activity concentration in fly ash, and (2) study of environmental levels of radioactivity in the vicinity of an established site of coal–fired thermal site power plant.

Etnier and Travis (1983) in their review article of health risk estimates of the book, Health Risks of Energy Technologies, reported that when judged solely on the basis of fatalities and injuries during normal operation and maintenance,

nuclear power appeared to produce the least health impact and coal-fired power plants the highest, with the renewable technologies (solar, geothermal, biomass) ranging between the two. In terms of deaths and disease or injury, data on the fuel-cycle approach standardized to a 1000-MW(e) power plant year, suggested that the coal fuel cycle was an order of magnitude more hazardous than the comparable nuclear fuel cycle (Hamilton, 1983)

Papastefanou and Charalambous (1984) studied the radioactivity due to uranium series that escaped from a Greek (Kardia Ptolemais) coal power plant burning lignites of about 7×10^6 tons per year with 12.8% ash content. Assuming 2% of the ash escaped into the atmosphere, the total escaping ^{226}Ra was estimated in the order of 148×10^{12} Bq or 148 TBq (40 Ci/y). Their data indicated, as estimated by Eisenbud and Petrow, Kolb, and Aurand, that coal power plants discharged relatively larger quantities of radioactive materials into the atmosphere than nuclear power plants of comparable size, during normal operation. About ten years later, Papastefanou (1996) reported that about 11,672 MBq/y of ^{226}Ra were discharged into the environment from four coal-fired power plants totaling 3.62 GWe in Ptolemais Valley, Northern Greece, in which the combustion of 1.1×10^{10} was required to produce an electrical energy of 1 GW/y. The collective committed equivalent dose to lung tissue per unit power generated resulting from atmospheric releases was estimated to be 1.1×10^{-2} man-Sv/GW.y), more than fifteen times higher than the average value for a modern type coal-fired power plant reported by UNSCEAR in1988.

Measurements for estimating the natural radioactivity discharges from twenty-nine coal-fired power plants operating in India, having about 10,000 MW (e) installed capacity, was carried out by Lalit and Mishra (1986). From the results, they estimated the radiation doses to the population residing within 88.5 km radius of each thermal power plant; collective dose equivalent commitment to the bones, lungs and thyroid of 206 man-Sv/y and to the whole body of 73 man-Sv/y.

Similar radiological impact studies were made by Cruz and Alvarez (1989) from Spanish coal-fired power plants providing estimates of released radioactivity as 2-3 TBq/y and that inhalation risks of radionuclides released from coal power plants, by power unit and in normal working conditions were higher from those of nuclear power plant (pressurized water reactor and boiling water reactor. The activity concentrations of ^{228}Ac, ^{226}Ra, and ^{40}K from two power plants in Hongkong included radiological assessments at the center of an ash lagoon (Tso and Leung, 1995) such as external gamma dose rate at the center of an uncovered ash lagoon of 0.165 μGy/h and concentration of ^{222}Rn at 2.9 Bq/m^3. Radioactivity measurements in coals and ashes from coal power plants located in the southern part of Turkey (Aycik and Ercan, 1995) and in Mugla, Turkey were made. Baba (2002) reported that a coal-fired power plant producing 5,000 tons of fly and bottom ash per day with average level of uranium in bottom ash and fly ash of 354.7 Bq/kg (28.72ppm) and 199.2 Bq/kg (16.13ppm), respectively; and thorium in fly ash and bottom ash of 176.2 Bq/kg (43.39ppm)

and 133.4 Bq/kg (32.85ppm), respectively. The TENORM concentrations in fly and bottom ash were 3 to 6 times more than that of feed coals.

Hedvall and Erlandsson (1992) reported the results of their investigation on radioactivity concentration in peat fuel and ash from a peat-fired power plant in central Sweden before and after the Chernobyl accident. In spite of the fall-out after the Chernobyl accident, more than 99% of the calculated annual effective dose equivalent from internal exposure was due to NORM/TENORM, equivalent to about 6 μSv.

Mandal and Sengupta (2003) reported that in India, the production of ash associated with the use of coal as fuel in thermal power plants was one of the major environmental problems because Indian power stations used poor quality coal with 5-50% ash and an average production of 100 million tons of ash per annum. Their radio-elemental study of a 1,260 MW Kolaghat thermal power plant in West Bengal, India gave the following results: a maximum of 55.2 Bq/kg Th and 49.9 Bq/kg U for Kolaghat coal, 152.8 Bq/kg Th and 117.0 Bq/kg U in fly ash, 125.46 Bq/kg Th (pre-monsoon), 148.0 Bq/kg Th (post-monsoon), 102.09 Bq/kg U (pre-monsoon), 124.23 Bq/kg U (post-monsoon), in ash pond.

In Victoria, Australia, 65 million tons of brown coal is burned annually for electricity production. This contains about 19.8 Bq/kg (1.6 ppm) U and 12.2-14.2 Bq/kg (3.0-3.5 ppm) Th. About 100 tons U and 200 tons Th are buried in landfill each year in the Latrobe Valley. Australia is reported to have an average of 830 Bq/kg of total radioactivity related to 22.2Bq/kg (1.8 ppm) U and 28.4 Bq/kg (7 ppm) Th in its coal; 100-600 Bq/kg range for New South Wales (NSW) coals;

1500 Bq/kg for fly ash and up to 570 Bq/kg for bottom ash in NSW (http://www.uic.com.au/nip59.htm).

A comparison of the radiological impact of airborne effluents of coal and nuclear plants (1000 MWe) was done by McBride, et al. (1978). Assuming a 1% ash release to the atmosphere, 12.35 Bq/kg (1 ppm) of U and 8.12 Bq/kg (2 ppm) of Th in the coal (approximate USA average based principally on Appalachian coal), they calculated the inhalation and ingestion dose commitments over a 50-year period in an area within 88.5 km radius from the plant. Population dose commitments from the coal plant are generally higher than those from pressurized water (PW) or boiling water (BW) reactors that meet government regulations. According to their study, the maximum individual 50-yr dose commitments from the model coal-fired power plant were greater than those from the PWR (except for the thyroid dose) but were less than those from the BWR, (except for the bone dose). In general, however, the whole body and organ dose commitments were within the same order of magnitude. The estimated 50-yr dose commitments to the whole body per year of plant operation were: coal plant, 19 μSv (1.9 mRem); BWR, 46 μSv (4.6 mRem); and PWR, 18 μSv (1.8 mRem). The annual dose resulting from background radioactivity in the United States, external plus internal radiation, is 1.3 mSv/y (130 mRem /y). They concluded that the public health significance of the dose commitments they estimated was relatively minor. However, coals having U and Th concentrations higher that 12.35 Bq/kg (1ppm) and 8.12 Bq/kg (2ppm) respectively, could result to higher dose commitments and methods for estimating these higher dose

commitments were presented. They also mentioned that the health effects associated with airborne releases of non-radioactive materials from coal-fired power plants (particulates, NOx, SO2 and etc.) would appear to be many times more significant than those associated with the radioactive releases from either coal-fired or nuclear power plants.

Beck and Miller (1980) argued however, that unlike nuclear power plants, the radioactivity released from coal combustion resulted entirely to redistribution of already existing radionuclides rather than the creation of new ones. Their extensive review of available data on radioactivity of coal and coal ashes at that time clearly indicated the enrichment of ^{210}Pb in fly ash relative to bottom ash. The releases of radionuclides from typical power plants including the analysis of their own data and results of a number of published assessments of potential health hazards led them to conclude that the radioactivity released by the combustion of coal in modern plants (after 1972) meeting the USA Environmental Protection Agency's particulate emission standards was not a matter of concern. However, their findings did not stop researchers in other parts of the world from conducting similar studies.

Cohen, B. (1980) showed that radon gas emissions were the predominant source of radiation exposure from nuclear, coal burning, or phosphate mining. If only effects over 500 years were considered, lives saved by removal of uranium in mining exceeded lives lost due to radon emissions from nuclear industry under regulations now being instituted. The net fatalities per GWe/y caused by all radioactivity releases were 0.017 for nuclear and 0.045 for coal burning. The

effects of radioactivity releases by one year of present annual operations were ten times larger for phosphate mining than for coal burning.

Travis, et al. (1979) made an assessment of ^{222}Rn releases from major natural and technologically enhanced sources in the United States. The most important natural source of ^{222}Rn was decay of ^{226}Ra in the soil and rocks of the earth's surface which resulted in about 40% of the total population dose from all sources of radon. The largest technologically enhanced contributor to population dose was airborne ^{222}Rn in building interiors with estimated release of 1036 TBq/y (2.8 x 10^4 Ci/y) that contributed to about 55% to the total population exposure to ^{222}Rn. Uranium mining and milling, 14.8 x 10^{15} Bq/y or 14.8 PBq (4 x 10^5 Ci/y), phosphate mines, 1.96 PBq Bq/y (5.3 x 10^4 Ci/y), phosphate fertilizer, 1.8 PBq/y (4.8 x 10^4 Ci/y), coal mines, 518 TBq/y (1.4 x 10^4 Ci/y), and coal-fired power plants, 518 TBq/y (1.4 x 10^4 Ci/y), contributed less than 3% each.

De Santis and Longo (1984) examined about thirty published reports from 1954 to 1980 on the radiological risks from coal-fired and nuclear plants and commented that there were some errors, under and over evaluations observed. According to their review, the reports appeared to be generally in the direction of maximizing coal risks and minimizing nuclear risks. The assumptions of McBride were the closest reasonable high-maximum estimate of global release and considered unrealistic the total release of 148 TBq (40 Ci/yr) as reported by Papastefanou. De Santis and Longo removed the apparent inconsistencies in their analysis and took full account of the Suess effect, the cleaning effect derived from the fact that coal is free from ^{14}C. Thus, the huge release of non-

radioactive carbon into the atmosphere dilutes the natural ^{14}C present, acting like a "negative release" of radioactivity from the plant. The radiological risks from coal-fired power plants were fully counterbalanced by the Suess effect, and were, in any case, small in comparison with those from nuclear plants. Considering the Suess effect, they concluded that a coal fired-power plant, even one that was not well run, did not produce any radiological effect. Instead, it has the overall effect of reducing the radiological risk incurred by the population from other sources. Risk comparison between two energy technologies must take into account all possible harmful effects of each technology, as well as its associated cycle. In the case of coal, the non-radiological risks must be taken into account and compared with the radiological risks from the nuclear cycle (De Santis and Longo, 1984).

Coal-fired power plants are considered the major competitor of nuclear power plants as near-term energy sources. The risks of the life cycles of these two types of power plants need to be considered equally. For this reason, Dornsife, et al. (1998) compared the cost per risk avoided of the decommissioning of coal-fired thermal power with nuclear power plant decommissioning in terms of disposal of wastes generated. A Boiling Water Reactor (BWR) was used as an example for nuclear power plant decommissioning since it was projected to produce the most wastes. The results of this study showed that coal ash presented much greater long-term risk due to the presence of very long lived-TENORM compared to the radionuclides in the BWR decommissioning wastes which were relatively short-lived. Considering that

TENORM was not regulated, the radioactivity in coal ash had been found to pose a much higher potential for public exposure than the radioactivity in BWR decommissioning wastes.

According to the projections of Blix (2001) in his paper "What views and uses of radiation sources in the 21st century?", the combination of increasing cost of oil and gas, increasing fear of green house CO_2 emissions linked to the burning of fossil fuels, the emergence of newer and even safer nuclear power plants and better educated people on radiation will point to nuclear power as a source of world's electricity in the near future. It is the low-energy density of the renewable sources that makes it expensive to exploit them and that requires large areas for solar cells, wind farms and biomass plantations. It is the high-energy density of uranium (1 kg of natural uranium corresponds to 50,000 kW of electricity) that allows a nuclear power plant to operate on an extremely small volume of fuel resulting in extremely low volume of wastes, in contrast with the low energy density sources - 1 kg of wood corresponds to 1 kW of electricity, 1 kg of coal to 3 kW, and 1 kg of oil to 4 kW of electricity. In terms of waste disposal, nuclear waste is not the greatest problem from the energy use of our generation as a whole according to Blix (2001), because the nuclear waste is so small a volume that it can be put back in the crust of the earth from where the uranium came. This cannot be done with the main alternative wastes from burning fossil fuels such as CO_2, SO_2, nitrogen oxides, heavy toxic metals, and huge amounts of ashes whereby the earth's surface and the atmosphere are the final disposal sites of these wastes (Blix, 2001).

In the USA where 52% of the capacity for generating electricity is fueled by coal, (compared with 14.8% for nuclear energy), Gabbard (2005) made the following projections of releases of radioactive material from coal combustion for 100 years (from 1940-2040 as follows:

U.S. release (from combustion of ~1.0 x 10^{11} kg (101,348 MMT of coal) were as follows:

U ~1.4 x 10^{8} kg (140,902 MT) containing ~ 9.3 x 10^{5} kg (935 MT) of ^{235}U;

Th ~ 3.2 x 10^{8} kg (324,316 MT)

Worldwide release (from combustion of ~ 5.8 x 10^{11} kg (578,257 MMT) were as follows:

U~ 8.0 x 10^{8} kg (803,939 MT) containing ~5.7 x 10^{5} kg (5,659 MT of ^{235}U);

Th ~ 2.0 x 10^{10} kg (1,978,926 MT)

Based on the National Council on Radiation Protection and Measurements (NCRP) Reports No. 92 and No. 95, the population exposure from the operation of 1000-MWe nuclear and coal-fired power plants is 4.90 man-Sv/year for coal plants and 0.048 man-Sv/year for nuclear plants. Thus, the population effective dose equivalent from coal plants is about 100 times compared to that from nuclear plants. For the complete nuclear fuel cycle, from mining to reactor operation to waste disposal, the radiation dose is cited as 1.36 man-Sv/year (Gabbard, 2005). The equivalent dose for coal fuel cycle - from mining to power plant operation to waste disposal will still be over three times than from a nuclear power plant, plus the carcinogenic chemicals, green house gas, oxides of sulfur

that cause acid rain, oxides of nitrogen that cause breathing problems created by burning coal make coal-fired power plant less attractive (Kruzelnicke, 2006).

Some investigations were performed to determine the activity concentration in soil samples collected from the vicinity of coal-fired power plants. Bem et al., (1998) reported that in Lodz region in Poland, the radionuclide concentrations in surface soils around fly ash disposal areas showed an abnormally high depositional flux of ^{210}Pb. They attributed this to the high emanation of ^{222}Rn from deposited fly ash with insufficient soil cover. The activity concentration of the radionuclides in ^{238}U and ^{232}Th series in the sites studied ranged from 7.5 to 77 Bq/kg. According to the report of Flues, et al., (2002), the activity concentrations of radionuclides in ^{238}U and ^{232}Th series in soil samples from the vicinity of a coal-fired power plant in Figueira, Brazil ranged from <9 to 282 Bq/g and for ^{40}K, < 59 to 412 Bq/kg. This power plant with a capacity of 10 MWe, has been operating for more than thirty five years. The enhanced level of TENORM was observable within the first kilometer from the power plant.

Papp, et al. (2001) reported an elevated activity concentration of 108 Bq/kg for of ^{238}U and ^{226}Ra in soil samples collected around a power plant in Ajka, Hungary, to be about five times higher than the uncontaminated deeper layers of soil. This power plant has been operational since 1943. Papp and Dezco (2003) made further studies and reported that the ^{238}U (^{226}Ra) activity discharge to the atmosphere from the same plant per unit electrical energy produced was 330-400 Bq/kg $(GW\ y)^{-1}$, which was 66-80 times more than the estimates of UNSCEAR (1988) for an old type power plant [5 Bq/kg $(GW\ y)^{-1}$].

Their estimates of dose rate in air from external exposure to terrestrial gamma rays outdoors at a height of 1 m from the ground in public areas, vegetable gardens, and backyards, were on average 32.8, 10.3 and 102 nGy/h, respectively. The annual effective dose was 21.8 μSv/y. The collective dose commitment per unit energy generated from outdoor exposure to the deposited uranium progeny was about 8-9 person-Sv $(GW\ y)^{-1}$, which was 67-76 times more than that evaluated by UNSCEAR (1988) for a typical old coal-fired power plant of 0.12 person-Sv$(GW\ y)^{-1}$.

Bem, et al. (2002) reported that several small coal-fired power plants in Lodz region in Poland resulted in a relatively small increase in natural radioactivity in the vicinity of the power plants. The average dose rate was 36±1.2 nGy/hr and at the edge of the region was slightly lower 30±09 nGy/hr. The technologically slightly enhanced radiation in the vicinity of the plant was further confirmed with the results of the gamma spectrometry measurements of the ^{238}U and ^{232}Th decay series radionuclides in the surface soil samples. Papaefthymiou, et al. (2005) also reported slightly higher natural radioactivity concentrations in Megalopolis City compared to Patras City in Greece and attributed this to the operation of coal-fired power plants A (operating since early 1970s) and B (operating since early 1990s) located in Megalopolis City.

The Multipartite Monitoring Team (MMT) activities periodically conducted in coal-fired power plants include ambient air monitoring for SO_2, NO_2, and TSP; verification of continuous monitoring of SO_2, NO_2, TSP and CO; noise monitoring; water quality monitoring for pH, temperature, color, turbidity, conductivity, salinity,

total dissolved solids, Cl^-, $(SO_4)^-$, $NO_3)^-$, total coliform, and trace elements (Hg, As, Cd, Cr, and Pb,; BOD, COD, oil and grease; ecological monitoring; socio-economic verification; and updating of morbidity and mortality data. The 2004 data of Balayan and Calaca, Batangas for morbidity are mostly on upper respiratory track infection and for mortality, pneumonia and cancer (MMT Report, 2005).

2.8 Uses of coal ash and associated radiological consequences

Coal ash has been utilized for various purposes i.e., manufacture of cement, concrete and bricks for building, dam and road construction, and for landfill. Specialized uses of fly ash are in tape making for fire-proofing and insulating high-voltage cables, insulation material for space shuttles and to increase the yield of rice paddies (Kruszelnicki, 2006).

Assessments have been done to determine the extent of radiological consequences of using fly ash as a component of cement. The main focus was to study the influence of fly ash on radon exhalation rate from cement materials. The radon exhalation rate was found to be significantly lower in cement containing fly ash than in ordinary cement (Stranden, 1983 and Kovler, et. al., 2005). Stranden (1983) also reported that in some countries where building blocks are made entirely of fly ash, the houses built of this material show enhanced radon concentration. Studies of USEPA have shown that radon releases from concrete blocks manufactured using coal fly ash are well below USEPA's radon action levels (USEPA, 2005).

According to the review article of Tokonami and Ishikawa on "Radiological aspects of using coal ash (slag) in building industry", surveys carried out in different countries of gamma dose in buildings constructed with coal ash (fly and bottom ash) show different results. In some buildings, the gamma dose was expected to be zero or insignificant and in certain cases, the annual gamma dose of several mSv could be expected. For example, the highest dose for a critical group in the United Kingdom was 250 μSv came from the use of fly ash in building materials; measurements in former Czechoslovakia gave values approaching 1000 nGy/hr in houses with outside walls containing coal slag; in Hungary, the annual radiation dose varied between 0.7 and 3.4 mSv when slag was used as filling–insulating material in houses; and that radionuclide concentration in light weight concrete produced using coal ash were: ^{226}Ra: 86 Bq/kg, ^{232}Th: 109 Bq/kg; and ^{40}K: 94 Bq/kg.

In order to decrease the radiation dose to the population and to prevent additional dose, materials used for building construction are classified in many countries. An example of such classification used in international practice that is based on radium equivalent (Ra eq) is as follows:

$$Ra\ eq = C_{Ra\text{-}226} + 1.26\ C_{Th\text{-}232} + 0.086\ C_{K\text{-}40} \quad \text{Eq. 1}$$

where C_x is activity concentration of the radionuclide expressed in Bq/kg.

The recommended applications and limit values are as follows:

I. House building: Ra eq < 370

II. Industrial building: Ra eq < 740

III. Road and highway construction: Ra eq <2200

IV. Soil clearing: Ra eq < 3700

V. Prohibited for any purpose Ra eq > 3700

Many countries have chosen an index which should be less or equal to 1 for the unlimited use of the materials for residential buildings. Based on activity concentration parameters of ^{226}Ra, ^{232}Th and ^{40}K in building materials, different values of activity concentration are used in the national legislation of some European countries to determine the index. The difference in values could be attributed to both the different levels of concentration of radionuclides in each country's typical building materials and the socio-economic consequences of banning the use and trade of the materials (Tokonami and Ishikawa, 2006). Based on the above, Tokonami and Ishikawa recommended that radiological survey of the ash and the building materials produced from ash, and subsequent classification based on the survey results were essential tasks to be done.

Just recently, the USEPA in cooperation with the Department of Energy (DOE), the Federal Highway Administration (FHWA), the American Coal Ash Association (ACAA), and the Utility Solid Waste Activities Group (USWAG) has issued a guide entitled "Using coal ash in highway construction: a guide to benefits and impacts". The use of coal combustion products (CCPs) in highway construction projects such as in concrete, road base, embankments, and other beneficial applications is encouraged. The increased use of these materials, which would otherwise be discarded as waste, can reduce greenhouse gases in the atmosphere, reduce energy consumption, and conserve natural resources. Some applications, such as road embankments and other non-encapsulated

(loose) uses, may require the evaluation of local hydro-geological conditions to ensure protection of human health and the environment. According to the American Coal Ash Association's annual coal combustion product survey, almost 122 million tons of coal combustion residues were generated in 2003, and more than 46 million tons were used as products in such beneficial applications as concrete, roofing tiles and shingles, bricks and blocks for building construction, wallboard, and specialty uses such as filler in carpet and bowling balls (USEPA, 2005).

L. Reijnders (2005) conducted a review on the disposal, uses and treatment of combustion ashes. Ashes from coal combustion can contain mobile compounds that may give rise to significant pollution on disposal or during use. Immobilization and forced extraction may be considered for metals and other polluting elements and destruction for persistent organic pollutants from the coal ash. Extraction of germanium from coal ash, for example has been pursued in Russia and China. For radioactive elements that may pose significant hazard on use, forced extraction is an option. China National Nuclear Corporation was commissioned Sparton Resources of Canada with the Beijing No.5 Testing Institute this year to undertake advanced trials on leaching uranium from coal ash out of the Xiaolongtang power station in Yunnan as the ash contained 1,976-2,223 Bq/kg (160-180 ppm) U - above the cut-off level for some uranium mines. Then, Sparton Resources of Canada was also commissioned by Wild Horse Energy to assess the potential for recovering uranium from European coal ash having 988-1,667 Bq/kg (80 - 135 ppm) U (http://www.uic.au.nip54.htm).

The use of coal ash as additive or substitute for cement will help reduce the future generation of greenhouse gases from the reduction of cement making and the forced extraction of useful metals from the coal ash, which is the object in mining industries, will help conserve our natural resources.

CHAPTER 3

METHODOLOGY

3.1 Sampling sites

Figure 3.1 shows the map location of coal-fired thermal power plants C, M, P and S in Luzon where feed coal and ash samples were obtained. Table 3.1 provides information about each Plant's operating capacity, start of operation, origin of coal used, areas of ash ponds and heights of stacks.

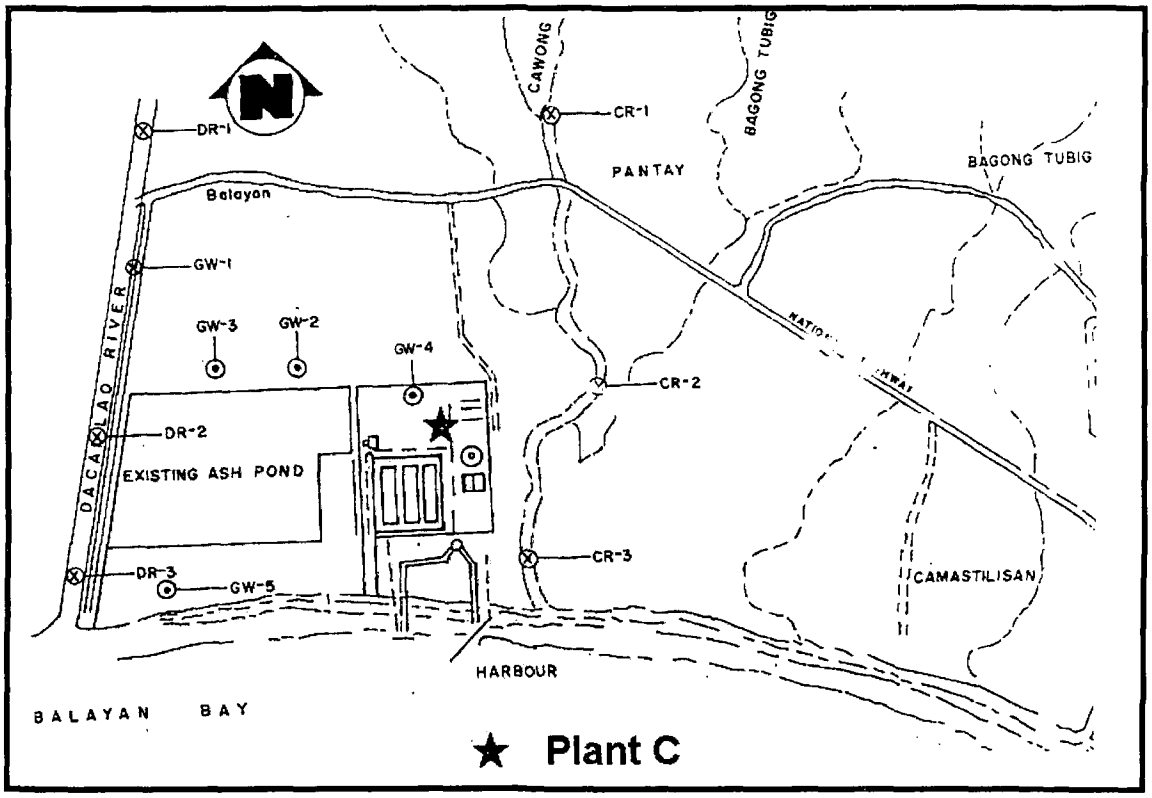
Fig. 3.1. Relative location of coal-fired thermal power plants.

Table 3.1. Description of sampling sites.

Plant	MW	Location	Year start	Origin of Coal	Ash pond area (m^2)	Stack height (m)
C - 1	300.00	Calaca, Batangas	9/5/84	Semirara, Indonesia	640,000	120
C - 2	350.00	Calaca, Batangas	6/5/95	Semirara		150
M - 1	300.00	Masinloc, Zambales	6/18/98	China	Not available	150
M - 2	300.00	Masinloc, Zambales	12/1/98	China		150
P - 1	367.5	Pagbilao, Quezon	3/7/96	Semirara Indonesia	146,492 77, 083*	220
P - 2	367.5	Pagbilao, Quezon	5/26/96	Semirara, Indonesia		
S - I	609.00	Sual, Pangasinan	10/23/99	China, Semirara	1,400,000	240
S- 2	609.00	Sual, Pangasinan	10/5/99	China, Semirara		

Source: http://www.doe.gov.ph; Plant C, P, and S brochures; personal communications
* Under development

The main study site is Plant C with Units 1 and 2 at 300 MW each. Plant C has an area of 167 hectares located along the shorelines of Balayan Bay, San Rafael, Calaca, Batangas, about 115 km south of Manila and about 270 km by sea from Semirara Island, Antique, the origin of the Plant's local coal requirements. It is bounded in the north by the National Highway, on the west by Dacanlao River, on the east by Cawong River, and Balayan Bay in the south as shown in Figure 3.2. The Pozzolanic Philippines purchases the plants' fly ash mainly for building construction purposes (BCFTPP, 1994).



Source: Batangas Coal-Fired Thermal Power Plant Multipartite Monitoring Activity Report, December 12-16, 2005

Fig. 3.2. Vicinity lay-out of Plant C.

3.2 Collection and sample preparation

About 2-3 kg of feed coal, bottom ash, fly ash, and ash pond samples were obtained from Plants C, M, P and S through the Plant's Environmental Safety Officer. All feed coal samples were pulverized. Plant P's bottom and fly ash samples were from Units 1 and 2, and ash pond samples are from ash ponds A and B. Plants M and S did not indicate from which Unit the bottom and fly ash samples were specifically collected and both plants did not provide samples from their ash ponds. All samples were placed in properly labeled polyethelene bags, indicating the sampling date, type of sample, and the country of origin of the feed coal.

Plant C's feed coal, bottom, fly and ash pond samples were collected from Unit 1 only during the sampling period in June 2005, and from both Units 1 and 2 during the sampling period in June 2006. Unit 2 was shut down during the sampling period in June 2005. Both sampling periods in June 2005 and June 2006 coincided with Plant C's scheduled Multipartite Monitoring activities. Sample collection is summarized in Table 3.2. Figure 3.3 (a), (b) and (c) show the portion of the ash pond area where samples were randomly taken.

Table 3.2. *Description* of sample and sampling dates

Plant	Type of samples	Sampling dates	Comments
C (Units 1 & 2)	Feed coal, bottom ash, fly ash, and ash pond	June 2005 (Unit 1); June 2006 (Units 1 & 2)	Ash pond sampling personally done, refer to Fig. 3.3 (a) and (c)
	On-site measurements of U, Th and K concentrations (ppm)	December 2005 and June 2006	Refer to Fig. 3.1, Sec. 3.2, and Appendix H.
M	Feed coal, bottom ash, fly ash (Unit not indicated)	July 2005	Samples delivered at PNRI
P (Units 1 & 2)	Feed coal, bottom ash, fly ash, ash pond	September 2005	Samples delivered at PNRI
S	Feed coal, bottom ash, fly ash (Unit not indicated)	August 2005	Samples picked up at Plant employee's residence

(a)

(b)

(c)

Fig. 3.3. Ash pond sampling areas (a) June 2005; (b) December 2005, ash pond with water; and (c) June 2006.

Split samples of 200-300 g were taken from each of samples obtained from four coal-fired power plants, packed separately and labeled in polyethylene bags. The split samples were brought to the National Institute of Radiological Sciences (NIRS), Inage, Chiba, Japan for high purity germanium HPGe gamma spectrometry (HPGe-GS) and inductively coupled plasma mass spectrometry (ICP-MS) analyses for the period September to December 2005. At NIRS, all samples were oven dried at 60 ^{0}C until weight was constant, pulverized using a mortar and pestle (except for the ash samples), and homogenized using a 500 µm mesh size sieve. Figure 3.4 shows the flow chart of sample preparation common to both ICP-MS and HPGe techniques and Table 3.3 presents the types

of samples obtained from each Plant, the types of analysis done, and the sub-sections wherein the type of analysis is described.

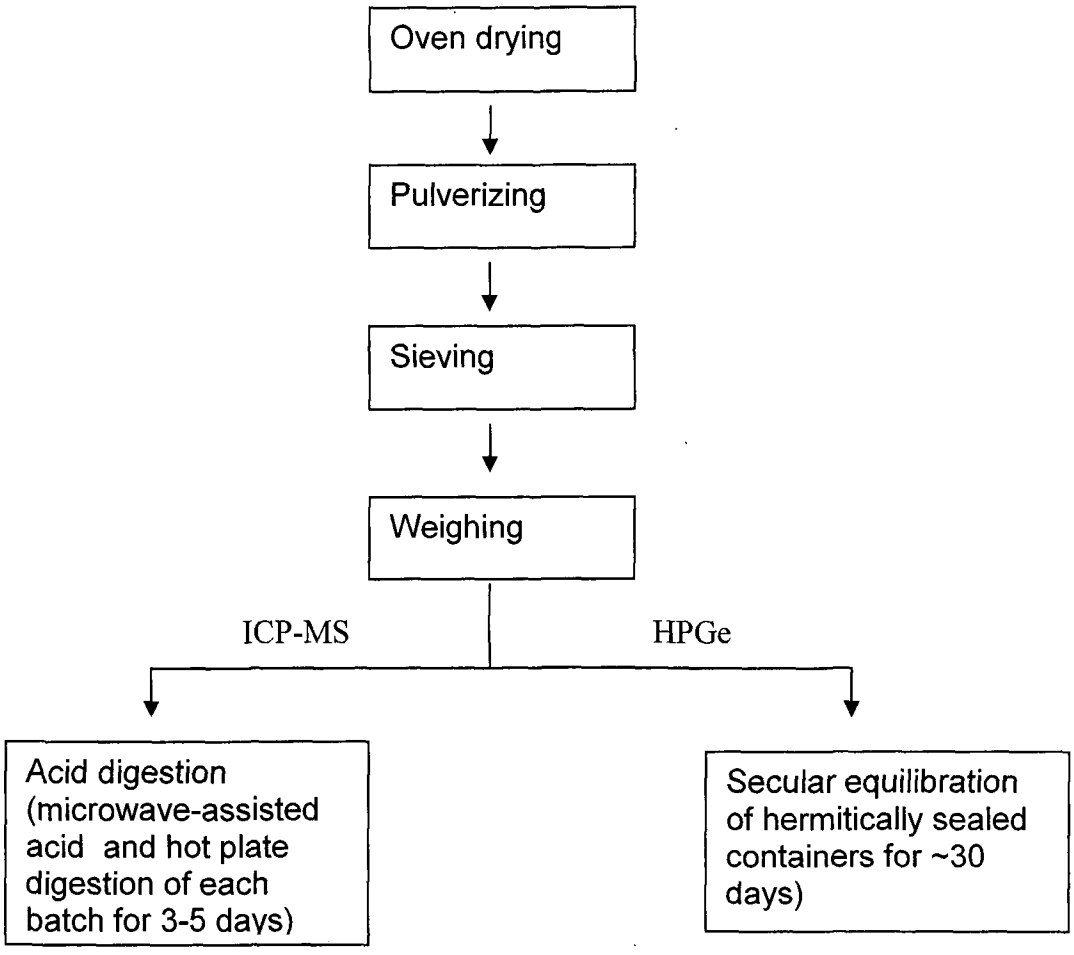


Fig. 3.4. Flow chart of sample preparation common to ICP-MS and HPGe analyses.

Table 3.3. Sample preparation and type of analysis

Plant	Type of samples	Sample preparation		Analysis	
		ICP-MS	HPGe GS	ICP-MS	HPGe GS
C (Units 1 and 2)	Feed coal (1), bottom ash, fly ash, ash pond,	Fig. 3.4 Sec. 3.2.1	Fig. 3.4 Sec. 3.2.2	Sec. 3.3.1, except ash pond samples	Sec.3.3.2
M	Feed coal, bottom ash, fly ash	Fig. 3.3 Sec. 3.2.1	Fig. 3.3 Sec. 3.2.2	Sec. 3.3.1	Sec.3.3.2
P (Units 1 and 2)	Feed coal, bottom ash, fly ash, ash pond	Fig. 3.3 Sec. 3.2.1	Fig. 3.3 Sec. 3.2.2	Sec. 3.3.1, except ash pond samples	Sec.3.3.2
S	Feed coal, bottom ash, fly ash	Fig. 3.3 Sec. 3.2.1	Fig. 3.3 Sec. 3.2.2	Sec. 3.3.1	Sec.3.3.2

3.2.1 Sample preparation for ICP-MS analysis

The split samples for ICP-MS analysis were further pulverized and homogenized using a 0.45 μm mesh size. The samples prepared for acid digestion are shown in Figure 3.5. About 0.1 g of each sample (weighed to a precision of 0.001 g) was digested with a combination of high purity acids (Tama Chemical Co.; Ltd, Japan): 20 mL HNO_3, 19.5 mL $HClO_4$, and 15 mL HF for ash samples; 18 mL HNO_3, 13.5 mL $HClO_4$, and 13.5 mL HF for bottom ash samples; and18 mL HNO_3, 18 mL $HClO_4$, and 9 mL HF for feed coal samples (ANSTO ENV-I-035-001, 2004). Bi-distilled water was used for cleaning and dilution purposes (Millipore Milli-Q water purification system, Auto Still WF-12, Yamato Scientific, Japan). Complete digestion of the samples was accomplished by a combination of closed 120 mL tetrafluormethaxil (TFM) pressure decomposition vessels in a microwave unit (Milestone Ethos-1600, Italy) and open Teflon

beakers on a hot plate. The parameters for microwave assisted acid digestion program (Ethos 1600 User Manual-Rev. 1/99) are presented in Table 3.4.

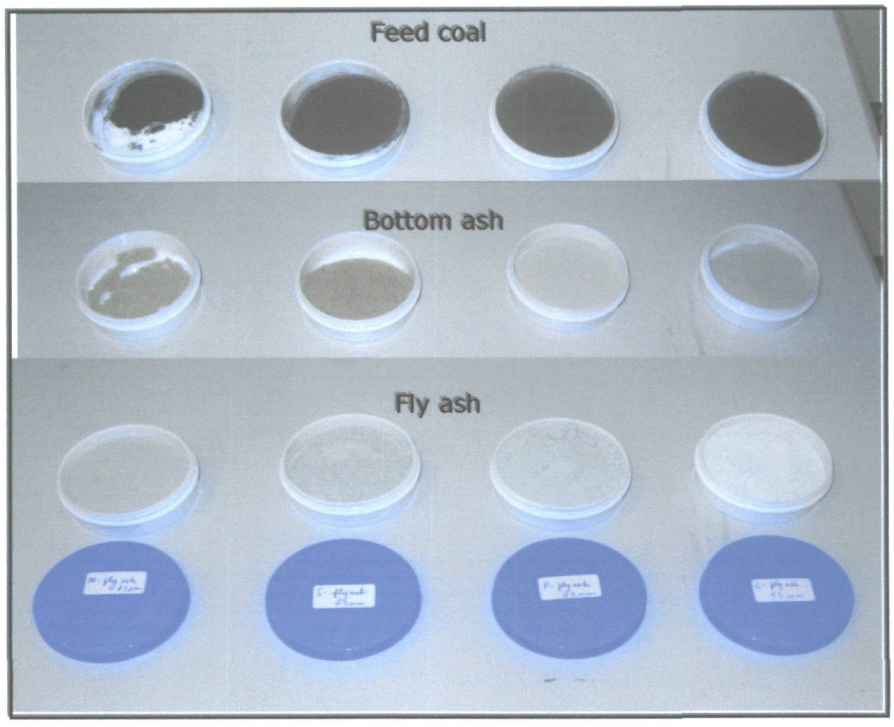


Fig. 3.5 Samples for acid digestion

Table 3.4 Input parameters of program for microwave assisted digestion

Time (min)	Power (W)	Temperature (^{0}C)
5	250	140
5	0	140
10	250	140
5	400	140
5	600	140

Each microwave digested sample was transferred to a Teflon beaker and evaporated to dryness on a hot plate at about 200^{0}C. Similar proportion of acids was added until complete sample decomposition was attained. Each completely

digested sample was diluted with 68% HNO_3 to yield a sample solution (about 10-20 g). Each sample was transferred to a pre-weighed and labeled sample bottle and was accurately weighed. A blank sample with the same mixture of acids was processed with each batch of samples. A reference material, JLK-1 lake sediment sample, supplied by the Geological Survey of Japan (GSJ) was digested with the same acid proportions for quality control.

The TFM vessels after acid digestion of each sample batch were cleaned by microwaving for 10 min at 500 W and 100 ^{0}C and then rinsed with high purity water. The vessels were transferred to a large beaker with HNO_3 solution and brought to sub-boiling for 1 hr, then transferred to another beaker with high purity water, and brought to sub boiling for another 1 hr. The Teflon beakers were cleaned in the same manner, except for the microwaving step. The entire sample preparation and cleaning of used vessels were done inside two adjacent fume hoods. The cleaned Teflon beakers, TFM vessels were allowed to dry in a particle and fume free enclosure (SS-MAC Airtech, Model MAC 11FR, Airtech, Japan).

3.2.2 Sample preparation for HPGe gamma analysis

About 100 g each of split sample was placed in U8 standard cylindrical containers (diameter = 56 mm; h = 68 mm) (Sanplatec Corp, Japan), inserted with spacers, tightly covered and hermetically sealed by applying glue inside and outside the lid, and then wrapped with thin plastic sheet in order to prevent the escape of radon, see Figure 3.6 (a). The sealed samples were allowed to sit for about thirty (30) days (equivalent to 7 half-lives of ^{222}Rn) in order that ^{226}Ra and

^{222}Rn and its short-lived gamma emitting decay products, ^{214}Bi and ^{214}Pb attain secular equilibrium. ^{222}Rn ($t_{1/2}$ = 3.8 days) and its short-lived gamma-emitting decay products, ^{214}Pb ($t_{1/2}$ = 26.8 m) and ^{214}Bi ($t_{1/2}$ = 19.7 m), establish secular equilibrium with its long-lived parent, ^{226}Ra ($t_{1/2}$ = 1,622 y) after 7 half-lives of ^{222}Rn or about 30 days in a hermitically sealed containers. ^{228}Ra and ^{228}Th will also attain secular equilibrium with its gamma emitting decay products. A total of twenty (20) samples and two (2) blank samples (empty containers) were prepared for *gamma* analysis.

The time by which ^{222}Rn establishes secular equilibrium with ^{226}Ra is based on the equation, $Q_B = Q_A (1 - e^{-\lambda_B t})$, where Q_A and Q_B are the respective activities in becquerels of the parent and daughter. As time increases, $e^{-\lambda t}$ decreases, and Q_B approaches Q_A. For practical purposes, equilibrium may be considered established after 7 daughter half-lives. At equilibrium, the activity of the parent is equal to that of the daughter. In the case of secular equilibrium, the activity of the parent remains to be substantially constant during the period that it is being observed. For secular equilibrium, it is required that the half-life of the parent must be very much longer than that of the daughter (Cember, 1988).

The remaining split samples at PNRI were also oven-dried, ground, and homogenized to 32 M mesh size. About 200 g each of split samples were placed in plastic containers (~ 60 mm diameter; 90 mm) and hermetically sealed. Two blank containers were similarly sealed. The sizes of the containers were similar to the 250 mL Nalgene bottle containing the multi-nuclide standard source as shown in Figure 3.6 (b) and (c). The sealed samples were also kept for about

thirty (30) days prior to analysis to allow ^{226}Ra, ^{222}Rn and its short-lived gamma emitting decay products, ^{214}Bi and ^{214}Pb attain secular equilibrium. A total of forty (40) samples and two (2) blank samples (empty containers) were prepared for PNRI HPGe analysis.

Additional nineteen (19) samples from Plant C collected during the sampling period in June 2006 were similarly prepared for gamma analysis.

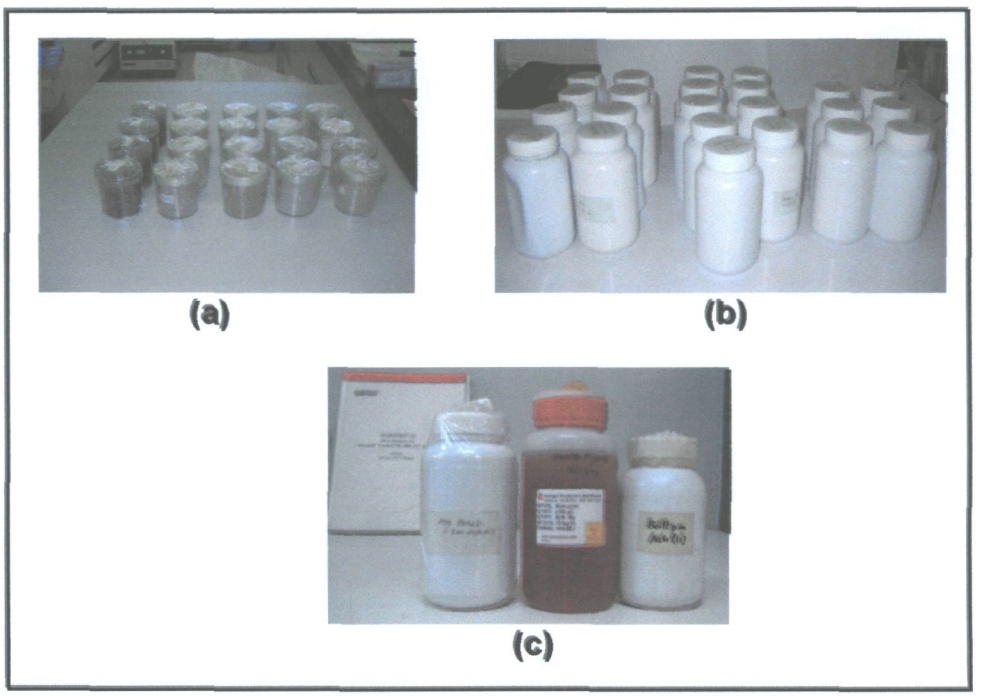


Fig. 3.6. (a) Samples for NIRS HPGe gamma analysis;
(b) Samples for PNRI HPGe gamma analysis; and
(c) Samples with the multi-nuclide standard source.

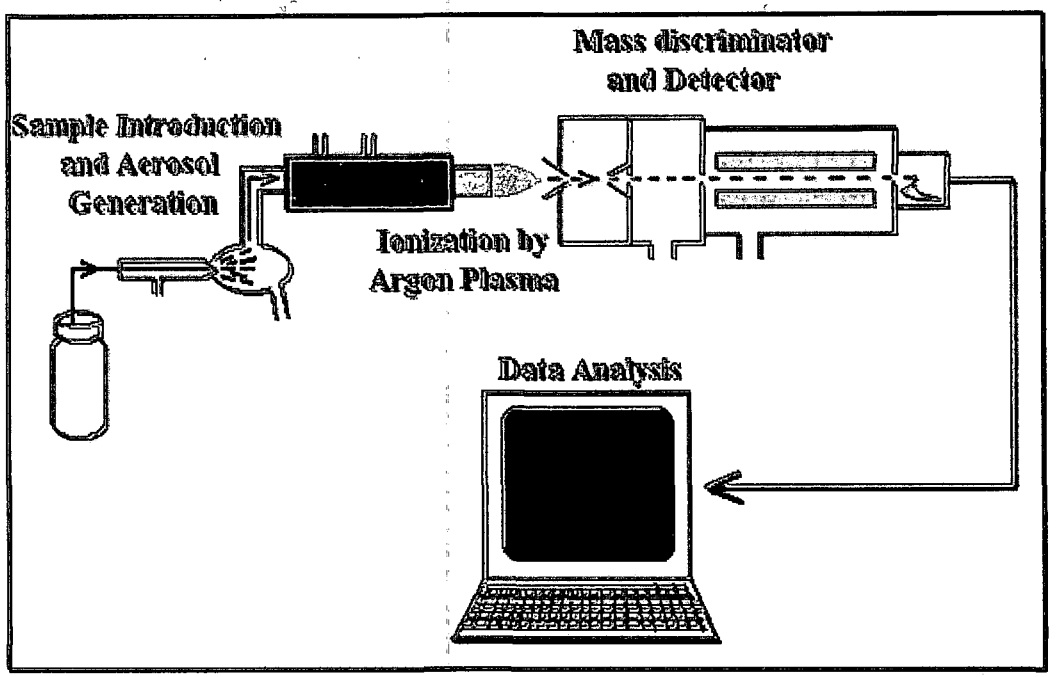
3.3 Data acquisition and activity calculation

3.3.1 Measurement using NIRS ICP-MS

Inductively coupled plasma mass spectroscopy (ICP-MS) was developed in the late 1980s that combines the easy sample introduction and quick analysis with the accurate and low detection limits of a mass spectrometer. It is capable of

trace multi-element analysis, often at the part per trillion level of detection. The samples are decomposed to neutral elements in a high-temperature argon plasma and analyzed based on their mass to charge ratios. Although the majority of ICP-MS applications involve analysis of liquid samples, over the years the technique can also handle solid samples. The solid samples are introduced into the ICP by way of laser ablation system which can be purchased as an accessory. If the ICP-MS has no laser ablation system accessory, solid samples must be decomposed, for example, by acid digestion, from which aqueous solutions are prepared (Worley and Kvech, 2005).

There are four main processes in ICP-MS. These are: sample introduction and aerosol generation; ionization by an argon plasma source; mass discrimination; and the detection system. The schematic diagram of the sequence of processes is shown in Figure 3.7.



Source: http://www.earth.man.ac.uk/facilities/agu/ICP-MS

Fig. 3.7. Schematic diagram of ICP-MS main processes

One of the most critical areas of the ICP-MS is the sample introduction system. While there are many ways of introducing the sample, the desired result is the same- to generate a fine aerosol of the sample so it can be efficiently ionized in the plasma discharge. The sample introduction system is considered the weakest ICP-MS component because only 1-2 % of the sample finds its way into the plasma (Thomas, 2001). According to McCurdy and Potter (2001), the optimization of ICP-MS for the determination of trace metals in high matrix samples depends on many factors. Dissolved solid levels must be given proper attention and controlled carefully, typically no higher than 0.2%, to avoid matrix deposition on the spectrometer interface. The plasma temperature must be high enough so that during the residence time, in the order of a few milliseconds, of the aerosol sample droplet in the plasma region, the plasma must be able to dry,

decompose, dissociate, atomize, and ionize the aerosol sample to give, as far as possible, 100% conversion of sample analyte components into singly charge positive ions. The potential for the formation of polyatomic interferences from matrix components are strongly influenced by the design and operating conditions of the ICP-MS sample introduction and plasma. Hence, with an ICP-MS designed for matrix tolerance and using operating conditions that are optimized for efficient matrix decomposition, accurate determination of many trace elements at the single ug/L levels found in natural materials is made possible.

With this development, the ICP-MS has become one of the most powerful and increasingly established analytical techniques including its ability to provide a very sensitive multi-elemental determination of long-lived radionuclides at trace and ultra-trace concentration for environmental samples such as water, geological, biological and medical samples, nuclear materials and radioactive waste. For environmental research, the main field of application is the determination of radionuclide concentration, e.g. U^{238}, U^{234}, U^{235}, Th^{230}, Th^{232} and their decay radionuclides, and precise abundances of NORM as terrestrial sources of radioactivity. The determination of long-lived radionuclides is also of increasing importance for radioactive waste control and radioactive waste management for final storage (Becker, 2002).

Pawlak and Gabriela (2002) carried out a comparison of ICP-MS with the US Environmental Protection Agency (USEPA) accepted radiochemical method EPA908.0 based on data from laboratory control standards, national proficiency

test samples, and environmental and drinking water samples from the State of Utah. The results demonstrated that the ICP-MS is a superior analytical tool for the determination of uranium in drinking and environmental waters at concentrations required by the USEPA. The ICP-MS method also showed simplified sample preparation, high sensitivity and accuracy, and good precision. Because it can be performed with less sample volume, faster results, lower detection sensitivity and relatively lower cost, the ICP-MS was selected as the primary method for the determination of U^{235}, U^{238}, and total uranium concentration of collected samples of surface soil, subsurface soil, ground water, surface water, sediment and bog peat in the first round of characterization of an approximately 186,200 m^2 (46 acres) EPA Superfund Site (Downey, 2005). Bailey and Stokes (2002) started using ICP-MS as part of environmental dose rate evaluation and considered ICP-MS as a potentially powerful complement to other methods of dose rate assessment. They believed that ICP-MS approach offers some advantages over and above the use of nuclear methods such as instrumental neutron activation analysis (INAA) presently used widely.

The determination of ^{232}Th and ^{238}U in Philippine feed coal and ash samples was the first attempt of NIRS to use ICP-MS technique in preparation for their forthcoming research project on NORM. The ICP-MS instrument used in this experiment was a Hewlett Packard, Model HP 5000 (Hewlett Packard-Yokogawa Analytical Systems, Ltd, Tokyo, Japan) shown in Figure 3.8. The instrument operation was fully controlled by a computer through a dedicated Microsoft Windows – HP 4500 ChemStation Software which also processed the QA/QC

results. The data acquisition and optimization parameters of the ICP-MS are summarized in Table 3.5.

Prior to ICP-MS analyses, standard solutions were prepared from SPEX multi-element plasma standard (Spex CertiPrep, NJ, USA) at 0, 25, 50, 100, 250 ppt to derive calibration curves. The standard solutions, blank, coal and ash samples were measured 3 times for a period of 9 s each. After digestion of the first batch of samples, measurements were conducted immediately using a different instrument (referred to as ICP-MS 2) from the ICP-instrument (referred to as ICP-MS 1) assigned to the researcher. A sample ICP-MS print-out is shown in Appendix A. The results of the analysis using ICP-MS 1 and ICP-MS 2 are presented in Appendix B to show the reliability of ICP-MS measurements.

The activity concentration (AC) of ^{232}Th and ^{238}U in samples was calculated according to the example below.

Example of calculation of the activity concentration, AC (Bq/kg) of ^{238}U in a given sample

Type of sample: Plant C fly ash

m1 - mass of fly ash, 0.3397g

m2 - mass of digested fly ash solution, 19.9076g

m3 - mass of aliquot of fly ash solution, 0.1382g

m4 - mass of diluted aliquot of fly ash solution, 62.475g

C - ICP-MS data for ^{238}U in Plant C fly ash sample from Appendix B, 155.8 ppt

CF - correction factor, 1.285

SA - specific activity of ^{238}U - 0.0124 Bq/ug from the equation

Specific activity, $SA = 0.693\ N / A \times t_{½}$

where, $N = 6.023 \times 10^{23}$ atoms/mole

$A = 238$ g/mole

$t_{½}\ (^{238}U) = 4.51 \times 10^{9}$ y

AC (Bq/kg) = [(C (^{238}U) x m2 x m4) / (CF x m1 x m3 x 10^{6}) µg/g] x [SA (Bq/µg) x 1000 g/kg]

= 39.58 Bq/kg

Fig. 3.8. NIRS ICP-MS set-up

Table 3.5. ICP-MS parameters for data acquisition and optimization conditions

Plasma RF power (kW)	1.30
Argon flow (L/min) Plasma Auxiliary Carrier Nebulizer Sampling distance, mm Peri-pump (rps)	 16.0 1.0 1.23 Babington type 6.0 0.1
Data acquisition mode Number of points per peak Dwell time per point, s Scan mass range, a.m.u.	Peak jumping mode 3 9 88-238

3.3.2 Measurement using HPGe GS

NIRS HPGe GS

As shown in Tables 1 and 2, some of the decay products of ^{238}U and ^{232}Th emit gamma rays of specific energy during their decay. Because gamma rays are uncharged, its detection is primarily based on the different mechanisms of its interaction with the absorbing material. There are four major mechanisms for the interaction of gamma energy that are considered significant for detection purposes. Two of these mechanisms, photoelectric absorption and Compton scattering involve interactions only with the orbital electron of the detector (absorber), and predominates when the gamma-ray energy does not greatly exceed 1.02 MeV, the energy equivalent of the rest mass of two electrons. In the case of higher gamma ray energies, pair production, which is a direct conversion of the energy into a positron and an electron, occurs. When the gamma energy

is very high, $E>>2m_0 c^2$, it may be absorbed by the nuclei of the absorber atoms, initiate a nuclear reaction that results in the emission from the excited nuclei of other radiations.

The types of gamma radiation detectors that have been utilized for the determination of naturally occurring radioisotopes and their activity concentration are scintillator-based detector such as sodium iodide (NaI), and solid state detectors using advanced material semi-conductors such as High Purity Germanium (HPGe) and the recently popular Cadmium-Zinc-Telluride (CaZnTe or CZT) crystals. These detectors mainly rely on the production of photoelectric ionization on the material by the gamma ray; electron-hole pairs are created in the semiconductors while electron-ion pairs are created in scintillators. Both types of detectors are capable of recording the energies of incoming gamma rays. The incoming gamma radiation in such detectors produces pulses of light or electric charges proportional to the kinetic energy of the incoming gamma radiation. As seen in Figure 3.9, the associated electronic components – preamplifiers, amplifiers, analog to digital converters (ADCs), and multi-channel analyzers (MCAs) shape and amplify the signal from a detector, perform analog to digital conversion, and segregate the generated pulses according to their amplitude (height) that is proportional to the energy of the incoming gamma radiation. Most MCA are built with the number of channels (correspond to gamma energies), varying by a factor of 2 over the range of 128 to 4096 each with a storage capacity of 10^5 to 10^6 counts per channel (Cember, 1988).

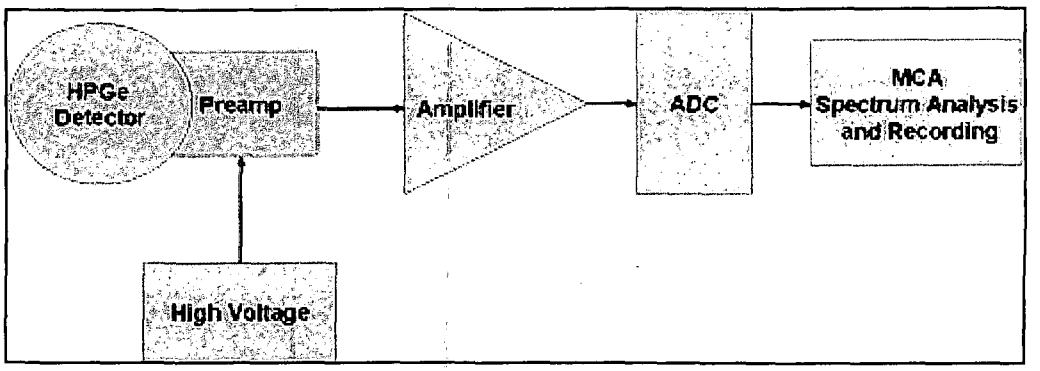


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Fig. 3.9. Components of a typical gamma-ray spectrometry system.

Figure 3.10 shows a histogram of the segregated pulses that are recorded with the X-axis representing energy and the Y-axis representing count rate i.e., intensity of incoming gamma radiation. The obtained distribution of the incoming gamma radiation as pulses (counts) versus their energies is a gamma spectrum. The spectrum is a signature of the original radioisotope, hence can be compared to the reference spectra stored in the isotope library of the detector system software. The photopeaks represent the full energy of the incoming gamma radiation, the fingerprints of the original radioisotopes. The sharper the peaks, the higher the resolution of the detection system i.e., better ability to distinguish two radioisotopes emitting gammas of similar energies. The resolution of gamma spectrometry systems is a function of detector type. HPGe detectors have the highest resolution while scintillator-based detectors, i.e. NaI detectors, have the lowest.

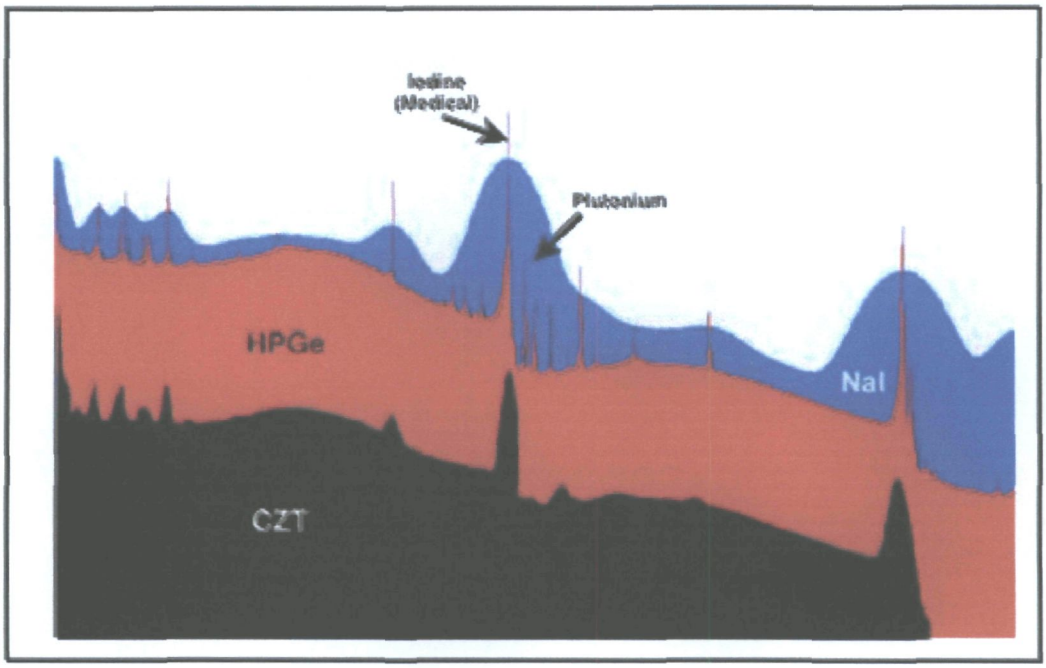

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Fig. 3.10. Radioisotope "fingerprints". Gamma spectra obtained by different types of detector systems.

In order to reduce electronic noise, HPGe detectors must be cooled with liquid nitrogen, making them the most difficult to use in portable field instruments. The scintillator-based detectors operate at room temperature, but with resolution 30 times less than HPGe detectors. The CZT detectors, which can be operated at room temperature, provide a compromise solution. Their resolution is less than HPGe detectors, but much better than scintillator-based detector. The latest in portable high- resolution detector technology for field gamma spectrometry are mechanically-cooled HPGe systems that do not require liquid nitrogen for cooling, instead battery operated mechanical cooling system (heat pump) is incorporated into the detector unit (http://saver.tamu.edu).

HPGe is an ultrapure germanium semiconductor detector or solid state detector with impurity levels as low as 10^{10} atoms/cm^3 that became widely available in the early 1980s (Knoll, 1989). Techniques have been developed to make available large HPGe detectors with depletion or sensitive layer of 1 cm or more. The advantages of large-size HPGe detector is the ability to absorb entirely the incident gamma energy in order to obtain a photopeak, and the corresponding much larger number of information carriers for a given incident gamma ray event that is critical to energy resolution. Consequently, the best energy resolution achievable today is realized through the use of solid state detectors (Knoll, 1989, http://saver.tamu.edu/documents.php). The key considerations of a good spectral data are that the peaks of interest are well shaped and have good "signal to noise" ratio. The minimum detectable activity (MDA) of the detector system is one measure of the quality of a spectrum. The resolution, background and efficiency of the detector are related to the MDA (Cooper, 1970 and www.ortec-online.com, 2005).

At NIRS, the HPGe GS used to indirectly determine the activity concentrations of TENORM in feed coal and ash samples in sealed standard containers, was a closed-end co-axial (ORTEC GEM-100210). The detector was connected to a 16k multi-channel analyzer (MCA) (ORTEC, 7700-010) with a range of 0-4000 keV. The computer software used for gamma-ray spectral analysis was Gamma Studio (Seiko EG & G, 2000). The relative efficiency was 100% at 1.33 MeV relative to that of a standard 3-inch diameter, 3- inch long NaI(Tl) detector. The detector was shielded with 10 cm of lead, inner lined with

20 mm of iron and 5 mm of acrylic plate. The NIRS HPGe GS set-up is shown in Figure 3.11.

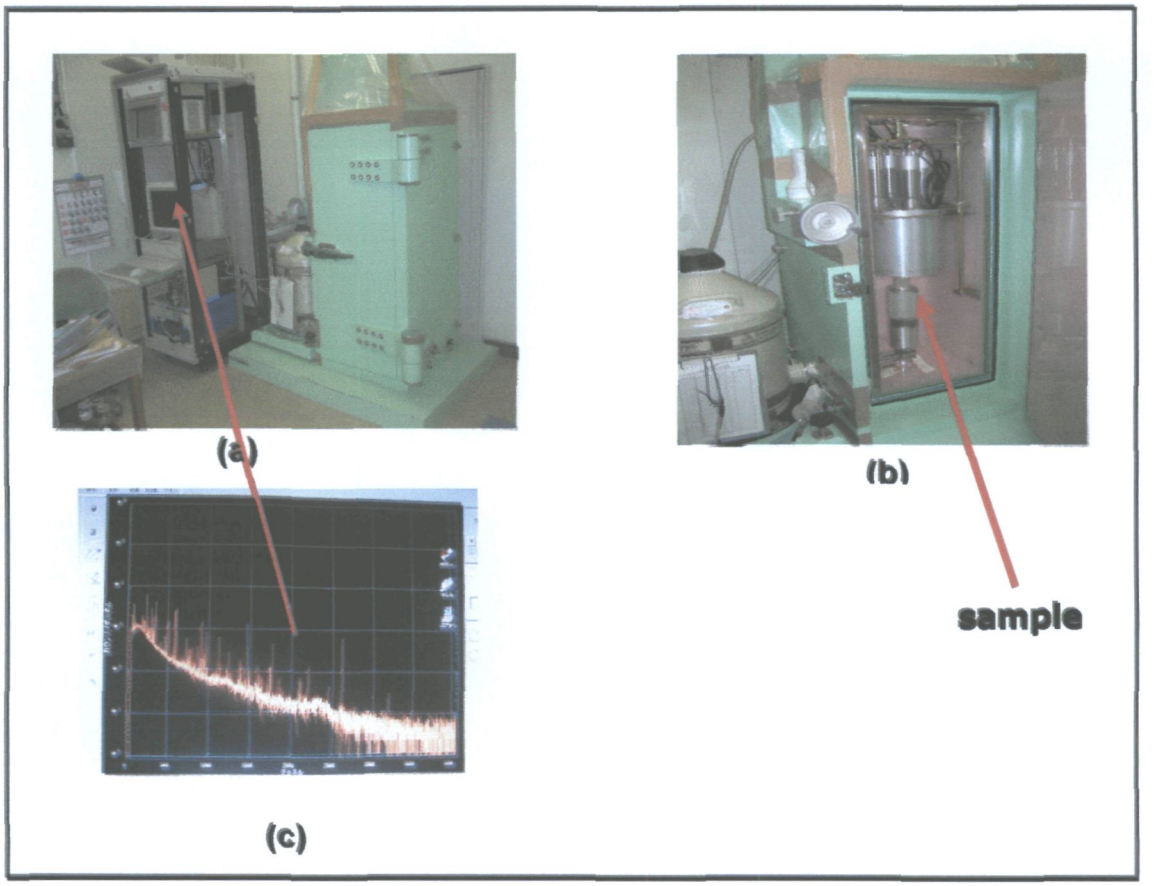


Fig. 3.11. (a) NIRS HPGe GS set-up; (b) sample location; and (c) typical full-energy spectrum as seen on the computer monitor.

To determine the energy dependence of detector efficiency, a 100 g multi-nuclide standard source with quoted gamma energies ranging from 60 keV to 1333 keV, MXO33U8PS, 0288 supplied by Japan Radioisotope Association, with an overall uncertainty of less than 5% (k=2), was used. The standard sample had the same dimensions as the U8 standard cylindrical containers (56 mm diameter; 68 mm) for samples. The detector efficiency with respect to the gamma energy or

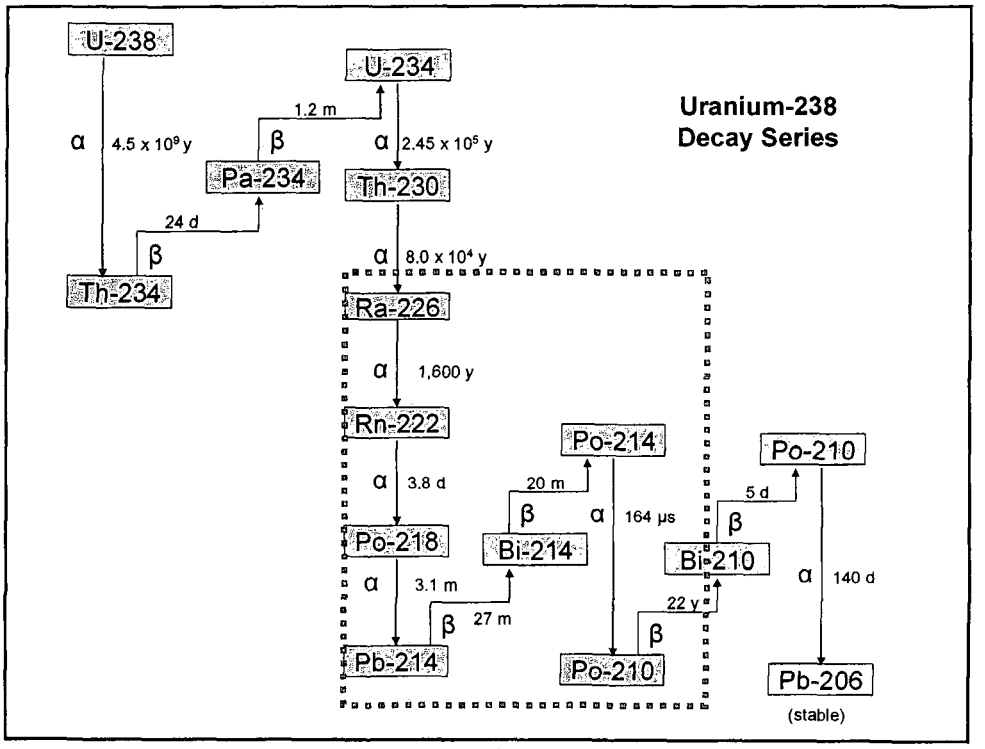
photo-peak of the radionuclides of interest was entered into the computer and was included in the computer generated print-out. Energy calibration versus channel was done using ^{137}Cs and KCl reference sources. The counting time for each sample was pre-set 80,000 sec. Measurements of blank samples (empty containers) were carried-out three (3) times, mid-way and twice towards the last part of the experiment from October 28 to December 2, 2005. A sample print-out of the NIRS HPGe GS is shown in Appendix D.

Table 3.6 lists all the radionuclides and gamma ray energies that were actually measured along with the decay chain origin, the post-combustion source, and the decay product that actually emits each gamma ray. Figures 3.12 (a) and (b) illustrate the portions (enclosed in dashed lines) of ^{232}Th and ^{238}U decay series whereby secular equilibrium was attained in the samples. The gamma-emitting daughters or decay products in secular equilibrium with ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K were counted simultaneously and the degree of decay chain disequilibrium in the ashes due to combustion was determined. The AC of ^{226}Ra was determined indirectly from the mean of the ACs of its gamma emitting decay products in secular equilibrium i.e., ^{214}Pb (295.2 keV), ^{214}Pb (351.9 keV) and ^{214}Bi (609.3.keV), ^{228}Ra from the AC of its decay product, ^{228}A (911.2 keV), and ^{228}Th from the mean of the ACs of the decay products, ^{212}Pb (238.6 keV), ^{212}Bi which is assumed to be equal to the mean of ^{208}Tl (583.2 keV), and ^{208}Tl (2614.53 keV) divided by 0.36, see Table 2.3 (Chapter 2) and Fig. 3.12 (b). The AC of ^{40}K was determined directly from its gamma (1461 keV). The gamma

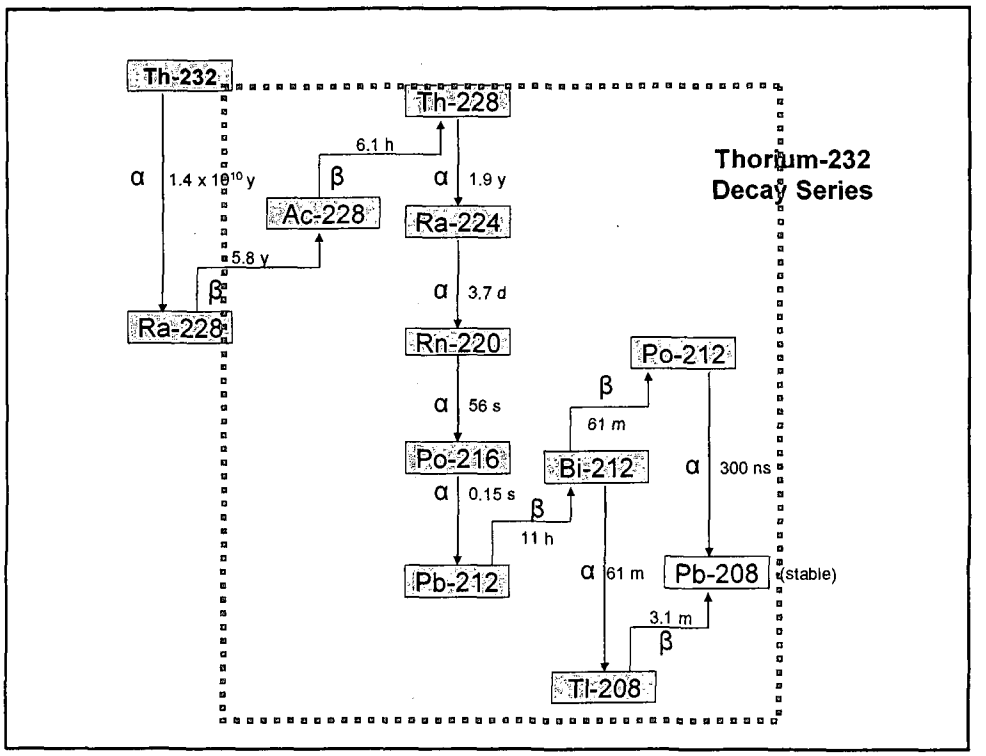
Table 3.6. Naturally occurring radionuclides observed in feed coal and ash samples.

Natural decay chain origin	Source after combustion	Gamma-emitting nuclide	Gamma energy (keV)
^{232}Th	^{228}Ra	^{228}Ac	911
^{232}Th	^{228}Th	^{212}Pb	238
^{232}Th	^{228}Th	^{208}Tl	583
^{232}Th	^{228}Th	^{208}Tl	2614
^{238}U	^{226}Ra	^{214}Pb	295
^{238}U	^{226}Ra	^{214}Pb	352
^{238}U	^{226}Ra	^{214}Bi	609
^{40}K*	^{40}K	^{40}K	1461

*No decay chain



(a)



(b)

Fig. 3.12 (a) ^{238}U decay series; (b) ^{232}Th decay series showing portions (enclosed in dashed lines) to attain secular equilibrium in samples in the laboratory

PNRI HPGe GS

The PNRI HPGe GS was a co-axial EG and G Ortec brand, with Model No. CPVDS30-20190 and Serial No. 2640, connected to a multi-channel analyzer (MCA), Personal Analyzer II (PCA II) with channels corresponding to energy range of 0-2000 keV. The detector and preamplifier were placed inside a lead shield and cooled with liquid nitrogen. The computer software used for gamma-ray spectral analysis was ORTEC Maestro-32, MCA Emulator for Microsoft Windows 98, 2000, NT, and XP (2003). The quoted resolution and

relative efficiency of the detector for 1333 keV (Co-60) were 1.9 keV and 20%, respectively. The PNRI HPGe GS set-up is shown in Figure 3.13.

Fig. 3.13. PNRI HPGe GS set-up.

The efficiency calculation (based on FINDPEAK Computer Code by L. Leopando, PNRI, Jan. 2000 version) for the PNRI HPGe detector was previously generated using a 250 mL (250.2 g) multi-nuclide standard source with quoted gamma energies ranging from 60 keV- 1836 keV, with overall uncertainty of less than 5%. The container of the standard source was a 250 mL wide mouth Nalgene bottle (Isotope Products Laboratories, USA). The reference date of the standard source was 15 Aug. 2005. The gamma energy versus channel calibration was done using ^{137}Cs and ^{60}Co reference sources. Measurements of blank samples (empty containers) were carried-out in between counting times from Sept 2005 – Dec 2006. The counting time for each sample was 80,000 sec. The same gamma-emitting radionuclides in the samples were analyzed as in the NIRS HPGe GS, except ^{208}Tl (2614.5 keV). A sample spectrum generated from

the PNRI HPGe GS is shown in Figure 3.14. A sample PNRI HPGe GS printed output that contains the data used in the calculation of the activity concentration is presented in Appendix E.

The activity concentration (AC) was calculated using the equation below:

AC (Bq/kg) (E_γ) = [sample count – blank count] / [m x E_γ x BR_γ]

Where, m = mass of sample

E_γ = efficiency at full energy or photo-peak count

BR_γ = gamma branching ratio or gamma emission probability

An attempt was made to calculate the expanded relative uncertainty, U (k=2) of all HPGe measurements using the following standard deviations:

u1– standard deviation of sample photo-peak counts taken from system print-out

u2– standard deviation of blank photo-peak taken from system print-out

u3 – uncertainty in weighing the sample ~ 2% mass of sample (estimated)

u4 – uncertainty in weighing the sample container) ~ 2% (estimated)

u5 – uncertainty of detector efficiency at photo-peak ~ 5% (estimated)

u6 - uncertainty of BR (branching ratio) values taken from the Table of Isotopes, 8th ed, 1996

U (k=2) = 2 x AC x square root of the sum of squares of u1 to u6

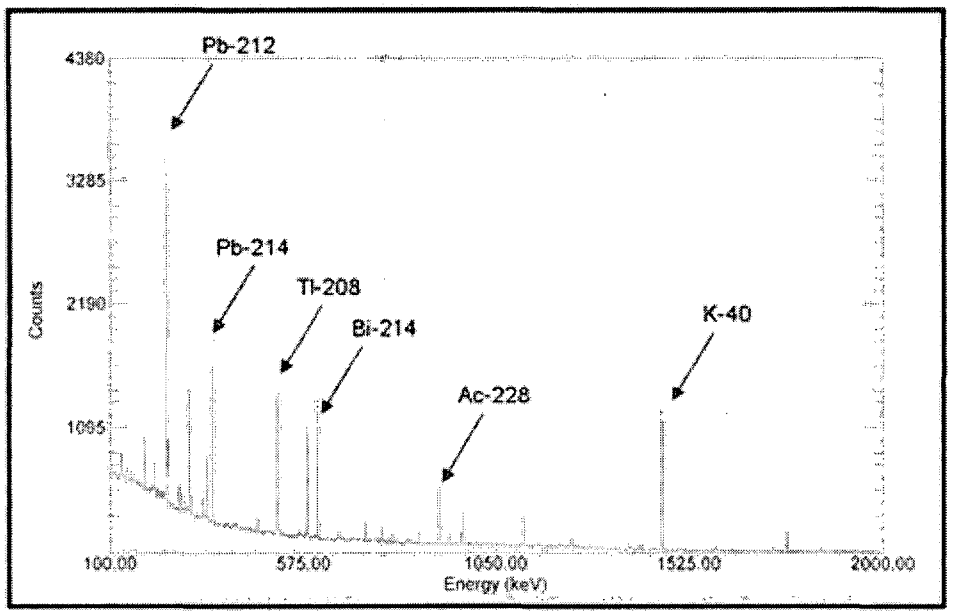


Fig. 3.14. Pulse height spectrum of gamma rays from the decay products in equilibrium with ^{226}Ra, ^{228}Ra, and ^{228}Th in bottom ash sample, generated by PNRI HPGe GS

3.4 Absorbed gamma dose rate determination using portable gamma ray spectrometer

Absorbed gamma dose rates inside and in the vicinity of Plant C were measured during the Multipartite Monitoring Activities in December 2005 and June 2006. The locations of the measurements were along the terrestrial transect lines (TL) established by Plant C for the survey of vegetation and collection of insect samples.

The portable gamma ray spectrometer used is shown in Figure 3.15. It consists of a GR-256 spectrometer console and a GPS-21 NaI detector. A detailed description of its operation and calibration is discussed elsewhere (Reyes, 2001). The instrument directly gives measurements in % for K and parts per million (ppm) for Th and U. The data obtained were used to calculate the

gamma absorbed dose rate in air in nanogray per hr (nGy/hr) at 1 meter above the ground in various locations inside and in the vicinity of Plant C. For each location, the activity concentration was calculated from an average of five (5) measurements of concentration in pct for K, and ppm for U and Th. Measurements were performed in about fifty locations. The coordinates of each location were determined using a portable global positioning system (GPS). Figure 3.16 shows the locations on the map where measurements were performed. Some photos of these locations are shown in Appendix H.

Shown below are the conversion factors of portable gamma spectrometry (PGS) measurements (ppm for U and Th and pct for K-40) to gamma absorbed dose rate (nGy/hr) at 1 m above the ground.

Dose rate (^{40}K) = data PGS (pct) x 313 (Bq/kg)/pct x 0.0417nGy/hr

Dose rate (^{238}U) = data PGS (ppm) x (12.35 Bq/kg) x 0.462nGy/hr

Dose rate (^{232}Th) = data PGS (ppm) x (4.06 Bq/kg) x 0.0.604nGy/hr

Total dose rate (nGy/hr) = dose rate (^{40}K) + dose rate (^{238}U) + dose rate (^{232}Th)

Conversion factors:

^{40}K	^{238}U	^{232}Th
1 pct = 313 Bq/kg	1 ppm =12.35 Bq/kg	1ppm = 4.06 Bq/kg
1 Bq/kg = 0.0417 nGy/h	1 Bq/kg = 0.462 nGy/h	1 Bq/kg = 0.604 nGy/h

Fig. 3.15. (a) Portable gamma spectrometer (PGS) instrument on a calibration pad; and (b) close–up of the PGS control pads.

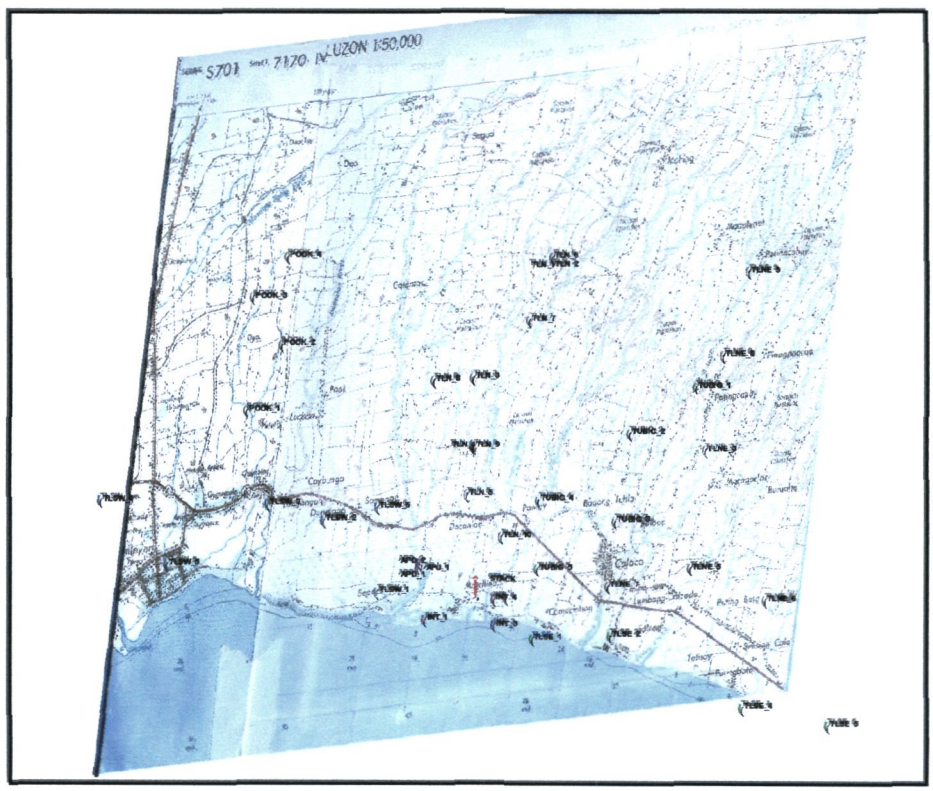


Fig. 3.16 Map location of absorbed gamma dose rate in air measurements in the vicinity of Plant C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Activity concentration of feed coal, bottom ash and fly ash samples of four coal-fired thermal power plants (NIRS analysis), 2005 sampling

4.1.1 NIRS ICP-MS and HPGe

Activity concentration (AC) of ^{232}Th and ^{238}U measured by ICP-MS

The activity concentration, i.e. activiity per unit mass of feed coal (FC), bottom ash (BA), and fly ash (FA) from four coal fired thermal power plants in the Philippines, were measured directly by mass in the case of ^{232}Th and ^{238}U using ICP-MS, indirectly in the case of ^{226}Ra, ^{228}Ra, ^{228}Th through their gamma emitting decay products using HPGe, and directly for gamma-emitting ^{40}K using also HPGe.

Table 4.1 presents the mass concentration (MC) determined by NIRS ICP-MS, and the calculated AC (Bq/kg) of ^{232}Th and ^{238}U in FC, BA and FA samples collected in 2005 from four coal-fired thermal power plants, C, M, P, and S. The FA samples from Plant C were taken from the different ESP stages: 1st, 2nd and 3rd stages.

The relative ACs of the three types of samples from four coal-fired thermal power plants are illustrated in Figure 4.1. Plant S used feed coal from Shinwa, China with the highest AC followed by Plant M which also used feed coal from Tianjin, China. Plants C and P using feed coal from the Philippines and Indonesia

Table 4.1. Mass and activity concentrations of ^{232}Th and ^{238}U in FC, BA and FA samples from Plants C, M, P and S measured by NIRS ICP-MS.

Type of samples	No. of samples	MC (µg/g)		AC (Bq/kg)			
		^{232}Th	^{238}U	^{232}Th	U (k=2)	^{238}U	U (k=2)
Plant C-Unit 1; Origin of coal: Semirara, Philippines; Sampling date: 15-18 Jun 2005							
FC	1	0.65	0.21	2.62	0.26	2.61	0.10
BA	1	10.33	2.43	41.66	1.67	30.21	1.21
ESP 1st	1	17.23	4.81	69.49	2.78	59.8	2.39
ESP 2nd	1	16.81	5.63	67.79	2.71	69.99	4.20
Plant M; Origin of coal: Tianjin, China; Sampling date: 8 August 2005							
FC	1	2.06	0.47	8.31	0.33	5.84	0.12
BA	1	15.15	4.47	61.1	1.22	55.57	1.66
FA	1	15.64	6.69	63.08	3.78	83.17	0.00
Plant P; Origin of coal: Indonesia; Sampling date: September 2005							
FC	1	0.79	0.23	3.19	0.32	2.86	0.11
BA	1	17.99	4.66	72.55	4.35	57.93	3.48
FA	1	38.67	21.56	155.96	6.24	268.03	10.72
Plant S; Origin of coal: Shinwa, China; Sampling date: August 2005							
FC	1	3.91	1.1	15.77	0.32	13.67	0.82
BA	1	20.05	8.06	80.86	3.23	100.2	4.01
FA	1	21.57	10.65	86.99	5.22	132.4	10.59
Reference sample (lake sediment, JLK-1)	1	19.39	3.85	78.1	3.13	47.86	2.87
Recommended values of N. Imai, et al. (1996)		19.5	3.83				
Error with recommended values		0.56	0.52				

U (k=2) - Expanded relative uncertainty at 95% confidence level

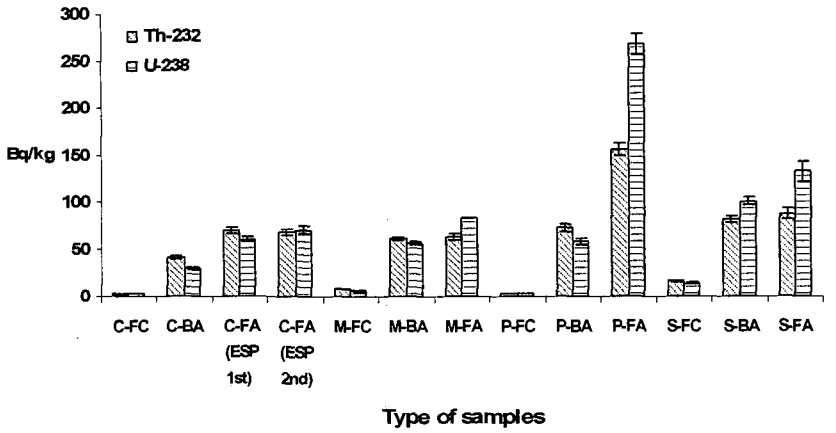


Fig. 4.1. Comparison of ACs of ^{232}Th and ^{238}U in FC, BA and FA samples from Plants C, M, P and S.

respectively, had the lowest AC of ^{232}Th and ^{238}U. The BA sample from Plant S had the highest AC of ^{232}Th and ^{238}U while the FA sample from Plant P had the highest AC of ^{232}Th and ^{238}U. BA and FA samples from Plants C and M had comparable ACs of ^{232}Th and ^{238}U.

Activity concentration (AC) of ^{226}Ra (^{238}U series), ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K measured by HPGe GS

Because of the relative ease of sample preparation and less cost involved using the HPGe GS as compared to ICP-MS, the same number of split samples analyzed by ICP-MS plus additional FA and ash pond samples from Plants C and P were analyzed by this indirect method.

The ACs of ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K in split samples of FC, BA and FA from Plants C, M, P, and S determined by NIRS HPGe GS are presented in Table 4.2 and illustrated in Figures 4.2-4.4. In general, the results show that the ACs of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K are all enhanced in the BA and FA samples as compared with the ACs in the FC samples from Plants C, M, P, and S. The

behavior of ^{238}U with respect to ^{226}Ra and ^{232}Th with respect to ^{228}Ra after combustion can be deduced from Figures 4.2 and 4.3. Before combustion, ^{232}Th, ^{228}Ra and ^{228}Th appear to be generally in equilibrium in feed coal samples, except for Plant C, as seen in Figure 4.2. In Figure 4.3, ^{238}U and ^{226}Ra show similar behavior (equilibrium in FC samples, except for Plant C). After combustion, the equilibrium was disturbed and the degree of partitioning of the radionuclides between BA and FA were disturbed. The degree of partitioning was influenced by their volatility and geochemical association, as explained by Coles, et al. (1979).

Table 4.2. ACs (Bq/kg) of ^{226}Ra, ^{228}Ra, and ^{228}Th measured by NIRS HPGe

Type of sample	No. of samples	^{238}U series		^{232}Th series				^{40}K	
		^{226}Ra		^{228}Ra		^{228}Th			
		AC	U	AC	U	AC	U	AC	U
Plant C-Unit 1; Origin of coal: Semirara, Phil.; Sampling date: 15-18 Jun 2005									
FC	1	11.70	1.39	13.65	4.99	11.35	3.96	80.23	10.91
BA	1	29.90	2.20	37.04	4.83	33.55	7.33	259.76	28.54
Econ	1	36.01	2.44	41.54	5.21	40.47	7.70	244.96	26.72
ESP 1st	1	53.43	3.43	61.96	7.46	55.86	10.85	369.08	40.87
ESP 2nd	1	56.31	3.64	74.04	8.85	57.62	10.54	382.20	39.39
Plant M; Origin of coal: Tianjin, China; Sampling date: 8 August 2005									
FC	1	6.74	1.24	6.44	1.88	5.64	2.86	30.74	6.44
BA	1	106.73	6.74	59.48	7.62	58.33	11.16	217.09	25.10
FA	1	109.57	6.82	67.19	8.56	62.22	11.32	229.85	26.93
Plant P; Origin of coal: Indonesia; Sampling date: September 2005									
FC	1	1.84	1.27	1.72	1.66	<MDL		13.90	5.70
BA	1	51.58	3.55	55.79	7.13	56.51	10.81	203.94	23.55
FA	1	50.79	3.35	65.22	7.87	60.71	11.16	197.71	22.17
Plant S; Origin of coal: Shinwa, China/Semirara; Sampling date: August 2005									
FC	1	10.11	1.46	12.08	2.48	8.87	3.27	51.80	8.88
BA	1	83.27	5.26	66.64	8.16	62.95	11.69	400.93	43.06
FA	1	131.13	8.09	87.70	10.45	82.07	14.93	354.47	38.18
Total	**14**								

U (k=2)-Expanded relative uncertainty at 95% confidence level
MDL-Minimum detection limit (4.66 x std. deviation of mean background count)

Figure 4.2 also shows that (except for ^{232}Th in Plant P FA sample) ^{232}Th, ^{228}Ra, and ^{232}Th are partitioned comparably in the BA and FA samples of the four Plants. In contrast, ^{238}U is significantly higher in all FA samples compared to BA samples as seen in Figure 4.3. In the same Figure, ^{226}Ra can be seen to be about equally partitioned in Plants M and P BA and FA samples, and slightly increased in Plants C and S FA samples compared to their BA samples.

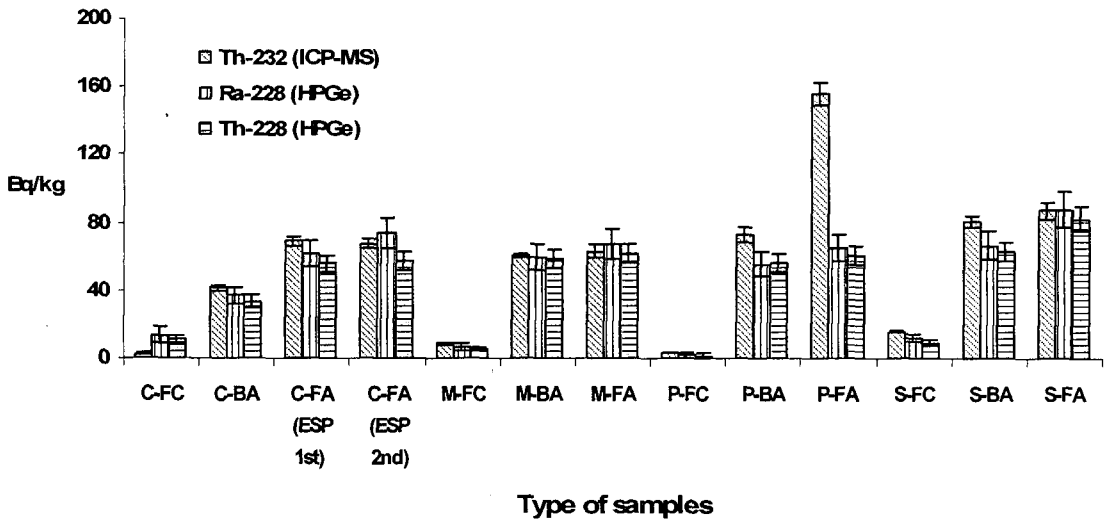


Fig. 4.2. Comparison of ACs of ^{232}Th, ^{228}Ra and ^{228}Th (^{232}Th series) in samples from Plants C (Unit 1), M, P, and S measured by NIRS ICP-MS and HPGe.

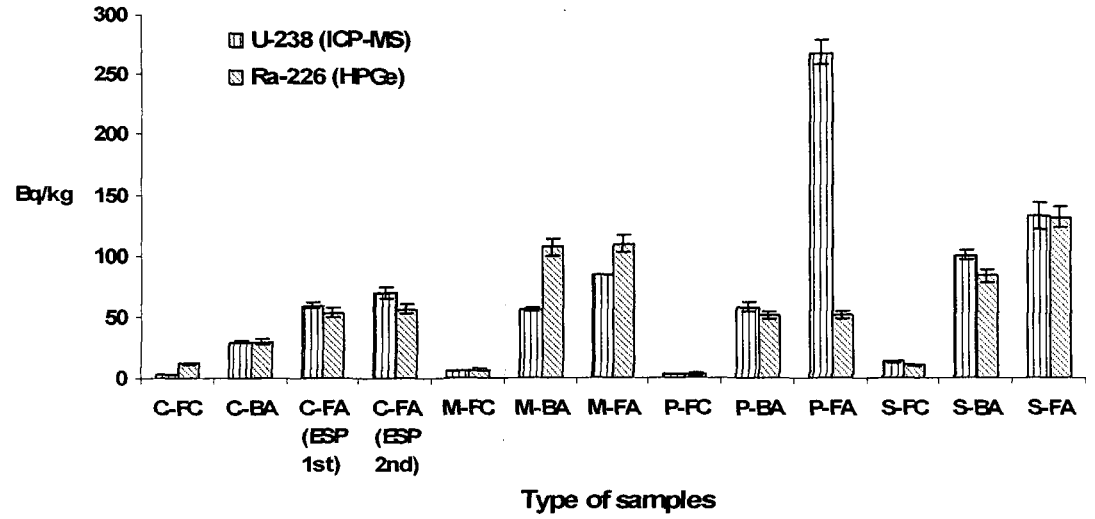


Fig. 4.3. Comparison of ACs of ^{238}U and ^{226}Ra (^{238}U series) in samples from Plants C (Unit 1), M, P, and S measured by NIRS ICP-MS and HPGe.

Fig. 4.4 presents the summary of AC results of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K in FC, BA and FA samples from Plants C, M, P, and S. It can be easily seen that, among the radionuclides, ^{40}K AC is highest in BA and FA samples from Plants C, M, P and S (except for ^{238}U in the FA of Plant P), and that ^{40}K is partitioned about equally in Plants M, P and S BA and FA samples.

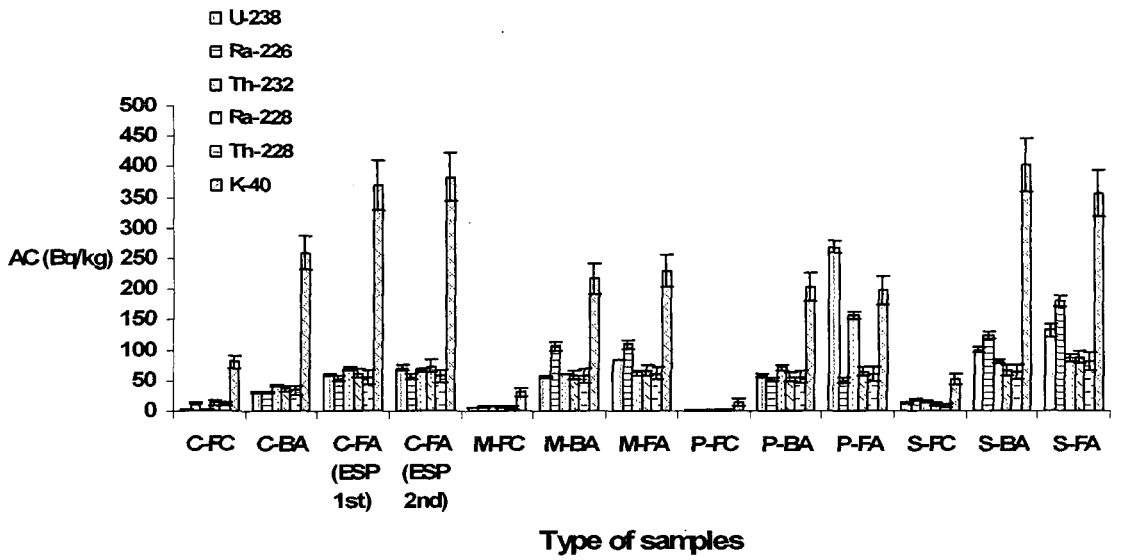
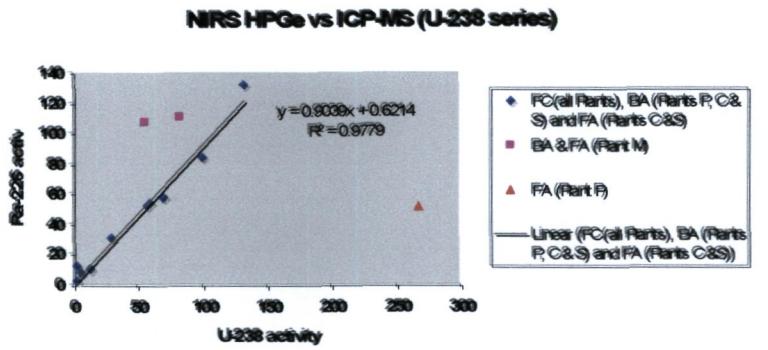


Fig. 4.4. Comparison of ACs of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K in FC, BA and FA samples from Plants C, M, P, and S measured by NIRS ICP-MS and HPGe.

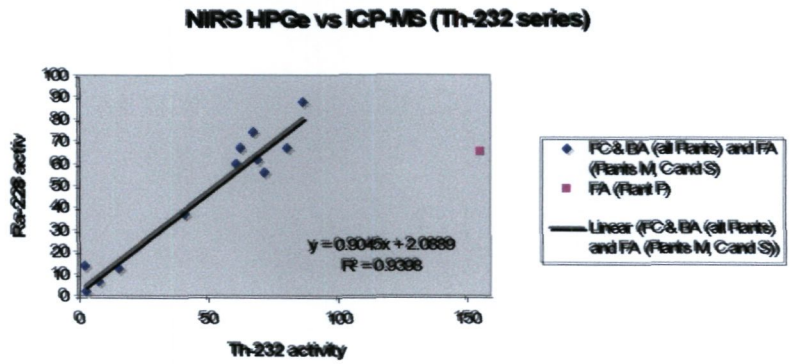
Comparison of NIRS ICP-MS and HPGe results

Figures 4.5 (a) and (b) show the correlations of ^{226}Ra with ^{238}U, and ^{228}Ra with ^{232}Th, respectively, of all samples analyzed by NIRS HPGe and ICP-MS. With the exception of a few data points, good correlation was obtained for the two analytical techniques used for both ^{238}U and ^{232}Th series. Slopes for the HPGe vs ICP MS data had values near unity (around 0.90) and intercepts were near zero (0.62 and 2.1 Bq/kg). These indicate an approximate one to one correspondence between the two techniques. Correlation coefficients (R^2) were also good for both ^{238}U and ^{232}Th series, with values of 0.94 and 0.98 respectively. The data points for Plant P FA sample were most aberrant in the correlation plots for the two series, with the FA and BA samples of Plant M aberrant to a lesser degree in the ^{238}U series. The results indicate that the HPGe analytical technique can generally be used for activity measurements for the two

series, instead of the more expensive ICP-MS method. However, the ICP-MS method is more direct and is assumed more accurate, since it measures mass concentrations, particularly for ^{238}U and ^{232}Th.



(a)



(b)

Fig. 4.5. Correlations of ACs in all samples from Plants C, M, P and S measured by NIRS HPGe and ICP- MS (a) ^{238}U series (b) ^{232}Th series.

HPGe is presently the method often used to estimate the ACs of ^{238}U and ^{232}Th based on their gamma emitting decay products. However, this is an indirect method and is based on the assumption that secular equilibrium exists between these two radionuclides and their decay products. In this study, Figures 4.5 (a) and (b) support the assumption (the values of R^2 and the slopes of the curves

are ~ 1. However, even for the limited scope of this study, there are exemptions (refer to same Figures).

In the coal, secular equilibrium between ^{238}U and ^{232}Th and their decay products may exist, especially when the coal is undisturbed for very long period of time. But this is not true for disturbed coal or relatively "young coal" e.g., lignites and sub-bituminous. Definitely, secular equilibrium also does not exist in combusted coal or in ashes. Therefore, ICP-MS is still the preferred method since ^{238}U and ^{232}Th can be directly determined.

4.1.2 AC enhancement in BA and FA samples

The actual enhancement of AC of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, ^{228}Th (^{232}Th series) and ^{40}K, due to loss of carbon during combustion in ash samples with respect to that in FC samples is presented in Table 4.3 and is illustrated in Fig. 4.6. The highest enhancement (among the AC's of ^{238}U, ^{226}Ra [^{238}U series], ^{232}Th, ^{228}Ra, and ^{228}Th [^{232}Th series]) occurred in Plant P FA sample. It was also this sample that was most aberrant in the HPGe versus ICP-MS correlation plots. The enhancement of ^{238}U AC is consistently higher in all FA samples compared to that in BA samples. The enhancement of ^{232}Th in Plants C and P FA samples is higher than that in the BA samples, and about the same in the BA and FA samples of Plants M and S. For ^{226}Ra, Plants C and S FA samples are slightly more enhanced compared to BA samples, while BA and FA samples of Plants M and P have about the same enhancement. ^{228}Ra in all FA samples is slightly more enhanced compared to BA samples. For ^{228}Th and ^{40}K, enhancement is about the same in the BA and FA samples of all Plants.

Table 4.3. Ratio of AC of radionuclides in BA and FA samples with that in FC samples (actual AC enhancement).

	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th	^{40}K
C-BA	11.57	2.55	15.90	2.71	2.96	3.24
C-FA (ESP 1st)	22.91	4.56	26.52	4.54	1.38	4.60
C- FA (ESP 2nd)	26.82	4.81	25.87	5.43	1.03	4.76
M-BA	9.52	15.84	7.35	9.24	10.33	7.48
M-FA	14.24	16.26	7.59	10.44	11.02	7.48
P-BA	20.26	16.89	22.74	32.42	36.34	14.67
P-FA	93.72	16.63	48.89	37.89	39.04	14.23
S-BA	7.33	8.24	5.13	5.52	7.10	7.74
S-FA	9.69	12.97	5.52	7.26	9.26	6.84

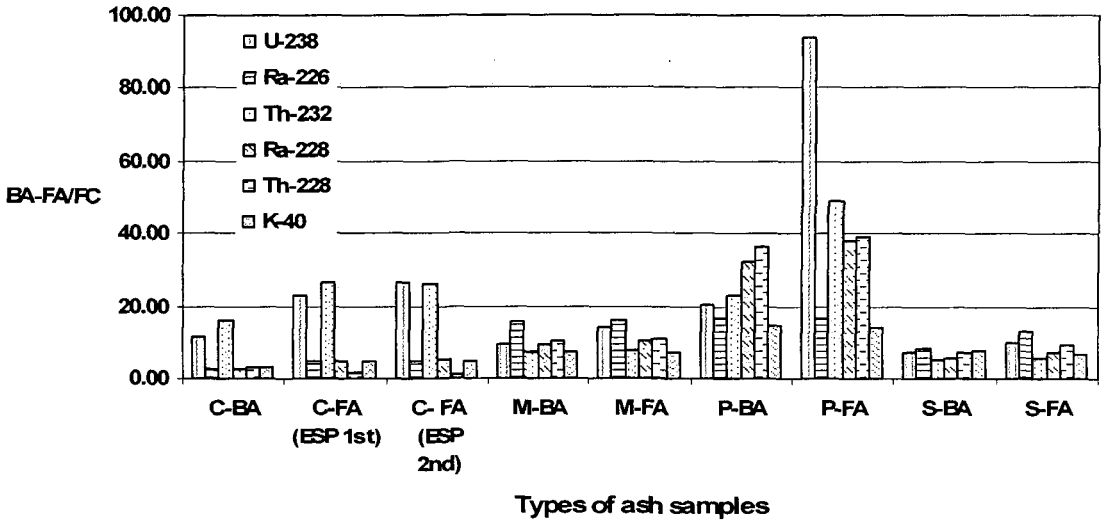


Fig. 4.6. Actual enhancement of radionuclides in ash samples with respect to that in FC samples due to loss of carbon from combustion.

4.1.3 Radionuclide partitioning in BA and FA

The degree of partitioning of the radionuclides between BA and FA could be attributed to the different physical and chemical characteristics of ^{238}U and ^{226}Ra and ^{232}Th and ^{228}Ra and their association with the alumino-silicate in the coal (Coles, 1978). Analysis of the partitioning is discussed below using

enrichment factor calculations and AC comparison of BA and FA samples per Plant.

Enrichment factor

The enrichment factor (EF), defined as the ratio of AC of the radionuclide [X] and ^{40}K in a BA or FA sample divided by the corresponding ratio in the FC sample, was determined according to the formula used by Coles, et al. (1978); Tso and Leung (1996); and Mandal and Sengupta (2003) as follows:

EF = {[X] ash sample/[40K] ash sample}/ {[X] feed coal/[40K] feed coal}

This in effect normalizes the apparent enrichment resulting from loss of carbon during the combustion process. ^{40}K is used for the normalization process because its concentration remains more or less constant in ash samples, hence assumed to be a tracer for the alumino-silicate dominated ash matrix (Coles, et al., 1978). The AC values of ^{40}K determined by NIRS HPGe were used in the EF calculation and the results are presented in Table 4.4. As shown in Figure 4.6, the AC ratios of BA and FA samples (relative to FC) for ^{40}K are approximately the same for each Plant.

For a particular radionuclide, an EF value >1 indicates enrichment in the ash sample relative to feed coal. The EF values vary considerably among ash samples from the four coal power plants. This variation could be attributed to the different geographical locations of coal origin used each plant that may have influenced the chemical and physical characteristics of ^{238}U, ^{232}Th and their decay products. (Coles, et. al., 1978). Another factor that may have influenced EF is the volatility of the radionuclides, which could vary depending on the coal

chemical and physical composition and the boiler temperature of the plant. The boilers of the four Plants, however, were operated at similar temperatures of about 550°C.

Figure 4.7 compares the EF of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, and ^{228}Th (^{232}Th series) in BA and FA samples from all plants. The EF in the FA samples is generally higher than the EF in BA samples. It can be observed that the EF of ^{238}U in Plant C ash samples increased along the ESP 1st and 2nd collection stages (decreasing particle size as the ESP stage approaches the stack), while the EF of ^{232}Th slightly decreased with decreasing particle size of fly ash.

In the report of Coles, et al. (1978), ^{238}U showed slight depletion (EF<1) in the bottom ash collected from two USA coal power plants. However, the EF of ^{238}U showed a very definite increase with decreasing particle size, whereas ^{232}Th and ^{226}Ra showed slight small particle preference in post ESP size-classified fly ash. As explained by Coles, et al., the depletion of ^{238}U in the bottom ash samples probably occurred due to volatilization and later condensation onto the finer fly ash matrix of Plants M and S. Based on this, the EFs of Plants M and S samples could be expected to be higher in the finer fly ash in the latter ESP stages towards the stack as in the case of Plant C ESP 3rd stage sample. This could also be true for Plant P. This can only be confirmed when more samples taken from the different stages of Plants M, P, and S are analyzed.

Table 4.4. EF values in BA and FA samples normalized with K-40.

	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th
C-BA	3.57	0.91	4.91	0.84	0.91
C-FA (ESP 1st)	4.98	1.14	5.77	0.99	1.07
C- FA (ESP 2nd)	5.63	1.16	5.43	1.14	1.07
M-BA	1.35	0.57	1.04	1.31	1.46
M-FA	1.90	0.55	1.02	1.40	1.47
P-BA	1.38	1.33	1.55	2.21	2.48
P-FA	6.59	1.35	3.44	2.66	2.74
S-BA	0.95	1.06	0.66	0.71	0.92
S-FA	1.42	1.90	0.81	1.06	1.35

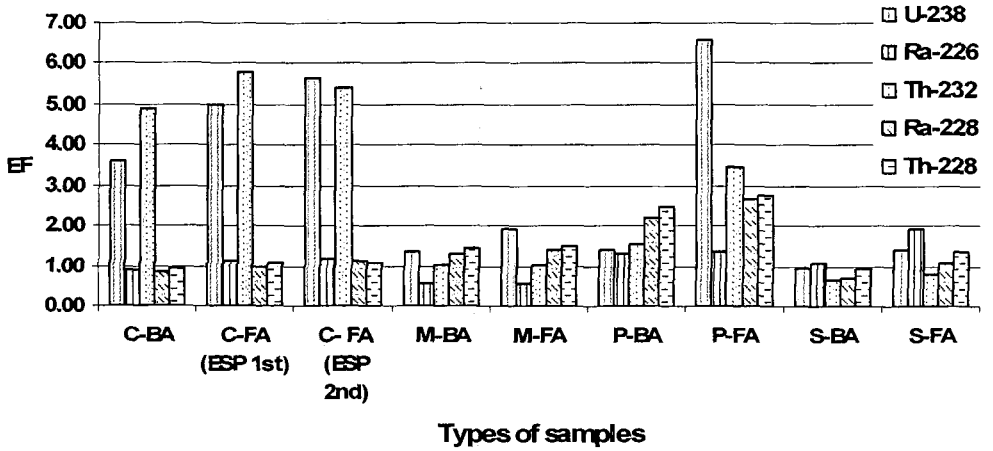


Fig. 4.7. Comparison of EFs of ^{238}U, ^{226}Ra (^{238}U series), ^{232}Th, ^{228}Ra, and ^{228}Th (^{232}Th series) in BA and FA samples from Plants C, M, P, and S

For ^{232}Th, the BA and FA samples of Plants M and S have lowest EFs which are less than or approximately equal to 1, thus showing depletion or no ^{232}Th enrichment. Plant C and Plant P ash samples, however, show enrichment for ^{232}Th, with Plant C having the highest EFs. For ^{238}U, all ash samples show enrichment (except the BA sample of Plant S) with the FA sample of Plant P having the highest EF. Except for Plant S FA sample, ^{226}Ra EF is about 1 or <1

for the rest of the BA and FA samples. ^{228}Ra and ^{228}Th EFs in Plants C, M and S BA and FA samples are about 1 and about 2-3 in Plant P BA and FA samples.

The behavior of ^{232}Th tends to confirm its classification as among the lithophilic elements (associated with aluminosilicate minerals) which show little or no enrichment on the smaller fly ash particles (Coles, et al., 1979). However, ^{232}Th is normally associated with the very chemically resistant mineral zircon ($ZrSiO_4$), which is ubiquitous in many common rocks. Zircon does not weather easily and is commonly found in sedimentary environments. These elements are not easily volatilized in the combustion zone, but instead form a melt of uniform composition that become both fly ash and bottom ash or slag (Klein, et.al., 1975). As a lithophilic element, Th is expected to be volume distributed in the aluminosilicate matrix of the fly ash. Seames and Wendt (2000) also reported that Th, similar with Cs, and Co, is reactive with aluminum compounds in the submicron particles. If Th existed in the coal as submicron particle, then it could be carried with the gases after combustion and follow the course of the fly ash (Coles, et al., 1978; Seames and Wendt (2000). If this is the case, Th could also be enhanced in the fly ash but to a lesser extent compared to U.

The results for ^{238}U in Plant C fly ash samples seem to indicate an increasing AC in the finer fly ash that agrees with the observation of Coles, et al., (1978) that U has the greatest small particle enrichment among elements that were neither lithophiles nor chalcophiles (elements associated with sulfide minerals). The small particle enrichment of U is the result of its bimodal phases in the coal (both organic and inorganic associations), with subsequent formation of

the volatile species (UO_3) from the uraninite ($UO_{2)}$ in the organic fraction, resulting to its high volatility upon combustion. This behavior of ^{238}U along the ESP fly ash collection system was also observed by Papastefanou and Charalambous, (1983), Manolopoulou and Papastefanou (1991), Karangelos, et al., (2004).

Beck, et al. estimated, based on Coles, et al. (1978) data, that the fly ash escaping from a typical modern 1000 MWe plant meeting the EPA particulate emission standards will be enriched in ^{238}U by a factor of 2 and ^{226}Ra by a factor of 1.5. No enrichment was expected for other radionuclides over the AC content of FC. Compared to the estimates of Beck, et al., the results in this study for ^{226}Ra (EF range; 1.1-1.9; Mean = 1.4) are similar while for ^{238}U (EF range; 1.4-6.6; Mean=5.4), are higher. ^{232}Th, however, which was predicted by Beck, et al. to have no enrichment, had an EF range of 0.8-5.8 (Mean=1.7). The variation of ACs of radionuclides in the fly ashes according to Tadmor (1986) is influenced by many factors as mentioned in Chapter 2 (Section 2.5) such as the ACs in the feed coal, the chemical characterisitics of the radionuclides, the fusibility temperature of ash, combustion conditions, and the filtration system of the power plants.

Relative enhancement of radionuclides based on AC_{FA}/AC_{BA} values

The ratios of AC_{FA}/AC_{BA} for ^{232}Th and ^{238}U are presented in Table 4.5 and comparison of the relative values is shown in Figure 4.8. All Plant samples have AC_{FA}/AC_{BA} >1 and all Plants have AC_{FA}/AC_{BA} for ^{238}U greater than the values for

^{232}Th. Like the EF results for Plant C, the AC_{FA}/AC_{BA} ratios increased for ^{238}U and slightly decreased for ^{232}Th, from the 1st to the 2nd ESP stage.

Based on the AC_{FA}/AC_{BA} values in Table 4.5 and as shown in Fig. 4.8, ^{238}U and ^{232}Th are not equally partitioned between BA and FA ash. This can be explained by the difference in their volatility. ^{238}U is more volatile than ^{232}Th hence ^{238}U is more enriched in the fly ash samples than ^{232}Th.

^{226}Ra and ^{228}Ra are generally slightly enriched in the ash samples (relative to the bottom ash), except for ^{226}Ra of Plants M and P. It was reported by Manolopoulou and Papastefanou (1991) Karangelos, et al. (2004) and Coles, et al. (1978) that ^{226}Ra tends to be more associated with the smaller fly ash particles than ^{228}Ra since ^{226}Ra resides in the uraninite portion of its ^{238}U parent to form a more mobile species as in the bimodal bound U, unlike the silicate-associated ^{228}Ra from the ^{232}Th decay series. The results for these two radium nuclides in this study have no consistent agreement with these literature observations.

AC_{FA}/AC_{BA} values for ^{40}K in Plants C and M ash samples is ~1 or is <1 in Plants M, P and S which confirms ^{40}K behavior classification as readily incorporated into the bottom ash and is partitioned about equally between the fly ash and bottom ash (Klein, et al., 1975; Coles, et al., 1978). However, Hedvall and Erlandsson (1991) observed that an increase in the furnace temperature of a peat-fired power plant caused a decrease in ^{40}K in the bottom ash. This plus other factors could have caused ^{40}K enhancement in the FA (relative to BA) of Plant C.

Table 4.5. **Relative values of radionuclide activity in fly ash samples using ratios of AC_{FA}/AC_{BA}.**

	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th	^{40}K
C ESP 1st	1.98	1.67	1.79	1.67	1.48	1.42
C ESP 2nd	2.32	1.63	1.88	2.00	1.72	1.47
M Fly ash	1.50	1.03	1.03	1.13	1.07	1.06
P Fly ash	4.63	2.15	0.98	1.17	1.07	0.97
S Fly ash	1.32	1.08	1.57	1.32	1.30	0.88

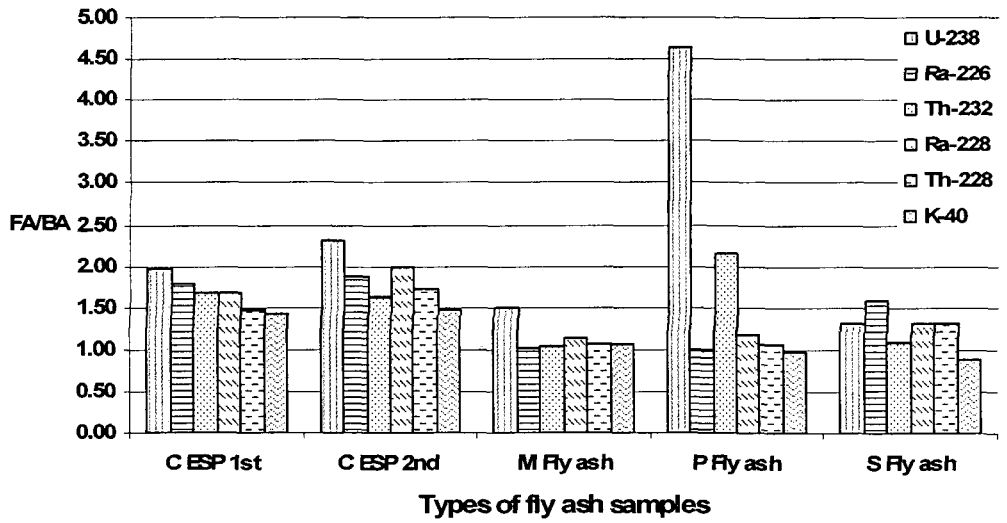


Fig. 4.8. Comparison of AC_{FA}/AC_{BA} values.

4.2 AC of FC, BA, and FA samples of four coal-fired plants (PNRI HPGe analysis), 2005 sampling

Split-samples from Plant C (Unit-1) and Plant P (Unit-1) collected in 2005, FA sample from the ESP 3rd stage of Plant C (Unit-1) , and additional sets of FC, FB, and FA samples from Plants M and S, also collected in 2005, a total of 31 samples, were analyzed by PNRI HPGe GS (gamma spectrometry). Table 4.6 and Figures 4.9, 4.10 and 4.11 present the results by PNRI HPGe spectrometry and comparison of the results by NIRS HPGe and PNRI HPGe.

Comparison of PNRI and NIRS HPGe results

In general, the ACs of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K determined by PNRI HPGe GS, follow the same trend as the ACs determined by NIRS HPGe GS. The additional results of ACs in the sample collected from the ESP 3rd stage of Plant C Unit-1 show that ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K tend to significantly increase towards the latter stages of Plant C Unit-1 ESP where FA particles are expected to be finer (see Figure 4.9).

The ACs of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K in Plant M samples of 1 September 2005 are generally much higher (by a factor of ~2) by PNRI HPGe than the ACs in Plant M samples of 8 August 2005 by NIRS HPGe, despite similar coal origin-China. On the other hand, the ACs in Plant S set of samples, although coming from the same bulk samples of August 2005, are higher (by a factor ~2) by PNRI HPGe compared to the ACs obtained by NIRS HPGe.

Figures 4.10 and 4.11 show that the ACs Comparing the results by PNRI HPGe GS are generally higher than the corresponding ACs by NIRS HPGe GS. The difference could be attributed to the use of slightly different geometry between the sample and the standard. At NIRS, standard container (U8) for samples and standard source (MX033U8PS, Certificate of Calibration, Japan Isotope Association, 2005) was used. Even if the samples were homogenized and standard container was used, the mass differed because the densities of the samples (FC, BA, and FA) were not exactly the same. The sample containers used at PNRI were not exactly the same with the standard source container. Moreover, the density of the 250 ml standard source used at PNRI was 1.0

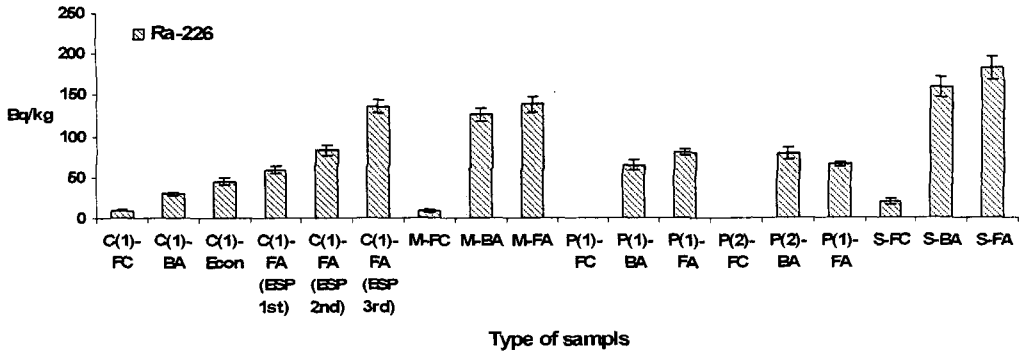
kg//m^3 (Certificate of Calibration, Isotope Products Laboratory, 2004) and the density of the ash samples at 1.5 kg/m^3 (EC, 2001). The source-to-detector geometries of NIRS and PNRI HPGe detectors may also differ. Not all information of the internal dimensions of the detector may be provided during its delivery, but even so, not all detector properties are known with sufficient confidence (Hardy, et al, http//.cyclotron.tamu.edu). According to Bjurman, et al. (1987), it can be difficult to compare AC values obtained at different laboratories as standard geometries are seldom used. For example, if samples are measured without sufficient homogenization, errors up to a factor of 3 can be introduced in the determination of AC; errors due to density variation (up to 10%), and radionuclide-specific coincidence effects (up to 40%) may arise. Systematic problems which may include calibration or correction for dead time could also influence the results.

NIRS HPGe versus PNRI HPGe plots in Figures 4.11 (a), (b) and (c) show very high correlation of ACs for both ^{226}Ra (R^2=0.93) and ^{228}Ra (R^2=0.91), and high correlation for ^{40}K (R^2=0.86). However, the slopes of the correlation lines give only 64 to 68% correspondence of NIRS HPGe relative to PNRI HPGe.

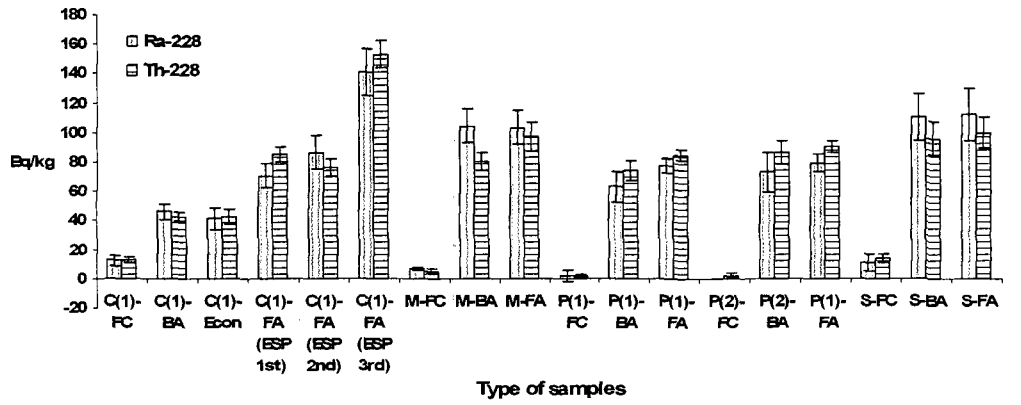
Table 4.6 ACs (Bq/kg) of ^{226}Ra, ^{228}Ra, and ^{228}Th measured by PNRI HPGe

Type of samples	No. of samples	^{238}U series		^{232}Th series					
		^{226}Ra		^{228}Ra		^{228}Th		^{40}K	
		AC	U	AC	U	AC	U	AC	U
Plant C-1; Origin of coal: Semirara, Phil.; Sampling date: 15-18 Jun 2005									
FC	5	9.57	1.43	**12.33**	3.41	**13.06**	1.96	**111.12**	13.36
BA	2	30.50	1.97	**45.95**	5.77	**42.48**	2.65	**272.23**	17.48
Econ	1	44.63	4.46	**41.09**	7.36	**42.70**	4.89	**270.04**	26.27
ESP 1st	2	59.39	3.68	**70.30**	8.44	**85.20**	4.92	**414.23**	21.75
ESP 2nd	1	82.48	5.85	**86.38**	11.56	**76.22**	5.93	**435.78**	27.08
ESP 3rd	2	135.05	8.13	**140.47**	15.94	**152.67**	9.36	**766.49**	42.43
Plant M; Origin of coal: China; Sampling date: September 1, 2005									
FC	2	9.08	2.00	**6.58**	0.70	**5.06**	1.75	**53.73**	23.54
BA	1	125.00	8.39	**104.17**	11.70	**79.97**	6.38	**419.10**	52.00
FA	4	137.88	9.63	**103.20**	11.60	**97.24**	9.86	**351.06**	44.70
Plant P-1; Origin of coal: Indonesia/Semirara; Sampling date: September 2005									
FC	1	<MDL		**1.63**	3.66	**1.92**	1.12	**14.90**	13.66
BA	2	64.50	5.91	**62.76**	10.23	**74.41**	6.91	**179.86**	30.94
FA	1	79.78	3.03	**77.06**	5.31	**84.26**	3.43	**251.52**	17.60
AP	3	76.96	5.75	**60.98**	8.92	**68.82**	5.60	**189.60**	25.20
Plant P-2; Origin of coal: Indonesia/Semirara; Sampling date: September 2005									
FC		<MDL		<MDL		**2.14**	1.14	**16.54**	12.85
BA	1	78.33	6.97	**72.90**	13.40	**86.15**	7.76	**284.15**	41.38
FA	1	65.10	3.00	**79.01**	6.20	**89.69**	4.18	**295.06**	22.53
AP	1	57.63	5.17	**50.99**	8.83	**66.02**	5.86	**203.44**	30.53
Plant S; Origin of coal: Shinwa, China/Semirara; Sampling date: August, 2005									
FC	2	19.87	3.56	**10.74**	5.61	**17.27**	2.94	**56.10**	26.35
BA	1	157.89	11.76	**109.67**	15.96	**129.51**	11.48	**638.30**	77.84
FA	2	181.11	14.28	**111.37**	17.74	**141.04**	10.03	**409.79**	58.03
Total no. of samples	**31**								

U (k=2)-Expanded relative uncertainty at 95% confidence level
MDL-Minimum detection limit =4.66 x std. deviation of mean background count (IAEA, 1999)



(a)



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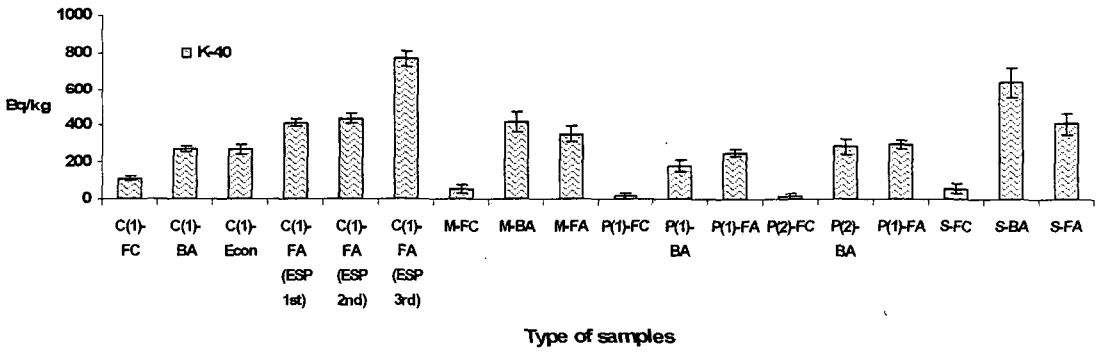
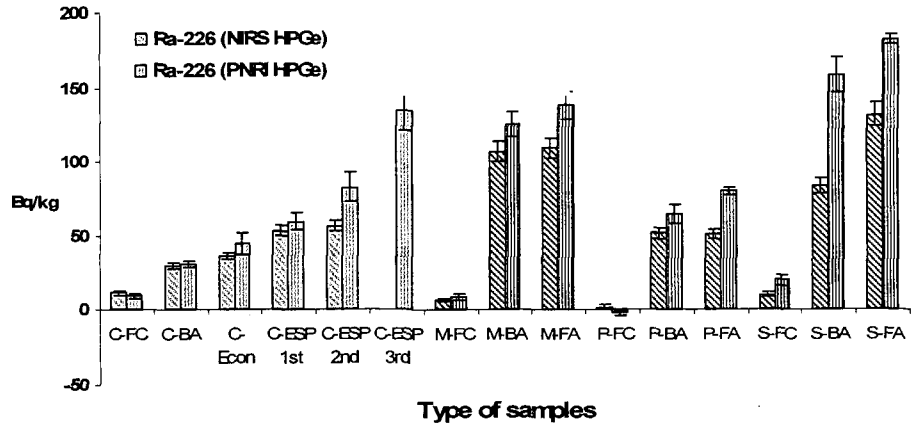
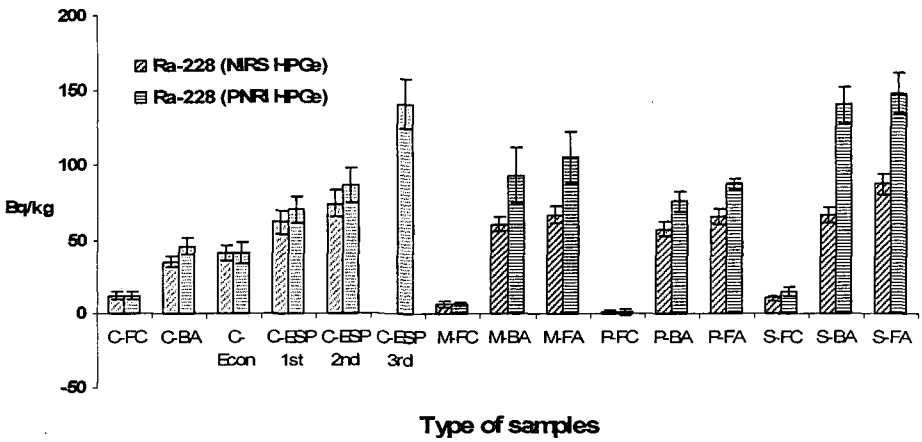


(c)

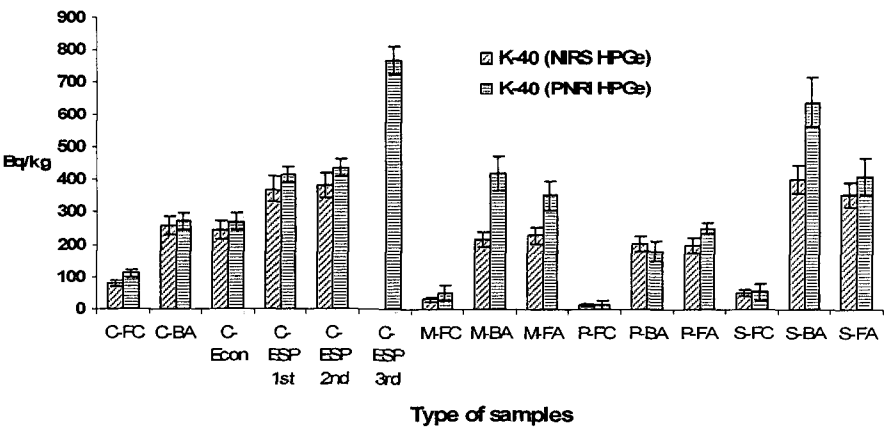
Figs. 4.9. ACs of (a) ^{226}Ra, (b) ^{228}Ra and ^{228}Th, (c) ^{40}K in samples from Plants C (Unit-1), M, P (Units 1 and 2), and S measured by PNRI HPGe.



(a)

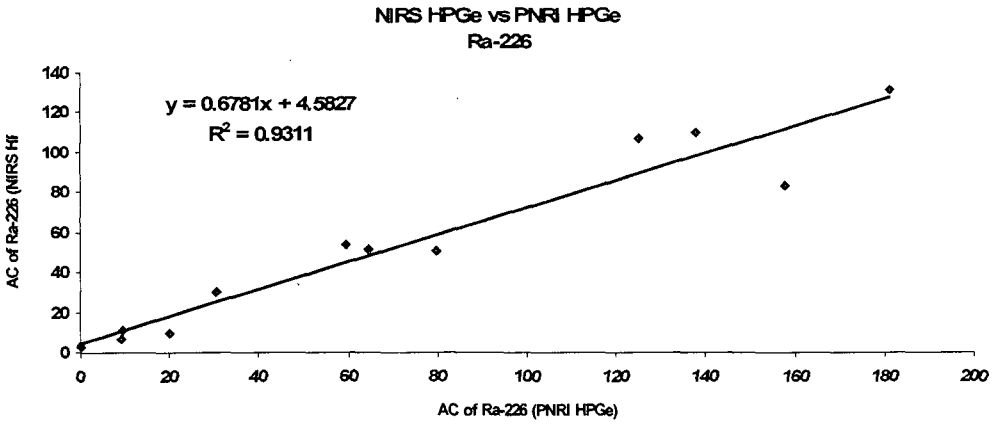


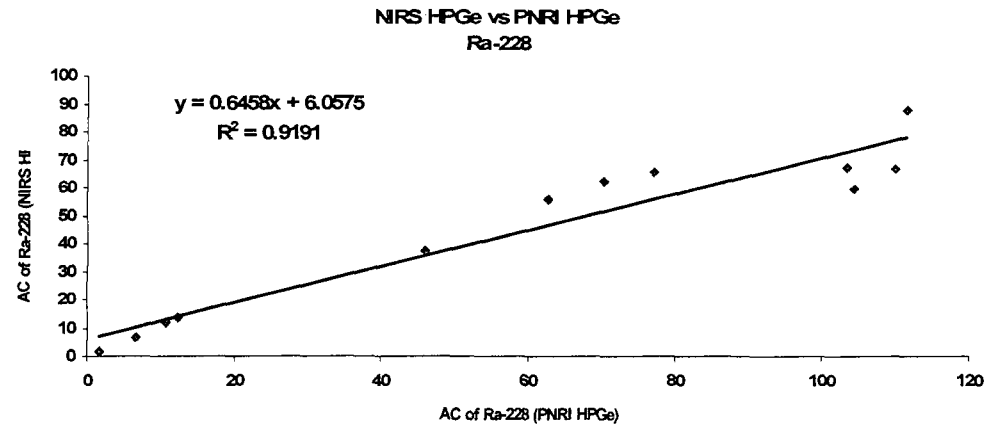
(b)

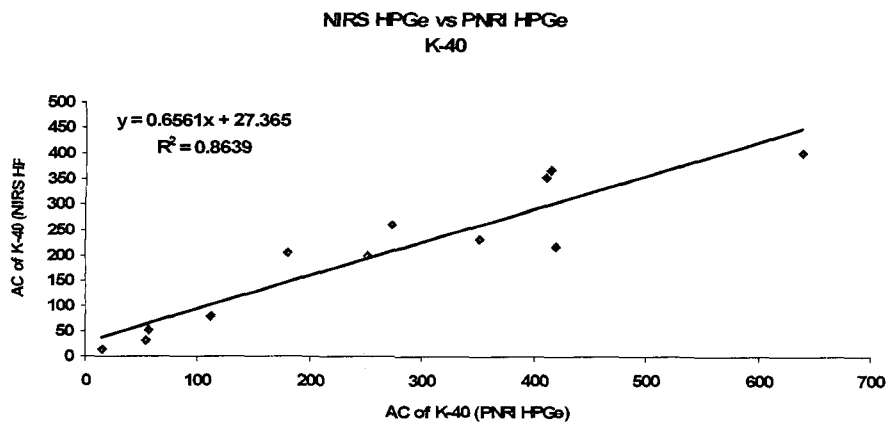


(c)

Figs. 4.10. Comparison of ACs of (a) ^{226}Ra, (b) ^{228}Ra, and (c) ^{40}K in samples from Plants C, M, P, and S measured by NIRS and PNRI HPGe.







Figs. 4.11. Correlations of NIRS HPGe and PNRI HPGe results for ^{226}Ra, ^{228}Ra and ^{40}K Plants C (Unit 1), M, P, and S samples.

4.3 Comparison of AC results with other works

The AC values in FC, BA and FA samples of the four coal-fired power plants obtained in this work are summarized and compared with the published world and country-specific AC values as presented in Table 4.7. The values obtained in this work are within the published data for ^{238}U, ^{232}Th, ^{226}Ra, and ^{228}Ra, except ^{40}K.

The AC of U in Plant S feed coal sample is higher than the mean uranium (U) content of coal samples from various mines located in 7 provinces of the Philippines of 5 Bq/kg (0.401 ppm) as reported by De la Rosa et al (1984) while that of Plant C, M and P are lower.

A more complete data on TENORM in the ashes from four coal-fired power plants in the Philippines was made possible because of the availability of the NIRS ICP-MS which proves to be a powerful technique for the measurement of ^{238}U and ^{232}Th, and the HPGe technique for the measurement of ^{226}Ra, and ^{228}Ra, and ^{40}K.

As can be gleaned from Table 4.7, this study was first to employ a direct mass concentration technique for ^{238}U and ^{232}Th (by ICP-MS) unlike studies in the literature which calculated the Ac's of these two radionuclides indirectly by Gamma Spectrometry (GS) or instrumental neutron activation analysis. There could be uncertainties in results among indirect measurements such as the case of NIRS and PNRI HPGe's.

Table 4.7. Comparison of AC values (Bq/kg) obtained in this study with that of the world and selected countries.

	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{40}K
This study (2005-2006)					
	By ICP-MS	**By HPGe**	**By ICP-MS**	**By HPGe**	**By HPGe**
Feed coal	2.6-13.7	1.84-11.70 (NIRS); <MDL-19.9 (PNRI)	2.6-15.8	1.72-13.65 (NIRS); <MDL-12.1 (PNRI)	13.90-80.23 (NIRS); 14.9-111.1 (PNRI)
Bottom ash	30.2-100.2	29.90-106.73 (NIRS); 30.0-157.9 (PNRI)	41.7-80.9	37.04-66.64 (NIRS); 35.5-66.5 (PNRI)	203.94-400.93 (NIRS); 179.86-638.3 (PNRI)
Fly ash	59.8-268.0	50.79-131.13 (NIRS) 50.8-181.1 (PNRI)	69.5-156.0	61.96-87.70 (NIRS); 65.2-140.5 (PNRI)	197.71-369.08 (NIRS); 251.52-414.23 (PNRI)
Ash pond	-	31.3-42.73 (NIRS); 33.04-63.48 (PNRI)	-	39.82-58.66 (NIRS); 41.75-74.71 (PNRI)	290.7-446.73 (NIRS); 390.35-561.54 (PNRI)
World (UNSCEAR, 2000)					
Feed coal	10-25	-	10-25	-	-
Bottom ash	200	-		-	-
Fly ash	200 400 (fly dust)	-	200 (fly dust)	-	-
UK fly ash	43.3-109.7	44.3-<400	19.1-39.6	-	-
USA (IAEA, 2003)					
Bottom ash	26.0	26.0	15.0	22.0	-
Fly ash	96.0	111.0	63	96.0	-
Brazil (IAEA, 2003)					
Coal	72.0	72.0	62.0	62.0	-
Bottom ash	156.0	120.0	96.0	84.0	-
Fly ash	144	192	80.0	144.0	-
Hongkong (Tso, M. W. and Leung, J. K. C., 1996) by HPGe					
Coal	-	17	-	20 (^{228}Ac)	24
Bottom ash	-	100	-	105	132
Fly ash	-	140	-	155	178
Kolaghat Power Plant, West Bengal, India (Mandal and Sengupta, 2003) by NaI (Tl)					
Coal	-	25-50	39-55	-	-
Ash pond	-	81-125	122-173	-	0.7-0.9 %
Fly ash	-	81.9-126	132-169	-	-
Greece (4 power plants) (Manolopoulou and Papastefanou, 1992) by Ge(Li) and INAA					
Lignite	117-399	44-236	-	9-41	59-227
Fly ash	236-950	142-605	-	27-68	204-382
Megapolis-A Power Plants, Greece, (Karangelos, et. al., 2004) by Ge(Li)					
Lignite	248-352	309-395	19-24	-	152-207
Bottom ash	658-715	583-743	41-47	-	334-460
Fly ash	944-1051	794-1028	50-57	-	403-516

4.4 More detailed study of Plant C, including 2006 sampling

4.4.1 2006 samples

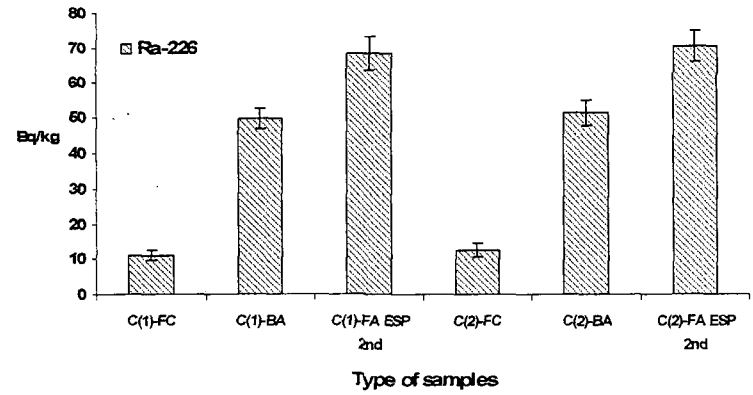
The ACs of ^{226} Ra, ^{228}Ra, ^{228}Th and ^{40}K in FC, BA and FA samples collected in June 2006 from Plant C Units 1 and 2 are presented in Table 4.8 and Figure 4.12. The fly ash samples from Unit 1 were from ESP 2nd and 3rd stages while that from Unit 2 were from 1st and 2nd stages. As can be seen from Figures 4.12 (a), (b) and (c), the behaviors of ^{226} Ra, ^{228}Ra, ^{228}Th, and ^{40}K are generally similar in the ash samples of Plant C Units 1 and 2 when both Units were fed with pure Semirara coal. Plant C Unit 1 can be fed with pure Semirara or Semirara mixed with imported coal while Plant C Unit 2 can be fed only with Semirara coal. During the sampling period of June 2005, only Unit 1 was operational and it was fed with Semirara coal. In June 2006, both Units were operational and both were fed with Semirara coal.

Despite the fact that Plant C Unit 1 was fed with the same Semirara coal in 2005 and 2006, ^{226} Ra, ^{228}Ra, and ^{40}K show different behaviors in 2005 and 2006, as shown in Figures 4.13 (a), (b) and (c). In 2005, the ACs of ^{226} Ra, ^{228}Ra, and ^{40}K in the FA sample from the ESP 3rd stage is enhanced with respect to the ACs in the FA sample from the ESP 2nd stage, while in 2006, there is no such enhancement.

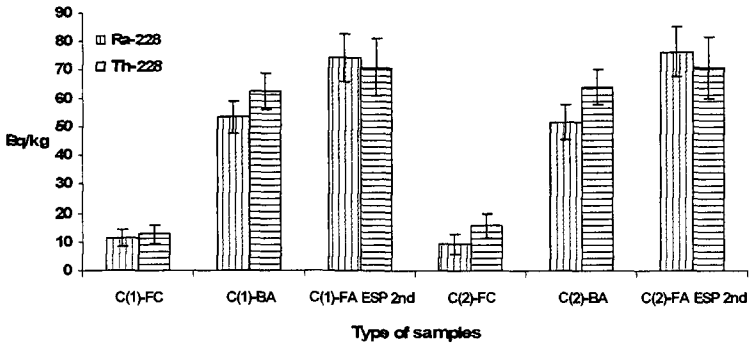
Table 4.8. ACs of ^{226}Ra, ^{228}Ra, and ^{228}Th in samples collected on 19-23 June 2006 from Plant C Units 1 and 2 measured by PNRI HPGe

Type of samples	No. of samples	^{238}U series		^{232}Th series				^{40}K	
		^{226}Ra		^{228}Ra		^{228}Th			
		AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)
Plant C-1; Origin of coal: Semirara, Phil.; Sampling date: 19-23 Jun 2006									
FC	**3**	**10.76**	1.47	**11.38**	3.19	**12.74**	1.48	**70.89**	25.85
BA	**2**	**49.80**	2.81	**53.22**	6.27	**62.36**	3.58	**420.72**	43.33
FA-ESP 2nd	1	**68.23**	4.99	**74.27**	10.16	**70.91**	5.59	**478.65**	59.23
FA-ESP 3rd	1	**66.93**	4.58	**76.67**	10.43	**66.92**	5.32	**496.10**	60.31
Plant C-2; Origin of coal: Semirara, Phil.; Sampling date: 19-23 Jun 2006									
FC	**3**	**12.38**	1.95	**9.47**	4.37	**15.58**	1.99	**105.17**	38.93
BA	**2**	**51.29**	3.53	**51.63**	6.17	**63.91**	3.94	**410.58**	42.33
FA-ESP 1st	1	**59.23**	4.34	**65.63**	8.95	**65.45**	5.12	**485.56**	53.85
FA-ESP 2nd	1	**70.28**	5.12	**76.33**	10.69	**70.74**	5.57	**558.36**	62.85
Total	14								

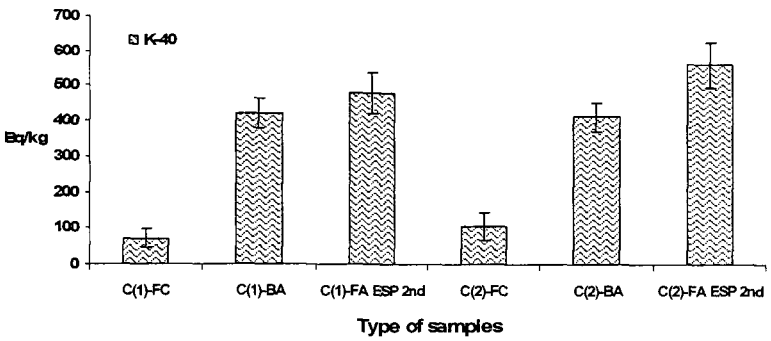
U (k=2)-Expanded relative uncertainty at 95% confidence level
MDL-Minimum detection limit (4.66 x std. deviation of mean background count)



(a)

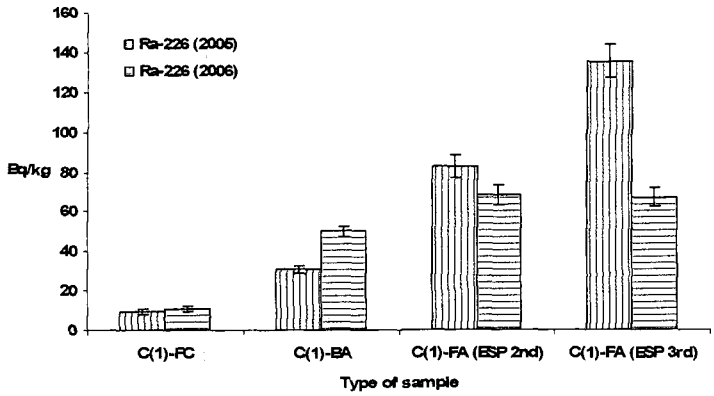


(b)



(c)

Figs. 4.12. ACs of (a) ^{226}Ra, (b) ^{228}Ra and ^{228}Th (c) ^{40}K, in Plant C Units 1 and 2 samples collected on 19-23 June 2006 and measured by PNRI HPGe.



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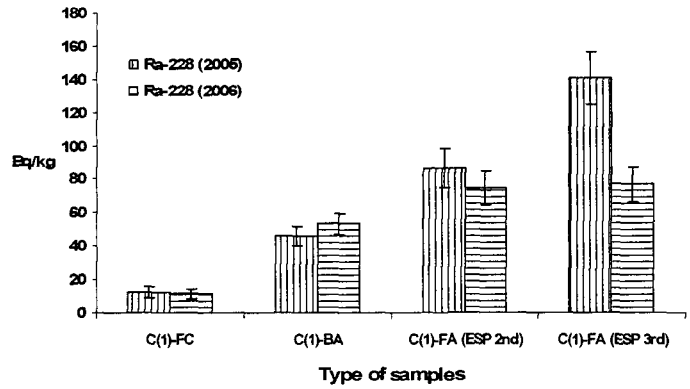

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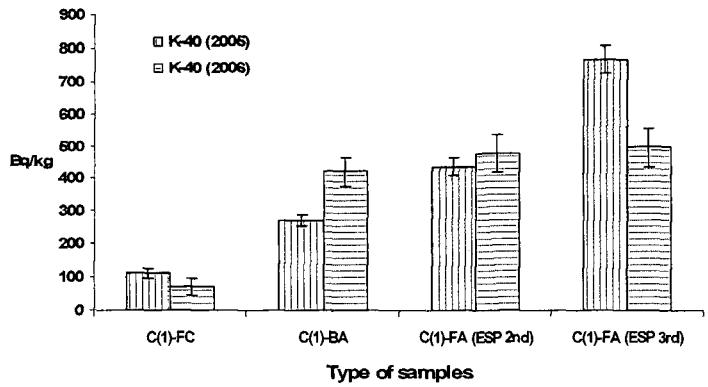


(c)

Figs. 4.13. Comparison of ACs of (a) ^{226}Ra, (b) ^{228}Ra and ^{228}Th and (c) ^{40}K, in Plant C Unit 1 samples collected in 2005 and 2006 and measured by PNRI HPGe.

4.4.2. Ash pond samples

Ash pond samples from Plant C were collected in 2005 and 2006. The 2005 samples were analyzed by NIRS and PNRI HPGe while the 2006 samples were analyzed by PNRI HPGe only and the results are presented in Table 4.9. The ACs of ^{226}Ra, ^{228}Ra and ^{228}Th in ash pond samples, in general, are lower than the ACs in FA samples of Plant C Units 1 and 2 for 2 sampling years (see Tables 4.2, 4.6 and 4.8), whereas for ^{40}K, the ACs are quite the same.

The ACs of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K in the samples taken at various accessible locations and depths of Plant C ash pond in 2005 tend to increase with depth down to about 1 m and tend to decrease from 1 m down to 2 m, as shown in Figure 4.14 (a), (b) and (c), also refer back to Figure 3.3 (a) for the sampling area.

For samples collected in 2006, (same location but different depths, refer to Figure 3.1 (c) similar behavior is observed for ^{228}Th and ^{40}K - a slight increase in AC then decrease with depth. However, the ACs of ^{226}Ra and ^{228}Ra decreases with depth, as shown in Figures 4.15 (a), (b) and (c). Similar trends of the radionuclides with depth were observed both in 2005 and 2006.

Plant C ash pond is periodically flooded with water to prevent ash pond dusts, especially during dry seasons. During the sampling period in June 2005, the ash pond was not flooded with water, hence sample collection was possible and gamma dose rate measurements was carried out but using another PGS. In December 2005, the ash pond was flooded with water so that no samples were collected. Only gamma dose rate measurements were done in accessible areas

of the ash pond. In June 2006, the ash pond was not flooded with water, so that ash pond samples were again collected. Gamma dose rate measurements were also done, this time with a different and calibrated PGS, results and discussion are in Section 4.2.

The decrease in ACs with depth could be the result of leaching or migration of more mobile radionuclides, i.e. Ra, to the underlying ash pond layers and to the underlying groundwater or downstream catchment, if the bottom of the ash pond is not lined with high density polyethylene (HDPE). The apparent variation of the ACs of the radionuclides in various depths of Plant C ash pond could be explained by the relative differences of mobility, solubility, and leaching characteristics of ^{226} Ra, ^{228}Ra, ^{228}Th and ^{40}K, and may also be due to their chemical and physical affinity in the ash matrix. The behaviors of ^{238} U and ^{232}Th in the ash pond may also be similarly influenced.

Burnett, et.al. (1995) reports that the behavior of radium in the laboratory is sample dependent; i.e., different solubility for different samples and that in general 10-50%, for example, of the radium in Florida phosphogypsum is water soluble. An assessment of gross Ra activity in ground waters around Yatagan Thermal Power Plant, India by Baba (2002) shows that the range of gross radium activity was 0.01-0.11 Bq/l: and that based on the generated contour map, the Ra activity tend to concentrate in the underlying ground water of the thermal power plant and ash pond. The values obtained however, are lower than the interim limit by USEPA for gross radium isotope activity of 0.55 Bq/l. Baba (2002) also

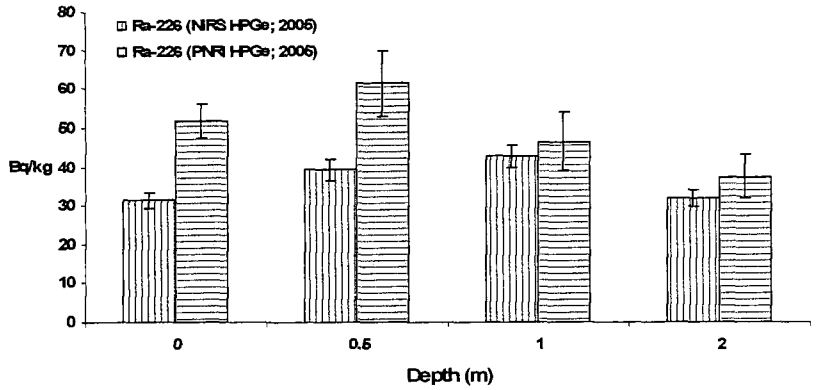
pointed out in his report that U is relatively more soluble than Th and can be leached out by percolating water.

Initial measurements of trace elements and radioactivity levels in drinking water near Tucbilek coal-fired power plant in Kutahya, Turkey by N. Ozturk and Y. Z. Yilmaz (2000) show that some water samples exceeded the World Health Organization (WHO) recommended activity concentration of 0.1 Bq/l for global α activity and approached the recommended activity concentration of 1 Bq/l for global β activity.

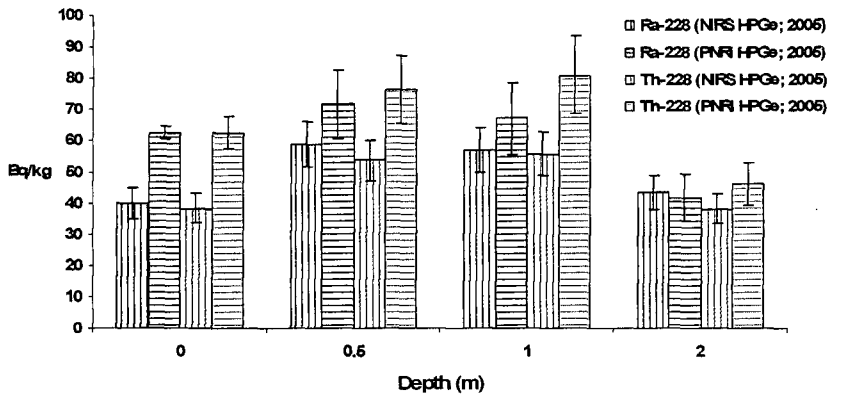
Table 4.9. AC of ^{226} Ra, ^{228}Ra, ^{228}Th and ^{40}K in samples from Plant C ash pond measured by NIRS and PNRI HPGe.

Plant C ash pond	No. of samples	^{238}U series		^{232}Th series					
		^{226}Ra		^{228}Ra		^{228}Th		^{40}K	
Depth (m)		AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)	AC Bq/kg	U (k=2)
NIRS HPGe; Sampling date: 15-18 June 2005									
0	1	**31.32**	2.16	**39.82**	4.98	**38.05**	4.73	**290.71**	31.36
0.5	1	**39.35**	2.74	**58.66**	7.24	**53.68**	6.67	**348.49**	37.77
1	1	**42.73**	2.95	**57.07**	7.10	**55.76**	7.06	**446.73**	47.81
2	1	**31.73**	2.15	**43.47**	5.44	**38.14**	4.81	**334.41**	35.97
PNRI HPGe; Sampling date: 15-18 June 2005									
0	4	**51.74**	4.19	62.50	2.08	**62.51**	5.15	408.70	16.72
0.5	1	**61.37**	8.56	**71.84**	11.06	**76.52**	10.73	**467.96**	33.33
1	1	**33.04**	7.54	**67.32**	11.45	**81.20**	12.63	**453.78**	33.01
1.5	1	**47.36**	6.49	**50.04**	8.00	**52.87**	7.46	**432.24**	27.26
2	1	**37.43**	5.66	**41.75**	7.37	**46.26**	6.84	**390.35**	27.00
PNRI HPGe: Sampling date: 19-23 June 2006									
0	1	**61.52**	8.48	**74.71**	12.97	**78.04**	11.66	**455.38**	42.29
0.5	1	**63.48**	10.26	**63.07**	11.60	**80.77**	13.48	**471.33**	36.08
1	1	**37.18**	7.41	**58.54**	10.73	**72.91**	12.10	**561.54**	42.14
1.5	1	**34.77**	6.47	**45.78**	9.39	**50.23**	8.34	**441.28**	31.27
2	1	**41.89**	7.69	**44.25**	8.01	**56.88**	10.05	**408.43**	29.20
Total	15								

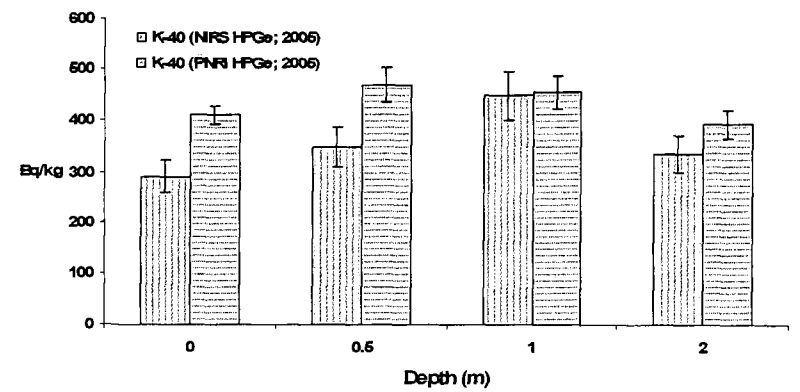
U (k=2)-Expanded relative uncertainty at 95% confidence level
MDL-Minimum detection limit (4.66 x std. deviation of mean background count)



(a)

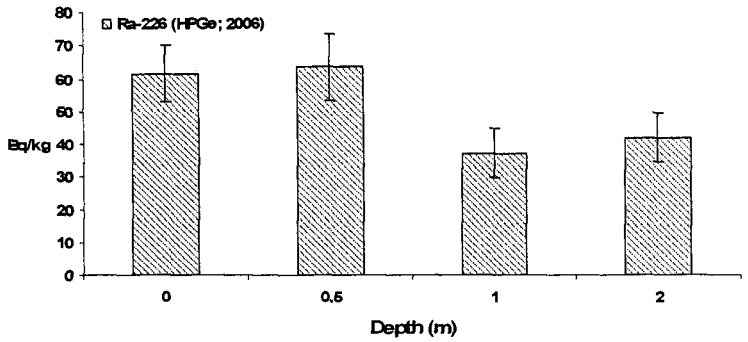


(b)

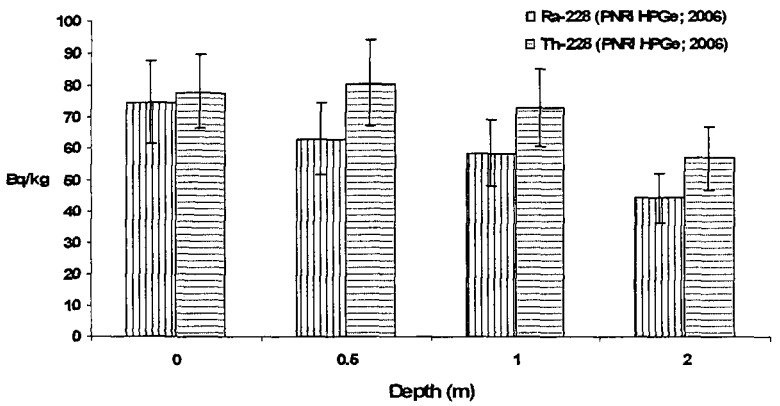


(c)

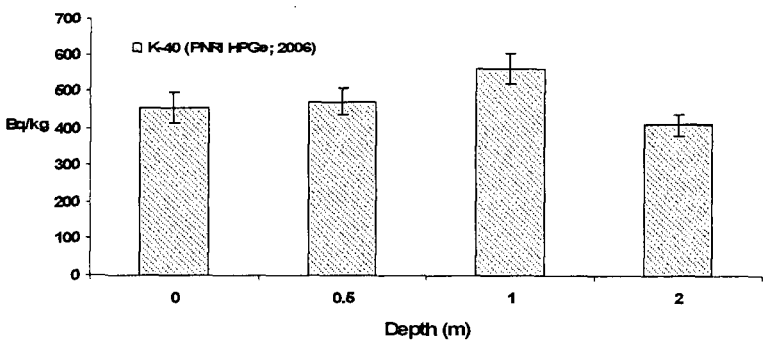
Figs. 4.14 ACs of (a) ^{226}Ra, (b) ^{228}Ra and ^{228}Th, (c) ^{40}K, in Plant C ash pond samples collected in 2005 and measured by NIRS and PNRI HPGe's.



(a)



(b)



(c)

Figs. 4.15 ACs of (a) ^{226}Ra, (b) ^{228}Ra and ^{228}Th (c) ^{40}K, in Plant C ash pond samples collected in 2006 measured by PNRI HPGe.

4.4.3 AC and absorbed gamma dose rate in air inside Plant C and its vicinity

The calculated absorbed gamma dose rate in air (nGy/h) at 1m above the ground surface in Plant C and vicinity is presented in Table 4.10. Using portable gamma spectrometer (PGS), measurements were made in five locations inside Plant C, at the truck loaded with fly ash, and about 40 sampling locations in the vicinity of Plant C. Most of the sampling locations were along the designated terrestrial line transects and air sampling locations of Plant C. Figure 4.16 presents the distribution of gamma absorbed dose rate in air.

The highest absorbed gamma dose rate in Plant C was 36.29 nGy/h measured near the Environmental Office building. Outside Plant C, the highest dose rate was 41.22 nGy/h measured at the grounds of the Provincial Science High School located about 1 km from the Plant. The lowest reading inside and outside Plant C was 29 nGy/h and 27 nGy/h, respectively, both higher than the reported minimum gamma dose rates in other areas in the Philippines, as presented in Table 4.11.

Flues, et al. (2002) reported small increment in natural radionuclide concentration in the surrounding soils of coal-fired power plants in Brazil that have been operating for more than thirty years. Similar report was made by Papp, et al. (2002) and Papp and Dezco (2003) for power plants operating in Hungary for more than fifty years. Bem, et. al (2002) also reported that several small coal-fired power plants in Lodz region in Poland resulted in a relatively small increase in natural radioactivity in the vicinity of the power plants. The average dose rate was 36$\pm$1.2 nGy/h and at the edge of the region was slightly

lower 30±09 nGy/h. The technologically slightly enhanced radiation in the vicinity of the plant was further confirmed with the results of the gamma spectrometry measurements of the ^{238}U and ^{232}Th decay series radionuclides in the surface soil samples. Papaefthymiou, et al. (2005) also reported that the slightly higher natural radioactivity concentrations measured in dust deposition in Megalopolis City compared to Patras City in Greece are attributed to the operation of coal-fired power plants A (operating since early 1970s) and B (operating since early 1990s) in Megalopolis City.

Plant C Unit-1 is the oldest coal-fired power plant in the Philippines which has been operating for about 23 years. Soil samples were collected by another researcher in each sampling location where gamma dose rate measurements were made. As of writing, the results of the of the soil sample analysis were not available yet.

Table 4.11 compares the data on gamma dose rate obtained in this work with available local and world data. The data in this work and that of Grasty and Reyes were obtained using the same PGS instrument. The dose rate due to cosmic rays was subtracted to reflect terrestrial gamma radiation dose rate only. The data from the Health Physics Section (HPS), PNRI were obtained using a different PGS and include the dose rate from cosmic rays. The quoted UNSCEAR data was calculated from the worldwide measurements of the concentrations of the relevant radionuclides (^{40}K, ^{238}U series, ^{232}Th series) in soil.

The gamma dose rates in air in Plant C and its vicinity, including that in the ash pond, are below the world average and are comparable to other local

data. Except for the ash pond data, it is yet uncertain whether the gamma dose rates are elevated due to the technologically enhanced radionuclides escaping from Plant C. However, the data obtained in this study can be used as baseline in future radiation level studies in the area.

Using the average value of the ACs of ^{40}K (422.24 Bq/kg), ^{226}Ra (55.03 Bq/kg), and ^{228}Ra (43.92Bq/kg) in Table 4.19, the gamma dose rate in air (D) in Plant C ash pond can also be calculated using the equation below:

$D = (0.462AC_U + 0.604AC_{Th} + 0.0417AC_K)$ nGy/hr (UNSCEAR, 2000),

D = 70.92 nGy/h (dry basis)

The conversion factor for dry to wet basis is 0.81 to account for representative soil moisture of 30% by volume and soil density of 1.6 g cm^{-3} (UNSCEAR, 2000). Applying this conversion factor for moisture in the ash pond gives a value of 57.44 nGy/h, which is quite in agreement with the results (44.84-56.08 Bq/kg) of the measured gamma dose rate in the ash pond in Table 4.10.

There is also additional exposure due to the potential release of ^{222}Rn from the ash pond. However, no radon measurement was done in this work. Beck and Miller (1980) also reported that radon did not appear to emanate significantly from fly ash and bottom – less than 2 percent compared to 15 percent for the average soil, and 20 percent for uranium mill tailings. Unless long term weathering modifies the physical composition of the impermeable glassy ash particles, the emanation of radon from ash does not constitute a significant potential perturbation to ambient ^{222}Rn levels (Beck and Miller, 1980).

The mean background gamma radiation in the Philippines, expressed as mean gamma dose rate, measured in 16 regions from 1982 to 2002 by PNRI, is 44nGy/h (with range from 21-124 nGy/h). This value corresponds to a mean annual effective dose equivalent of 0.46 mSv from background radiation alone (PNRI Data in Environmental Management Bureau, 2002) and is lower than the worldwide population-weighted average of 59 nGy/h (range of 10-200 nGy/h) that corresponds to a mean annual effective dose equivalent of 2.4 mSv, with typical range from 1-10 mSv (UNSCEAR, 2000).

According to UNSCEAR (2000), the maximum effective doses from natural radionuclides released from typical coal-fired power plant are: 12 μSv/y external irradiation; <0.4 μSv/y air dispersion pathways; and 4 μSv/y water dispersion pathways. UNSCEAR considers these exposure rates to constitute a negligible component of the total annual effective dose from all natural sources of radiation

The measured gamma dose rate on the surface of the truck containing fly ash was ~43 nGy/h. This can result to an estimated equivalent dose to the driver of 30960 nSv/y (~3 hrs/d to destination x 5 d/w x 48 w/y x 43 nGy/h x 1nSv/hr/1nGy/hr) or 0.031 mSv/y. This estimated dose to the truck driver can be considered trivial and of no radiological consequence of concern.

Table 4.10 Calculated activity concentration and absorbed gamma dose rate in air inside and in the vicinity of Plant C using portable gamma spectrometer.

Sampling location	GPS Reading		Concentration			Activity concentration (Bq/kg)			Total Dose Rate
	Easting	Northing	K (pct)	U (ppm)	Th (ppm)	K	U	Th	(nGy/h)
Inside Plant C; Sampling date: Dec 12-15, 2005									
1. Back gate	2600774.5	1541029	0.84	0.94	5.44	262.92	16.3	22.09	31.83
2. Env Off	261181	1541325	1.06	0.94	5.9	331.78	17.29	23.95	36.29
3. Near pier	261019.5	1540952	0.84	1.4	4.24	262.92	17.29	17.21	29.35
4. Flag pole	261090.5	1541377.5	0.9	1.14	5.94	281.7	14.08	24.12	32.82
5. Cargo truck			0.8	1.2	10.4	250.4	14.82	42.22	42.79
6. Stack	260833	1541453							
Plant C vicinity									
North Transect; Sampling date: Dec 12-15,2005									
1. 4000 m	261828.5	1545873	0.7	1.26	4.6	219.1	15.56	18.68	27.61
2. 3000 m	261828.5	1545873	0.68	1.18	5.86	212.84	14.573	23.79	29.98
3. 2000 m	260734.5	1544281.5	0.82	1.6	4.92	256.66	19.76	19.98	31.9
4. 1000 m	260734.5	1543355.5	0.92	1.94	4.98	287.96	23.96	20.22	35.29
5. 0 m	260646	1542714	0.9	1.74	5.12	281.7	21.5	20.79	34.23
Sampling date: Jun 19-24, 2006									
6. 4000 m	261823	1545878	0.8	1.7	6.8	250.4	20.99	27.61	36.82
7. 3000 m	261504	1545042	0.9	1	7	281.7	12.35	28.42	34.62
8. 2000 m	260195	1544252	1	0.9	6.9	313	11.12	28.01	35.11
9. 1000 m	260748	1543360	1.1	1.4	6.9	344.3	17.29	28.01	39.27
SW Transect; Sampling date: Dec 12-15, 2005									
1. 1000 m	259423	1541406.5	0.68	1.28	5.18	212.84	15.81	21.03	28.88
2. 2000 m	258688	1542372	0.68	1.66	4.38	212.84	20.5	17.78	29.09
3. 3000 m	257929.5	1542589	0.62	1.34	5.14	194.06	16.55	20.87	28.34
Sampling date: Jun 19-24, 2006									
4. 4000 m	255654	1542631	0.7	1.22	4.46	219.1	15.07	18.11	27.03
5. 3000 m	256550	1541789	0.7	1.06	5.48	219.1	13.09	22.25	28.62
6. Sampaga	259426	1542552	0.9	1.76	6.32	281.7	21.74	25.66	37.29
7. data pt	263697	1541728	1.08	1.4	6.6	338.04	17.29	26.8	38.27
8. BPSHS	261121	1542154	1.1	1.82	6.72	344.3	22.48	27.28	41.22
SE Transect; Sampling date: Dec 12-15, 2005									
1. 1000 m	261542.5	1540780.5	0.9	1.46	4.68	281.7	18.03	19.00	31.55
2. 2000 m	262612.5	1540821.5	1	1.8	5.68	313	22.23	23.06	37.25
3. 3000 m	263916	1543312	0.74	1.58	4	231.62	19.51	16.24	28.48

Table 4.10. Continued.

Sampling date: 19-24 June 2006									
4. 4000 m	264402	1539867	0.92	1.28	6.02	287.96	15.81	24.44	34.07
5. 5000 m	265574	1539644	1	1.76	6.24	313	21.74	25.33	38.40
6. Near Steel Plant	264721	1541303	1.04	1.76	5.6	325.52	21.74	22.74	37.35
7. Near Hway	262584	1541494	0.78	1	5.78	244.14	12.35	23.47	30.06
8. data pt	264145	1544583	0.9	0.94	5.6	281.7	11.61	22.74	30.84
9. data pt	264503	1545689	0.84	1.62	6.26	262.92	20.01	25.42	35.56
Baranggay Pook; Sampling dates: 19-24 June 2006									
1	257636	1543856	0.8	1.04	5.4	250.4	12.84	21.92	29.62
2	258112	1544714	0.72	1.54	6.06	225.36	19.02	24.60	33.04
3	257721	1545334	0.92	1.64	6.43	287.96	20.25	26.09	37.12
4	258207	1545880	1	1.36	6.9	313	16.80	28.01	37.73
Bagongtubig; Sampling date: 22 June 2006									
1	263772	1544163	0.92	1.3	6.16	287.96	16.06	25.01	34.53
2	262882	1543551	0.92	1.4	6.5	287.96	17.29	26.39	35.94
3	262671	1542365	0.76	1.28	5.5	237.88	15.81	22.33	30.71
4. 2 km	261623	1542646	0.96	1.08	5.48	300.48	13.34	22.25	32.13
5. 1 km	261609	1541726	1.1	1.56	6.38	344.3	19.27	25.90	38.90
Ash pond; Sampling date: December 12-15, 2005									
1. Ash Pond	259988	1541730	0.75	2.35	8.1	229.53	34.58	31.94	44.84
Sampling date: Jun 19-24, 2006									
2. Ash pond	260060	1541715	**0.78**	**2.72**	**9.58**	244.14	33.59	38.89	49.19
3. ~1.5 ft deep			0.9	3	11.1	281.7	37.05	45.07	56.08
4. Across road	260005	1541801	0.9	1.64	4.9	281.7	20.25	19.89	33.12

Table 4.11. Local and world data on absorbed gamma dose rate in air (nGy/h)

	***Plant C** (This work)		***Marinduque** (Grasty, R. L., 1997)	***Batan Island** (Reyes, R., 2005)	****Philippines** (EMB, 2002, data from HPS, PNRI)	*****World** (UNSCEAR , 2000
	Inside Plant	Outside Plant				
Range	29-36	27-41	22-44	12-111	21-124	18-93
Mean	33	33	30	56	44	57
	Lodz, Poland coal- fired power plant					
Mean		36				

* Same PGS was used as described in this work

** different PGS used from this work and include dose rate from cosmic rays

*** derived from world mean soil activity concentrations

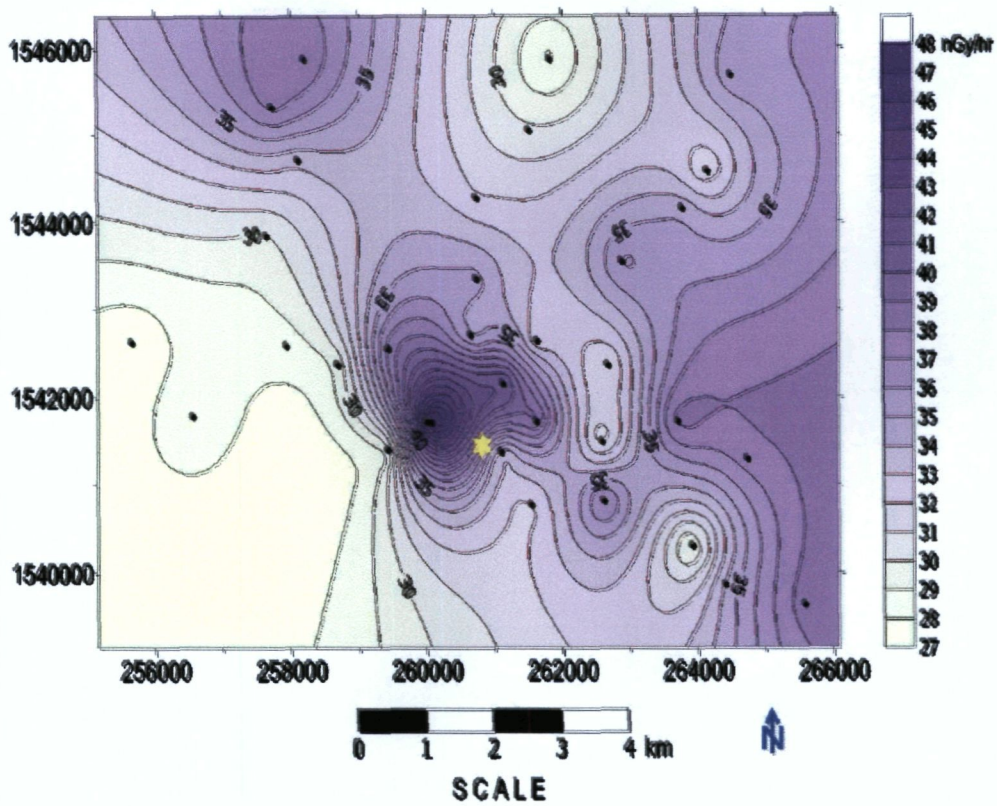


Fig. 4.16. Distribution of absorbed gamma dose rate (nGy/h) in air at 1 m above the ground inside and in the vicinity of Plant C measured by portable gamma spectrometer.

Plant C stack location **Sampling location**

4.5 ESTIMATES

Atmospheric discharge of TENORM

CPR Part 3, Standards for protection against radiation (PNRI, 2004) provides exempt levels of radionuclides in terms of activity concentration and total activity for moderate quantities of material, ~ 1 ton), anything greater than this amount is considered bulk quantities (IAEA, 2004). They have been derived using the dose criteria expected to be incurred by any member of the public of 10 μSv/y or less and the collective dose committed by one year is no more than about 1 man·Sv. The ash, for example in the ash pond, fall under bulk quantities,

hence the exempt levels in Part 3 cannot be applied. Appendices D-1 and D-2 in Part 3 on Derived clearance levels for airborne and liquid releases, respectively, apply to release rates not greater than 3 tons per year per facility and the appendices do not include all the radionuclides in the ^{238}U and ^{232}Th series, only ^{226}Ra and ^{232}Th are listed, hence cannot also be applied to the data obtained in this work.

Because of the above limitations of CPR Part 3, the recommendations of the EC (2001) and IAEA (2004) on exemption levels as presented in Table 4.12 are used to compare the measured ACs of radionuclides in the fly ash samples from the four coal-fired power plants. The AC values in fly ash are well below the recommendation for exempt levels by the IAEA and EC.

Table 4.12 Comparison of activity concentration (Bq/kg) of the radionuclides in fly ash samples obtained in this study with the recommended clearance and exemption AC's of the IAEA and the EC.

Radionuclides	Maximum AC in fly ash samples				Recommended clearance and exempt levels	
	Plant C	Plant M	Plant P	Plant S	IAEA (2004)	EC (2001)
^{238}U sec*	-	-	-	-	1000	500
^{238}U**	70.0	83.2	268.0	132.4	1000	5000
^{226}Ra+	135.0	137.9	79.8	181.1	1000	500
^{210}Pb+					1000	5000
^{210}Po	-	-	-	-	1000	5000
^{232}Th sec***	-	-	-	-	1000	500
^{232}Th	69.49	63.1	156.0	87.0	1000	5000
^{230}Th	-	-	-	-	1000	10000
^{228}Ra+	140.5	103.2	79.0	111.4	1000	1000
^{228}Th+	152.7	97.2	89.7	141.0	1000	500
^{40}K	369.08	229.85	197.71	354.47	10000	5000

*^{238}Usec consists of ^{238}U decay chain
**^{238}Usec and ^{235}Usec are in their fixed natural ratio (99.3% and 0.7% atomic fraction)
***^{232}Th consists of ^{232}Th decay chain
Ra-226+: Ra-226, Rn-222, Po-218, Pb-214, B-214, Po-214)
Th-228+: Th-228, Ra-224, Rn-220, Po-216, Pb-212, Po-212(64.1%), Tl-208 (35.9%)
Ra-228+: Ra-228, Ac-228

Table 4.13 presents the estimated discharges of radionuclides from Plant C, P and S and how these compare with the screening levels in Radiation Protection 135 (EC, 2003).

The radionuclide discharges are estimated as follows:

- Annual coal consumption of Plant C (600 MW total) is:

  ~ 5,000 tons/d x 365 d/y x 0.80 (assumed capacity factor) = 1,460,000 tons/y = 1,460,000,000 kg/y = **1.46×10^9 kg/y of feed coal**

- Estimated total ash production per year = 1.46×10^9 kg/y x 0.15 = **2.19×10^8 kg/y total ash**

- Fly ash (~75%) of total ash = **2.19×10^8 kg/y x 0.75 = 1.64×10^8 kg/y fly ash**

- Bottom ash = 2.19×10^8 kg/y x 0.25 **= 5.5×10^7 kg/y**

- For 95% efficiency of ESP, the amount of fly ash released into the atmosphere is 5% of fly ash produced = 1.64×10^8 kg/y x 0.05 = **8.2×10^6 kg/y**

- For ESP at 99% efficiency, the amount of fly ash released into the atmosphere is 1% of fly ash produced = 1.64×10^8 kg/y x 0.01 = **1.64×10^6 kg/y**

- Assuming that Plant C ESP has 95% efficiency, the estimated activity of **^{238}U** discharged from Plant C into the atmosphere (highest values of AC obtained in this study are used) = 70 Bq/kg x 8.2×10^6 kg/y **= 0.57 GBq/y**

The estimated atmospheric discharges are very much below the screening levels of RP 135 assuming the height of the stacks of Plant C is 200 m. Using as basis the RP135 recommendation, site-specific dose assessment need not be performed.

For Plant P:

- Annual coal consumption of Plant P (735 MW total) is:

  ~ 6,125 tons/d x 365 d/y x 0.80 (assumed capacity factor) = 1,790,000 tons/y = 1,790,000,000 kg/y = **1.79×10^9 kg/y of feed coal**
- Estimated total ash production per year = 1.79×10^9 kg/y x 0.15 = **2.68×10^8 kg/y total ash**
- Fly ash (~75%) of total ash = **2.68×10^8 kg/y x 0.75 = 2.01×10^8 kg/y**
- Bottom ash = 2.68×10^8 kg/y x 0.25 **= 6.7×10^7 kg/y**
- For 95% efficiency of ESP, the amount of fly ash released into the atmosphere is 5% of fly ash produced = 2.01×10^8 kg/y x 0.05 = **1.00×10^7 kg/y**
- For ESP at 99% efficiency, the amount of fly ash released into the atmosphere is 1% of fly ash produced = 2.01×10^8 kg/y x 0.01 = **2.01×10^6 kg/y**
- Assuming that Plant P ESP has also 95% efficiency, the estimated activity of **^{238}U** discharged from Plant P into the atmosphere (highest values of AC obtained in this study are used) = 268.03 Bq/kg x 1.00 x 10^7 kg/y = **2.68 GBq/y**

For Plant S, 1218 MW total with an estimated 10,150 tons of feed coal consumed per day

- Same assumptions are made as in Plants C and P

Table 4.13. Comparison of the estimated activity (GBq/y) discharged from the stacks of Plants C, P and S with the screening levels of RP 135 (screening level dose criterion of 300 μSv/y to critical groups).

Radionuclides	Estimated release rate of Plant C Stack height ~200m	Estimated release rate of Plant S Stack height ~200m	Estimated release rate of Plant P Stack height ~200m	Screening level for height of stack = 200m (RP 135) GBq/y
	~95% ESP efficiency	~95% ESP efficiency	~95% ESP efficiency	
^{238}U	0.57	2.20	2.68	2,300
$^{226}Ra+$	1.25	3.00	0.80	5,400
^{232}Th	1.1	1.40	1.56	1,900
$^{228}Th+$	0.56	1.85	0.90	1,700
$^{228}Ra+$	1.15	2.34	0.79	1,200

Table 4.14. Doses from estimated atmospheric discharges (GBq/y) from Plant C (Assumption: stack height = 200 m) based on doses per unit discharge rate of 1GBq/y of atmospheric release in RP 135 (EC, 2003).

	Estimated discharge GBq/y	**Estimated Dose Sv/y**
^{238}U	0.57	1.4×10^{-8}
^{226}Ra	1.25	2.4×10^{-7}
^{232}Th	1.1	4.1×10^{-7}
^{228}Th	0.56	1.8×10^{-7}
^{228}Ra	1.15	8.4×10^{-8}
Total		**9.3×10^{-7} (0.93 µSv/y)**
For 30 y (expected Plant C lifetime)		**2.79×10^{-5} (27.9 µSv)**

TENORM in Plant C ash pond

The area of Plant C ash pond is about 640,000 m^2 (64 ha) and the depth is approximately 6 m. The maximum volume of ash it can accommodate therefore is about 3,840,000 m^3. Assuming that 50% of the ash produced by Plant C per year is disposed in the ash pond, from Section 4.4, this is

- Ash disposed in ash pond 2.19×10^8 kg/y x 0.5 = 1.1×10^8 kg/y
- In 30 years, the amount of ash in the ash pond is 30 y x 1.1×10^8 kg/y = **3.3×10^9 kg**
- Using the maximum values of AC of radionuclides in Plant C ash pond samples, the estimated total activity of the radionuclides is presented in Table 4.15.

Table 4.15. Estimated activity (Bq) of radionuclides in Plant C ash pond after 30 y.

Radio-nuclide	Highest AC in ash pond samples, (Bq/kg)	Exempt AC Part 3) (Bq/kg)	*Estimated activity in 1 y (Bq)	*Estimated activity in 30 y (Bq)	Exempt activity (Part 3) (Bq)
^{238}U**	41.64	1×10^4	4×10^9	1×10^{11}	1×10^3
^{232}Th**	30.21	1×10^3	3×10^9	9×10^{10}	1×10^3
^{226}Ra+	63.5	1×10^3	7×10^9	2×10^{11}	1×10^4
^{228}Th	81.2	1×10^3	9×10^9	3×10^{11}	1×10^4
^{228}Ra+	71.84	1×10^4	8×10^9	2×10^{11}	1×10^5
^{40}K	561.54	1×10^5	6×10^{11}	2×10^{12}	1×10^6
Ash (kg/y)	1.1×10^8				

*Decay not taken into account
**ACs in bottom ash from Table 4.1

Assuming that the density of ash is 1.5 kg/m^3, the volume needed to accommodate 3.3 x 10^9 kg of ash is 2.2 x 10^9 m^3. This is more than the estimated capacity of the existing Plant C ash pond.

If the exempt levels for total activity (Bq) in CPR Part 3 are directly applied, Plant C will be subject to regulatory control since the total activities of the radionuclides in the ash pond for only 1 year exceed the exempt levels as presented in Table 4.15. On the other hand, the IAEA and EC recommendations for NORM/TENORM exempt levels expressed in terms of AC are not always equivalent with the exempt AC levels of same radionuclides of artificial origin or man-made. Furthermore, the IAEA and EC recommendations pose no further restrictions on accumulated activities for bulk quantities (> 1 ton) in any given location. There appears to be double standard for the same radionuclide depending on where it comes from. The same radionuclide, at the same AC, can either be sent to deep disposal if coming from nuclear power plant or released for use in building materials if coming from coal-fired power plant. Decommissioning

experts are increasingly concerned about double standards developing internationally which allow 30 times the dose rate from non-nuclear recycled materials than from the nuclear industry. For example, 0.3 to 1.0 mSv/y individual dose constraint is applied to recyclables with TENORM and 0.01 mSv/y is applied for the release of materials with the same kind of radioactivity from the nuclear industry (http:/www.uic.com.au/nip59.htm)

Classification of fly ash based on ACof ^{232}Th, ^{226}Ra, and ^{40}K

As discussed in Section 2.8, materials can be classified according to Radium equivalent (Ra eq) or Index (H). The radium equivalent (Ra eq) is determined using the highest AC values of ^{226}Ra, ^{232}Th and ^{40}K in fly ash samples from Plants C, M, P and S obtained in this study in order to find out whether the limit value of Ra eq < 370 Bq/kg is met. Using Eq.1 in Section 2.8, the values obtained for Ra eq are presented in Table 4.16.

Table 4.16. Radium equivalent (Ra eq) of fly ash samples from Plants C, M, P, and S.

Plant	Ra eq in fly ash (Bq/kg)
C	174.55
M	237.07
P	293.30
S	321.08

The results show that the Ra eq values of the fly ash samples from Plants C, M, P and S are all less than 370 Bq/kg. Thus, the fly ash from these Plants can be recommended for use in building residential houses.

The Index (H) can also be used to classify fly ash as discussed in Section 2.8. The value of H should be less or equal to 1 for unlimited use of the material

for residential buildings. Using the same ACs of ^{226}Ra, ^{232}Th and ^{40}K used in determining Ra eq, and applying the AC parameters of Finland and Norway (^{226}Ra: 300 Bq/kg, ^{232}Th: 200 Bq/kg and ^{40}K: 3000 Bq/kg) in Eq. 2 (refer to Section 2.8), the H values obtained for the fly ash samples from Plants C, M, P, and S are given in Table 4.17.

Table 4.17. Index (H) of fly ash samples from Plants C, M, P, and S.

Plant	H (Bq/kg)
C	0.8
M	0.9
P	1.1
S	1.2

Based on the H values, fly ash from Plants P and S cannot be recommended for use in residential building. However, if the AC parameters of Sweden are applied (^{226}Ra: 1000 Bq/kg, ^{232}Th: 700 Bq/kg and ^{40}K: 10000 Bq/kg), the fly ash from all Plants can be used for residential building. Applying the IAEA or EC recommended exempt values for ^{226}Ra, ^{232}Th and ^{40}K as AC parameters, will result to values of H also less than 1 for fly ash samples from Plants C, M, P, and S.

In order to decrease the radiation dose to the population and to prevent additional unnecessary dose, the Philippines should consider the classification of ashes and other industrial residues used in the construction of residential buildings according to their NORM/TENORM concentration.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The study was able to obtain new data on the levels of TENORM in the ashes arising from the operation of four major coal-fired thermal power plants in the Philippines using ICP-MS and HPGe techniques. Both techniques were used on the same samples to determine the activity concentrations (AC) of ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K in feed coal and ash samples from four coal fired power plants C, M, P and S in the Philippines. ICP-MS provided a powerful alternative technique for the direct determination of the AC of ^{232}Th and ^{238}U by their masses and complemented the capability of the HPGe for the indirect determination of the AC of ^{226}Ra, ^{228}Ra, ^{228}Th by their gamma emitting decay products, and the direct determination of AC of gamma-emitting ^{40}K.

The AC of ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K were all enhanced in the BA and FA samples relative to that in the FC samples of Plants C, M, P, and S, in agreement with studies of cited literature. The EF values obtained in this study for ^{232}Th and ^{238}U indicate that ^{238}U is generally more volatile than ^{232}Th hence, ^{238}U is generally more enhanced in the fly ash samples from four power plants. Further enhancement of AC of ^{238}U can be expected in the latter ESP stages and post ESP towards the stack. The enhancement is of radiological concern when the AC of TENORM approaches the values of internationally recommended action or screening levels. In this case, more detailed site investigation will have to be conducted.

The results also show that use of imported coals from China and Indonesia may have higher values of AC in fly and bottom ashes compared to using local coals. With the availability of ICP-MS, the information on TENORM levels in coal can be simultaneously determined with the other toxic trace elements. The TENORM information may be included by exporting countries in their certification of coal characteristics so that coal importers, including the Philippines, are better guided in the choice of coal supplies.

Considering the limited samples analyzed, it may be useful to do more detailed studies of AC in the fly ash from the different ESP stages of Plants P and S and that more samples are collected along the ESP collection stages, post ESP stages, and in the ash ponds, in a span of one to two years. The AC in fly ash of these Plants may approach or could exceed the recommended exempt levels due to enrichment. While the AC values obtained in this study for ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K are all lower than the international recommended exempt and screening levels, periodic environmental radioactivity monitoring however, is strongly recommended because of increasing accumulation of TENORM with continued operation of coal-fired power plants. TENORM in the ash ponds may leach and bio-accumulate due to weathering or biological processes. The fate of TENORM depends largely upon how the ashes are stored or disposed of. Further study is required on the stability of the ash under environmental conditions.

Certain TENORM, i.e. ^{238}U and ^{210}Po, are more concentrated on the finer fly ash particles that escape the emission control system of coal-fired thermal

power plants and are discharged into the atmosphere. The public is more likely to be exposed to these fine particles because of their longer atmospheric residence time compared with large particles and their eventual deep lung deposition. Since the leading cause of morbidity according to the Multipartite Monitoring Activity Report (2004) in two monitored towns near Plant C was upper respiratory track infection (8,371) and the leading causes of mortality in one of these towns, were pneumonia and cancer (147 and 50, respectively), it is also recommended that epidemiological studies be conducted among workers and residents in the localities near coal-fired power plants.

Because of the evident enhancement of NORM in by-products, residues and wastes in identified industries in Chapter 2, it is also recommended for PNRI, in cooperation with EMB, DENR, other relevant governmental agencies and concerned NORM/TENORM industries, to embark on a consolidated survey and inventory NORM/TENORM in the Philippines.

In the revision of relevant Philippine laws affecting radiation protection, the control and regulation of NORM that pose enhanced exposures to the general public should be incorporated. Meanwhile, PNRI may pursue the review of other countries' experience on NORM/TENORM regulation and also examine the available international recommendations in order to formulate policy and guidelines on NORM/TENORM with the objective of providing similar protection to the general public from the potential enhanced radiation exposures from NORM with that of artificial sources of radiation.

For Plant C, the results are summarized as follows:

- The EF values are highest for ^{232}Th and ^{238}U in ash samples but lowest in AC values among the four power plants;
- Based on correlation plots (Figure 4.5), most of the samples show secular equilibrium between $^{238}U$and ^{226}Ra, and between ^{232}Th and ^{228}Ra;
- Based on correlation plots (and t and U statistics), HPGe results of NIRS and PNRI are well correlated but with NIRS values about 64 to 68% 0f PNRI values (Figure 4.11);
- There was no significant variation of ACs of ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K between samples collected in 2005 and 2006 for Plant C when coal of the same origin was utilized. *Semirara* coals were utilized by Plant C at the time of sampling;
- The estimated atmospheric discharges of measured radionuclides from Plant C are well below the recommended EU screening levels, thus the estimated doses from the discharges may be of no radiological significance;
- The ACs of ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K tend to decrease with depth of ash pond. Leaching and infiltration of ground water may have occurred. It is also recommended that the analysis of water samples in the vicinity of the plants include U and Th.
- The measured absorbed gamma dose rates in air in the vicinity of Plant C are within local and world reported data. However, it is recommended that these data only serve as baseline and that

environmental radioactivity monitoring be done periodically during the operational lifetime of the plant;

- Based on the dose rate measurements of the truck that transports fly ash to construction sites, the driver will not receive radiation dose of radiological concern;
- Similarly, the estimated dose received by a worker from gamma exposure while working in the ash pond is of no radiological significance;
- The estimated total accumulated activity in the ash pond in 30 years is quite high. Periodic monitoring of radionuclide content in the ground waters not only of Plant C, but also in Plants M, P, and S and in their vicinities may be warranted.

The operational life time of power plants in the Philippines may be extended to more than fifty years as in other countries. The allocated ash pond may not be sufficient to accommodate all the ash that will be produced. Taking into consideration radiation protection alone, if TENORM levels are below the recommended exempt values, the ash may be utilized for construction purposes without restrictions. In this case, the ash may not be after all considered as hazardous waste but rather a resource if properly utilized and managed. This calls for the establishment of clear governmental policy and guidelines on the proper use of coal ash. A good model is that of USEPA's "Using coal ash in highway construction: a guide to benefits and impacts (2005). The forced

extraction of valuable metals, including ^{238}U from the voluminous ash may also be an option and requires further study.

Classification of fly ash for use in residential building should also be given due consideration.

TENORM is increasingly accumulating in the environment along with toxic trace elements such as As, Cd, Cr, Hg, Pb, etc. and major elements such as Na, Mg, Al, Si, K, Ca, Ti, Fe, etc. These materials have potential benefits and threats which may someday be of such significance that they should now be given due attention.

Appendix A

Sample NIRS ICP-MS print-out

定量ﾚﾎﾟｰﾄ - 要約

ﾌｧｲﾙ名　　1130Q51M.D
　　DEFAULT.M
測定日時　　Nov 30 105　01:36 pm
ｻﾝﾌﾟﾙ名
ﾀｲﾌﾟ　　: 未知試料
ﾗﾍﾞﾙ　　:
希釈倍率　　: 1.00
ｵﾍﾟﾚｰﾀ名　　:
測定ﾓｰﾄﾞ　　: [illegible]
検量線ﾀｲﾄﾙ　　:
検量線ﾀｲﾌﾟ　　: 絶対検量線法 (重み付けなし)
検量線日時　　: Nov 30 05　11:14 am
BKg ﾌｧｲﾙ　　: --------
干渉補正　　: OFF
ﾊﾞﾗﾝｸﾌｧｲﾙ　　: --------

元素	質量数	内標	ｶｳﾝﾄ	濃度	RSD(%)	時間(sec)	回数
Sr	88		1,599,023 P	17,980	0.16	9.0	3
Cd	111		130.3334 P	17.08	6.15	9.0	3
Cs	133		1,908.339 P	27.88	2.04	9.0	3
Bi	209		4,268.706 P	92.31	1.24	9.0	3
Th	232		22,669.27 P	399.6	1.82	9.0	3
U	238		27,314.19 P	443.7	2.50	9.0	3

Appendix B

ICP-MS data

Sample type	Mass of sample aliquot (g)	ICP-MS data		RSD*	
Batch 1		^{232}Th	^{238}U	^{232}Th	^{238}U
Ref. material	0.2465	139.6	27.69	0.02	0.03
C fly ash	0.3397	608.6	155.8	0.00	0.00
M fly ash	0.38	418	119.4	0.03	0.00
P fly ash	0.1928	506.6	282.5	0.02	0.02
S fly ash	0.288	419.9	207.3	0.03	0.04
Blank 1		-2.16	1.05	0.02	0.46
Batch 2					
C bottom ash	0.1059	391.5	92.18	0.02	0.02
M bottom ash	0.0989	208.3	92.03	0.01	0.01
P bottom ash	0.1093	576.5	138.6	0.03	0.03
S bottom ash	0.1201	223.1	89.66	0.02	0.02
C ESP 2nd	0.1169	221	73.95	0.02	0.03
Blank 2	0.1059	-6.60	0.27	0.08	0.14
Batch 3					
C feed coal	0.1144	39.32	12.48	0.05	0.02
M feed coal	0.1103	144.9	33.05	0.02	0.01
P feed coal	0.1058	40.47	11.58	0.03	0.04
S feed coal	0.1061	165.2	46.51	0.01	0.03
C ESP 1st	0.1094	797.2	222.7	0.02	0.02
Blank 3		-6.64	-1.84	0.07	0.09
Std Solution					
0		-6.59	-1.56	0.04	0.06
25		16.57	23.04	0.10	0.04
50		38.89	46.19	0.03	0.02
100		85.41	92	0.04	0.02
250	1^{st} run	243	252.1	0.02	0.01
	2^{nd} run	236.8	243.9	0.02	0.01
	3^{rd} run	236.4	243.4	0.01	0.02
	4^{th} run	234	242	0.01	0.03

***Relative standard deviation**

Appendix C

Mass concentration (µg/g) of ^{232}Th and ^{238}U and relative standard deviation (RSD) obtained from NIRS ICP-MS 1(used in this work) and ICP-MS 2

	ICP-MS 1 µg/g		ICP-MS 2 µg/g		RSD (ICP-MS 1)		RSD (ICP-MS 2)	
Batch 1	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U
JLK-1 lake sediment (Reference material)	19.39	3.85	19.62	3.88	0.02	0.03	0.06	0.05
C fly ash	12.55	3.21	12.16	3.09	0.00	0.00	0.04	0.04
M fly ash	15.64	4.47	16.17	4.49	0.03	0.00	0.05	0.06
P fly ash	38.67	21.56	38.81	21.12	0.02	0.02	0.04	0.04
S fly ash	21.57	10.65	26.28	12.81	0.03	0.04	0.04	0.04
Blank 1	-2.16	1.05	1.71	0.21	0.02	0.46	0.30	0.51

Appendix D

Sample NIRS HPGe GS print out

P-ash pond(Nov 29-Nov 30).CHN

P-ash pond(Nov 29- Nov 30)

Acquired:2005-11-29 13:11:47 Real Time:80000.0(sec) Live Time:79370.9(sec)

核種名	ｴﾈﾙｷﾞｰ (keV)	ﾋﾟｰｸﾁｬﾈﾙ (ch)	ﾋﾟｰｸ面積 (cnt)		検出限界 (cnt)	検出効率 (%)r	サム効果補正係数	自己吸収補正係数	減衰補正係数	放射能 (Bq/g)		検出限界 (Bq/g)		Pr Mark
Am-241	59.54	59.77	1064.9±	69.9 >	190.2	2.8384	1.000000	1.000000	1.000000	1.311648E+00±	8.687582E-02 >	2.364230E-01	1	NF
*Th-231	84.21	84.46	181.2±	55.8 >	156.9	4.4642	1.000000	1.000000	1.000000	7.833717E-01±	2.410220E-01 >	7.213959E-01	1	
*Th-228	84.37	84.63	181.2±	55.8 >	156.9	4.4931	1.000000	1.000000	1.000000	4.199833E+00±	1.292174E+00 >	3.867572E+00	1	
*Th-234	92.80	93.06	1897.8±	86.8 >	233.8	4.9251	1.000000	1.000000	1.000000	8.042987E+00±	4.112404E-01 >	1.107414E+00	1	
*Ra-226	186.18	186.44	1238.8±	99.9 >	284.9	6.2133	1.000000	1.000000	1.000000	7.611772E+00±	8.136553E-01 >	1.750721E+00	1	
*Pb-212	238.63	238.92	497.8±	87.2 >	257.5	5.8006	1.000000	1.000000	1.000000	2.604280E-01±	4.583523E-02 >	1.347268E-01	1	
*Ra-224	240.98	241.38	497.8±	87.2 >	257.5	5.6464	1.000000	1.000000	1.000000	2.888991E+00±	5.082429E-01 >	1.494557E+00	1	
*Pb-214	351.99	352.04	5269.9±	98.1 >	202.5	4.3924	1.000000	1.000000	1.000000	4.118844E+00±	7.668174E-02 >	1.583080E-01	1	
*Tl-208	583.14	583.09	3176.0±	70.6 >	132.3	3.2038	1.000000	1.000000	1.000000	4.042287E+00±	8.988293E-02 >	1.683297E-01	1	
*Cs-134	604.66	605.39	533.9±	48.6 >	132.8	3.1318	1.000000	1.000000	1.000000	2.201695E-01±	2.003811E-02 >	5.477139E-02	1	
*Bi-214	609.31	610.04	4393.3±	76.7 >	131.8	3.1168	1.000000	1.000000	1.000000	3.852280E+00±	6.899976E-02 >	1.156856E-01	1	
*Bi-212	727.27	728.11	753.4±	44.5 >	109.6	2.7904	1.000000	1.000000	1.000000	5.398388E+00±	3.188221E-01 >	7.856392E-01	1	
*Nb- 95	765.79	766.65	313.0±	39.0 >	108.8	2.7018	1.000000	1.000000	1.000000	1.462165E-01±	1.820626E-02 >	5.081094E-02	1	
*Tl-208	860.37	860.36	347.0±	39.2 >	108.1	2.5121	1.000000	1.000000	1.000000	1.450289E+00±	1.638559E-01 >	4.517500E-01	2	
*Ac-228	911.20	910.97	2346.1±	66.9 >	94.1	2.4235	1.000000	1.000000	1.000000	4.517255E+00±	1.095279E-01 >	1.811858E-01	1	
*Zn- 65	1115.52	1116.71	295.3±	31.4 >	83.5	2.1358	1.000000	1.000000	1.000000	3.433078E-01±	3.650032E-02 >	9.702458E-02	1	
*K - 40	1460.75	1460.41	2401.0±	52.8 >	63.3	1.8043	1.000000	1.000000	1.000000	1.571293E+01±	3.452155E-01 >	4.141008E-01	1	
*Tl-208	2614.50	2614.06	1488.1±	41.0 >	46.1	1.2539	1.000000	1.000000	1.000000	1.498261E+00±	4.124171E-02 >	4.839000E-02	3	

Appendix E

Sample PNRI HPGe GS print out

Detector #1 ACQ 24-Nov-2006 at 17:57:58 RT = 80000.0 LT = 79936.7
mcb1
S-fly ash, 154.6 g (Nov 24-25, 2006)

ROI#	RANGE(keV)		GROSS	NET	+/-	CENTROID	FWHM	FW(1/5)M	LIBRARY (keV)		cA	+/-
1	42.19	52.19	7925	1554	82	47.74	0.00	3.54	Sm-153	48.30	0.88	0.05
2	58.19	68.19	14500	521	110	63.25	1.62	2.93	Hf-181	63.20	0.12	0.02
3	72.19	98.19	53673	7629	410	77.00	1.12	3.59	Pb-214	77.11	0.89	0.05
4	124.19	134.19	11234	632	97	129.29	1.69	3.44	No close library match.			
5	139.18	159.18	20807	773	225	154.19	1.37	2.57	Xe-138	153.75	0.16	0.05
6	181.18	191.18	12264	2850	103	186.30	1.62	3.02	Ra-226	185.99	1.09	0.04
7	204.18	214.18	9281	782	88	209.67	1.76	2.65	Np-239	209.75	0.30	0.03
8	234.18	244.18	20795	8248	136	239.07	1.41	2.51	Ba-131	239.63	4.28	0.07
9	254.18	283.18	18282	1247	263	270.69	1.99	2.91	Rb-89	272.45	1.01	0.21
10	291.18	301.18	12154	5600	105	295.72	1.85	2.74	Pb-214	295.22	0.36	0.01
11	323.18	344.18	12223	2418	169	338.91	1.77	2.78	Cs-136	340.57	0.06	0.00
12	347.18	357.18	13997	9619	115	352.56	1.93	2.91	Pb-214	351.99	0.32	0.00
13	405.18	415.18	3971	193	57	410.25	1.29	2.78	Eu-152	411.09	0.11	0.03
14	459.18	469.18	3388	539	53	463.59	2.02	3.10	Cs-138	462.79	0.02	0.00
15	507.18	517.18	6928	3817	80	511.88	2.64	4.15	Rh-106M	511.80	0.06	0.00
16	579.18	589.18	5108	2824	68	584.25	1.65	3.12	Ba-131	585.02	2.86	0.07
17	605.18	615.18	9189	7007	93	610.49	2.00	3.21	Ru-103	610.33	1.65	0.02
18	723.17	733.17	2305	580	44	728.61	2.29	3.62	J-134	730.60	0.33	0.03
19	765.17	775.17	2298	534	44	769.88	2.06	3.25	Bi-214	768.36	0.14	0.01
20	782.17	813.17	4977	614	139	796.33	1.86	3.10	Cs-134	795.76	0.01	0.00
21	856.17	868.17	1775	360	44	862.06	2.17	3.53	No close library match.			
22	907.17	919.17	3330	1768	59	912.99	2.17	3.44	No close library match.			
23	930.17	942.17	1720	344	44	935.86	2.08	3.26	Ag-110M	937.48	0.01	0.00
24	965.17	977.17	2691	739	54	970.87	1.89	2.93	J-135	972.61	0.77	0.06
25	1116.17	1128.17	2484	1409	51	1122.41	2.10	3.43	Ta-182	1121.28	0.05	0.00
26	1151.17	1163.17	1246	148	37	1157.46	2.41	4.17	Bi-214	1155.19	0.11	0.03
27	1234.17	1246.17	1572	506	41	1240.52	2.49	3.94	Co-56	1238.28	0.01	0.00
28	1277.17	1289.17	989	151	33	1283.51	1.91	3.98	Bi-214	1280.96	0.13	0.03
29	1374.16	1386.16	1046	359	34	1380.43	2.15	3.50	Bi-214	1377.65	0.11	0.01
30	1398.16	1417.16	1218	348	48	1410.55	2.53	4.11	Eu-152	1408.08	0.02	0.00
31	1457.16	1469.16	3566	2982	60	1463.62	2.31	3.82	K-40	1460.75	0.35	0.01
32	1506.16	1518.16	718	174	28	1512.36	2.66	4.16	Bi-214	1509.19	0.10	0.02
33	1658.16	1670.16	436	107	22	1664.12	1.54	4.58	Bi-214	1661.28	0.12	0.02
34	1727.16	1739.16	510	261	23	1732.84	2.31	4.16	Bi-214	1729.60	0.11	0.01
35	1762.16	1774.16	1477	1195	39	1767.93	2.57	4.00	Xe-138	1768.26	0.09	0.00
36	1844.16	1858.16	478	176	25	1850.89	2.70	4.12	Xe-138	1850.86	0.15	0.02

Appendix F
NIRS HPGe data and results

F.1 ^{238}U series and ^{40}K

Activity concentration (AC) of Ra-226 taken from the mean of the ACs of its gamma emitting decay products Pb-214, Bi-214, and K-40 in feed coal and ash samples determined by NIRS HPGe Gamma Spectrometry (1)

PLANT	ORIGIN	SAMPLING DATE	SAMPLE TYPE	NO. OF SAMPLES	U-238 SERIES								K-40	
					Pb-214 (295.2 keV)		Pb-214 (351.9 keV)		Bi-214 (609.3 keV)		Ra-226		K-40 (1460.8 keV)	
					Eff=0.012	BR=0.185	Eff=0.011	BR=0.358	Eff=0.007	BR=0.448	Ave: Pb-214, Bi-214		Eff=0.018	BR=0.107
					AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)
					Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
C (Unit 1)	Semirara, Indonesia	15-18 Jun 05	Feed coal	1	**10.20**	3.10	**14.82**	2.23	**10.10**	1.70	**11.70**	1.39	**80.23**	10.91
			Bottom ash	1	**31.95**	4.51	**31.22**	3.67	**26.54**	3.11	**29.90**	2.20	**259.76**	28.54
			Economizer	1	**37.49**	4.71	**37.28**	4.19	**33.26**	3.70	**36.01**	2.44	**369.67**	39.48
			ESP 1st stage	1	**53.13**	6.23	**56.73**	6.15	**50.41**	5.43	**53.43**	3.43	**369.08**	40.87
			ESP 2nd stage	1	**58.87**	6.88	**58.78**	6.40	**51.28**	5.55	**56.31**	3.64	**382.20**	39.39
			0.0*	1	**30.82**	4.06	**33.75**	3.82	**29.38**	3.31	**31.32**	2.16	**290.71**	31.36
M	Tianjin, China	20 Jul 05	Feed coal	1	**8.07**	2.98	**7.86**	1.78	**4.29**	1.31	**6.74**	1.24	**30.74**	6.44
			Bottom ash	1	**108.78**	12.35	**111.64**	11.99	**99.79**	10.61	**106.73**	6.74	**217.09**	25.10
			Fly ash	1	**110.45**	12.29	**116.47**	12.36	**101.78**	10.70	**109.57**	6.82	**229.85**	26.93
P	Semirara, Indonesia	9 Sep 05	Feed coal	1	**2.65**	3.08	**3.46**	1.80	**-0.58**	1.30	**3.05**	1.27	**13.90**	5.70
			Bottom ash	1	**57.99**	7.29	**51.69**	5.86	**45.06**	5.08	**51.58**	3.55	**203.94**	23.55
			Fly ash	1	**51.59**	6.31	**53.62**	5.90	**47.17**	5.14	**50.79**	3.35	**197.71**	22.17
			Ash pond	1	**42.91**	5.35	**43.97**	4.92	**38.69**	4.30	**41.86**	2.82	**159.14**	18.24
S	Shinwa, China	1 Aug 05	Feed coal	1	**10.65**	3.44	**11.16**	2.09	**8.50**	1.70	**10.11**	1.46	**51.80**	8.88
			Bottom ash	1	**86.00**	9.73	**87.47**	9.39	**76.35**	8.13	**83.27**	5.26	**400.93**	43.06
			Fly ash	1	**132.28**	14.52	**140.12**	14.79	**120.98**	12.65	**131.13**	8.09	**354.47**	38.18

Eff-Efficiency

BR-Branching ratio

U (k=2)-Expanded relative uncertainty at 95% confidence level

negative AC means blank count is greater than sample count

Appendix F. Continued.
NIRS HPGe data and results

F.2 ^{232}Th series

Activity concentration (AC) of Ra-228 and Th-228 in feed coal and ash samples taken from the mean of the ACs of their gamma emitting decay products by NIRS HPGe Gamma Spectrometry (2)

PLANT	SAMPLE TYPE	Th-232 series															
		Pb-212 (238.6 keV)		Tl-208 (583.2 keV)		Tl-208 (2614.533 keV)		Tl-208		Bi-212		Th-228		Ac-228 (911.2 keV)		Ra-228	
		Eff=0.014	BR=0.433	Eff=0.00722	BR=0.852	Eff=0.013	BR=1.00	Ave		Tl-208/0.36	U/0.36	Ave: Pb-212, Tl-208		Eff=0.005	BR=0.266	In equilib w/ Ac-228	
		AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)
		Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
C (Unit 1)	Feed coal	10.96	2.65	4.82	0.76	3.63	0.74	4.22	1.06	11.73	2.94	11.35	3.96	13.65	4.99	13.65	4.99
	Bottom ash	33.98	4.66	12.17	1.42	11.68	1.46	11.93	2.04	33.13	5.66	33.55	7.33	37.04	4.83	37.04	4.83
	Economizer	41.74	4.37	13.88	1.55	14.34	1.67	14.11	2.28	39.20	6.34	40.47	7.70	41.54	5.21	41.54	5.21
	ESP 1st	57.40	5.94	19.60	2.42	19.51	2.19	19.56	3.27	54.32	9.08	55.86	10.85	61.96	7.46	61.96	7.46
	ESP 2nd	60.91	6.32	19.97	2.15	19.14	2.14	19.56	3.04	54.32	8.43	57.62	10.54	74.04	8.85	74.04	8.85
M	Feed coal	5.57	1.62	1.86	0.56	2.26	0.64	2.06	0.85	5.72	2.36	5.64	2.86	6.44	1.88	6.44	1.88
	Bottom ash	61.71	6.50	19.88	2.26	19.69	2.35	19.78	3.27	54.96	9.07	58.33	11.16	59.48	7.62	59.48	7.62
	Fly ash	66.86	7.10	20.92	2.15	20.54	2.33	20.73	3.17	57.59	8.81	62.22	11.32	67.19	8.56	67.19	8.56
P	Feed coal	1.04	1.65	0.32	0.58	1.17	0.63	0.74	0.85	2.07	2.37	1.55	2.89	1.72	1.66	1.72	1.66
	Bottom ash	59.37	6.27	19.04	2.16	19.59	2.32	19.31	3.17	53.65	8.80	56.51	10.81	55.79	7.13	55.79	7.13
	Fly ash	66.03	6.96	20.12	2.21	19.75	2.24	19.94	3.14	55.38	8.73	60.71	11.16	65.22	7.87	65.22	7.87
	Ash pond	51.44	5.42	16.23	1.81	15.17	1.79	15.70	2.55	43.61	7.08	47.52	8.92	50.66	6.27	50.66	6.27
S	Feed coal	9.48	1.52	3.16	0.72	2.77	0.75	2.97	1.04	8.25	2.90	8.87	3.27	12.08	2.48	12.08	2.48
	Bottom ash	66.27	6.91	22.25	2.44	20.68	2.36	21.46	3.39	59.62	9.42	62.95	11.69	66.64	8.16	66.64	8.16
	Fly ash	86.60	9.11	27.69	2.96	28.13	3.06	27.91	4.26	77.54	11.83	82.07	14.93	87.70	10.45	87.70	10.45

Eff-Efficiency

BR-Branching ratio

U (k=2)-Expanded relative uncertainty at 95% confidence level

negative AC means blank count is greater than sample count

Appendix G
PNRI HPGe data and results

G.1 ^{238}U series and ^{40}K

Activity concentration (AC) of Ra-226 in feed coal and ash samples taken from the mean of the ACs of its gamma emitting decay products and K-40 determined by PNRI HPGe Gamma Spectrometry (!)

PLANT	SAMPLE TYPE	NO. OF SAMPLES	U-238 Series								K-40	
			Pb-214 (295.2 keV)		Pb-214 (351.9keV)		Bi-214 (609.3 keV)		Ra-226		K-40 (1460.8 keV)	
			Eff=0.01196	BR=0.185	Eff=0.01067	BR=0.358	Eff=0.00693	BR=0.448	Ave: Pb, Bi		Eff=0.0031	BR=0.107
			Act conc	U (k=2)	Act conc	U (k=2)	Act Conc	U (k=2)	Act conc	U (k=2)	Act Conc	U (k=2)
			Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
C (Unit -1)	Feed coal	5	9.35	2.85	10.12	2.82	9.23	1.55	9.57	1.43	111.12	13.36
	Bottom ash	2	29.61	3.92	33.28	3.16	28.61	3.07	30.50	1.97	272.23	17.48
	Economizer	1	47.72	8.84	49.87	8.42	36.29	5.46	44.63	4.46	270.04	26.27
	EP silo 1st	2	52.07	2.83	68.12	9.11	58.00	5.56	59.39	3.68	414.23	21.75
	EP silo 2nd	1	98.06	12.49	76.97	8.58	72.42	8.86	82.48	5.85	435.78	27.08
	EP silo 3rd	2	122.08	13.42	172.57	17.05	110.50	11.11	135.05	8.13	766.49	42.43
M	Feed Coal	1	9.88	4.67	9.24	2.75	8.11	2.56	9.08	3.33	53.73	23.54
	Bottom ash	1	142.44	17.60	124.60	13.60	107.96	11.80	125.00	14.33	419.10	52.00
	Fly ash	1	131.51	15.86	169.93	20.48	112.22	12.79	137.88	16.38	351.06	44.70
P (Unit 1)	Feed Coal	2	-3.19	-2.71	-1.35	-1.47	-1.88	-1.69	-2.14	1.17	14.90	13.66
	Bottom ash	1	45.86	7.85	96.60	14.50	51.04	6.52	64.50	5.91	179.86	30.94
	Fly ash	4	86.46	5.74	91.28	6.15	61.59	3.48	79.78	3.03	251.52	17.60
	Ash pond	1	80.72	10.43	90.02	11.95	60.15	6.75	76.96	5.75	189.60	25.20
P (Unit 2)	Feed Coal	2	-0.83	-3.26	-1.59	-1.75	-2.08	-1.89	-1.50	1.39	16.54	12.85
	Bottom ash	1	66.93	10.50	106.28	16.17	61.79	8.14	78.33	6.97	284.15	41.38
	Fly ash	3	86.55	6.64	47.04	4.44	61.71	4.15	65.10	3.00	295.06	22.53
	Ash pond	1	41.70	6.69	83.50	12.69	47.67	5.94	57.63	5.17	203.44	30.53
S	S-feed coal	1	15.88	5.45	27.21	8.69	16.50	2.95	19.87	3.56	56.10	26.35
	S-bottom ash	1	137.93	18.21	206.36	28.12	129.38	11.08	157.89	11.76	638.30	77.84
	S-fly ash	1	218.09	6.21	158.65	4.74	166.59	2.97	181.11	2.79	409.79	58.03

Appendix G. Continued.
PNRI HPGe data and results

G.2 ^{232}Th series

Activity concentration (AC) of Ra-228 and Th-228 in feed coal and ash samples taken from the mean of the ACs of its gamma emitting decay products by PNRI HPGe Gamma Spectrometry (2)

PLANT	SAMPLE TYPE	NO. OF SAMPLES	Th-232 series											
			Pb-212 (238.6 keV)		Tl-208 (583.2 keV)		Bi-212		Th-228		Ac-228 (911.2 keV)		Ra-228	
			Eff=0.01376	BR=0.433	Eff=0.00722	BR=0.852	Tl-208/0.36		Ave: Pb-212, Bi-212		Eff=0.00469	BR=0.266	same as Ac-228	
			Act conc	U (k=2)	Act conc	U (k=2)	Act Conc	U (k=2)	Act Conc	U (k=2)	Act conc	U (k=2)	Act Conc	U (k=2)
			Bq/kg	Bq/kg	Bq/kg	Bq/kg					Bq/kg	Bq/kg	Bq/kg	Bq/kg
C (Unit -1)	Feed coal	5	**12.33**	3.41	**4.96**	0.69	13.78	1.91	**5.34**	1.96	**12.33**	3.41	**12.33**	3.41
	Bottom ash	2	**45.95**	3.84	**14.04**	1.32	39.01	3.67	**42.48**	2.65	**45.95**	5.77	**45.95**	5.77
	Economizer	1	**41.09**	7.74	**15.95**	2.15	44.31	5.98	**42.70**	4.89	**41.09**	7.36	**41.09**	7.36
	EP silo 1st	2	**103.35**	7.87	**24.14**	2.12	67.06	5.90	**85.20**	4.92	**70.30**	8.44	**70.30**	8.44
	EP silo 2nd	1	**83.73**	8.84	**24.74**	2.85	68.72	7.90	**76.22**	5.93	**86.38**	11.56	**86.38**	11.56
	EP silo 3rd	2	**182.07**	14.18	**44.38**	4.40	123.26	12.23	**152.67**	9.36	**140.47**	15.94	**140.47**	15.94
M	Feed Coal	1	**3.49**	1.92	**2.38**	1.05	6.62	2.93	**5.06**	1.75	**6.6**	2.2	**6.58**	0.70
	Bottom ash	1	**82.52**	8.98	**27.87**	3.26	77.42	9.06	**79.97**	6.38	**104.2**	35.1	**104.17**	11.70
	Fly ash	1	**121.06**	17.71	**26.43**	3.12	73.42	8.65	**97.24**	9.86	**89.2**	30.1	**103.20**	11.60
P (Unit 1)	Feed Coal	2	**1.13**	1.06	**0.97**	0.71	2.70	1.98	**1.92**	1.12	**1.63**	3.66	**1.63**	3.66
	Bottom ash	1	**88.78**	9.85	**21.61**	3.49	60.03	9.69	**74.41**	6.91	**62.76**	10.23	**62.76**	10.23
	Fly ash	4	**97.65**	5.36	**25.51**	1.54	70.86	4.27	**84.26**	3.43	**77.06**	5.31	**77.06**	5.31
	Ash pond	1	**84.08**	8.97	**19.28**	2.41	53.55	6.71	**68.82**	5.60	**60.98**	8.92	**60.98**	8.92
P (Unit 2)	Feed Coal	2	**2.17**	1.61	**0.76**	0.58	2.10	1.62	**2.14**	1.14	**-1.17**	-3.50	**-1.17**	-3.50
	Bottom ash	1	**106.82**	11.69	**23.57**	3.68	65.48	10.21	**86.15**	7.76	**72.90**	13.40	**72.90**	13.40
	Fly ash	3	**105.62**	6.62	**26.55**	1.84	73.75	5.12	**89.69**	4.18	**79.01**	6.20	**79.01**	6.20
	Ash pond	1	**79.10**	9.06	**19.06**	2.68	52.95	7.45	**66.02**	5.86	**50.99**	8.83	**50.99**	8.83
S	S-feed coal	1	**19.80**	3.75	**5.31**	1.63	14.74	4.52	**17.27**	2.94	**10.74**	5.61	**10.74**	5.61
	S-bottom ash	1	**169.55**	18.21	**32.21**	5.03	89.47	13.97	**129.51**	11.48	**109.67**	15.96	**109.67**	15.96
	S-fly ash	1	**183.30**	19.76	**35.56**	1.25	98.79	3.49	**141.04**	10.03	**111.37**	17.74	**111.37**	17.74

Appendix G. Continued.
PNRI HPGe data and results

G.3

Activity concentration (AC) of Ra-226, Th-228, Ra-228, and *K-40 in Plant C samples by PNRI HPGe Spectrometry*

Coal origin: Semirara ; Sampling Date: 19-23 June 2006

SAMPLE TYPE	PLANT	NO. OF SAMPLES	U-238 Series									
			Pb-214 (295.2 keV)		Pb-214 (351.9keV)		Bi-214 (609.3 keV)		Ra-226		K-40 (1460.8 keV)	
			Eff=0.01196	BR=0.185	Eff=0.01067	BR=0.358	Eff=0.00693	BR=0.448			Eff=0.0031	BR=0.107
			Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
Feed coal	Unit 1	3	8.53	2.59	14.47	3.01	9.97	1.91	10.76	3.14	70.89	25.85
	Unit 2	3	10.73	3.63	16.07	4.02	10.78	2.23	12.38	3.46	105.17	38.93
Bottom ash	Unit 1	2	52.84	6.07	51.60	4.37	45.20	3.89	49.80	5.50	420.72	43.33
	Unit 2	2	51.00	6.30	61.17	7.57	41.81	3.87	51.29	6.28	410.58	42.33
Fly ash	Unit 1: ESP 2nd	1	80.66	11.16	65.92	7.46	58.32	6.65	68.23	8.40	478.65	59.23
	Unit 1: ESP 3rd	1	64.73	8.46	71.00	7.97	65.26	7.34	66.93	7.89	496.10	60.31
	Unit 2: ESP 1st	1	71.28	9.80	55.07	6.26	51.51	5.86	59.23	7.29	485.56	53.85
	Unit 2: ESP 2nd	1	83.72	11.44	68.65	7.74	58.68	6.70	70.28	8.60	558.36	62.85

SAMPLE TYPE	PLANT	NO. OF SAMPLES	Th-232 series									
			Pb-212 (238.6 keV)		Tl-208 (583.2 keV)		Th-228		Ac-228 (911.2 keV)		Ra-228	
			Eff=0.01376	BR=0.433	Eff=0.00722	BR=0.852			Eff=0.00469	BR=0.266		
			Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
Feed coal	Unit 1	3	15.04	1.74	3.76	0.86	12.74	1.48	11.38	3.19	11.38	3.19
	Unit 2	3	18.14	2.63	4.69	1.08	15.58	1.99	9.47	4.37	9.47	4.37
Bottom ash	Unit 1	2	69.78	5.36	19.78	1.71	62.36	3.58	53.22	6.27	53.22	6.27
	Unit 2	2	74.41	6.00	19.23	1.84	63.91	3.94	51.63	6.17	51.63	6.17
Fly ash	Unit 1: ESP 2nd	1	79.36	8.46	22.49	2.63	70.91	5.59	74.27	10.16	74.27	10.16
	Unit 1: ESP 3rd	1	75.33	8.06	21.06	2.50	66.92	5.32	76.67	10.43	76.67	10.43
	Unit 2: ESP 1st	1	74.47	7.89	20.32	2.35	65.45	5.12	65.63	8.95	65.63	8.95
	Unit 2: ESP 2nd	1	78.46	8.37	22.69	2.65	70.74	5.57	76.33	10.69	76.33	10.69

Appendix G. Continued.
PNRI HPGe data and results

G.4

Activity concentration (AC) of Ra-226 taken from the mean of the ACs of its gamma emitting decay products, and K-40 in samples from Plant C ash pond collected in 2005 and 2006 by PNRI HPGe Spectrometry (1)

Gamma Spectrometry	SAMPLING DATE	DEPTH (m)	NO. OF SAMPLES	U-238 Series								K-40	
				Pb-214 (295.2 keV)		Pb-214 (351.9 keV)		Bi-214 (609.3 keV)		Ra-226		K-40 (1460.8 keV)	
				Eff=0.012	BR=0.185	Eff=0.011	BR=0.358	Eff=0.007	BR=0.448	Ave: Pb-214, Bi-214		Eff=0.003	BR=0.107
				AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)
				Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg		
NIRS HPGe	2005 Jun	0.0	1	**30.82**	4.06	**33.75**	3.82	**29.38**	3.31	**31.32**	2.16	**290.71**	31.36
		0.5	1	**40.19**	5.28	**42.69**	4.86	**35.16**	4.01	**39.35**	2.74	**348.49**	37.77
		1.0	1	**43.48**	5.63	**47.15**	5.32	**37.55**	4.27	**42.73**	2.95	**446.73**	47.81
		2.0	1	**36.89**	4.34	**32.01**	3.69	**26.28**	3.05	**31.73**	2.15	**334.41**	35.97
PNRI HPGe	2005 Jun	0.0	3	63.26	5.71	48.05	3.38	43.92	3.49	51.74	4.19	408.70	16.72
		0.5	1	**75.71**	11.65	**54.68**	6.70	**53.73**	7.33	61.37	8.56	**467.96**	33.33
		1.0	1	**38.18**	7.48	**14.49**	7.73	**46.46**	7.42	33.04	7.54	**453.78**	33.01
		1.5	1	**59.88**	8.88	**43.02**	5.21	**39.18**	5.37	47.36	6.49	**432.24**	27.26
		2.0	1	**47.05**	8.08	**35.48**	4.54	**29.77**	4.36	37.43	5.66	**390.35**	27.00
PNRI HPGe	2006 Jun	0.0	1	**59.65**	9.73	**64.27**	8.06	**60.63**	7.65	**61.52**	8.48	**455.38**	86.10
		0.5	1	**66.55**	10.63	**80.38**	14.04	**43.50**	6.11	**63.48**	10.26	**471.33**	72.98
		1.0	1	**44.19**	8.81	**24.63**	5.13	**42.73**	8.28	**37.18**	7.41	**561.54**	85.37
		1.5	1	**32.94**	6.76	**42.58**	8.53	**28.79**	4.12	**34.77**	6.47	**441.28**	63.21
		2.0	1	**28.09**	6.81	**63.48**	11.36	**34.11**	4.91	**41.89**	7.69	**408.43**	59.11

Appendix G. Continued.
PNRI HPGe data and results

G.5

Activity concentration (AC) of Th-228 and Ra-228 taken from the ACs of their gamma emitting decay products in samples from Plant C ash pond collected in 2005 and 2006 by NIRS and HPGe Spectrometry (2)

HPGe	SAMPLING DATE	DEPTH (m)	NO. OF SAMPLES	Th-232 series													
				Pb-212 (238.6 keV)		Tl-208 (583.2 keV)		Tl-208 (2614.5 keV)		Bi-212		Th-228		Ac-228 (911.2 keV)		Ra-228	
				Eff=0.014	BR=0.433	Eff=0.0072	BR=0.852	Eff=0.013	BR=1.00	(Tl-208/0.36)		Ave: Pb-212, Bi-212		Eff=0.005	BR=0.266	same as Ac-228	
				AC	U (k=2)	U (k=2)	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)	AC	U (k=2)
				Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg					Bq/kg	Bq/kg	Bq/kg	Bq/kg
NIRS	2005 Jun	0.0	1	**40.18**	4.26	**12.55**	1.42	**13.31**	1.56	35.92	2.93	38.05	4.73	**39.82**	4.98	**39.82**	4.98
		0.5	1	**57.15**	6.03	**18.42**	2.05	**17.73**	2.08	50.21	4.06	53.68	6.67	**58.66**	7.24	**58.66**	7.24
		1.0	1	**59.63**	6.41	**18.59**	2.08	**18.78**	2.19	51.90	4.19	55.76	7.06	**57.07**	7.10	**57.07**	7.10
		2.0	1	**40.80**	4.34	**12.98**	1.48	**12.56**	1.51	35.47	2.94	38.14	4.81	**43.47**	5.44	**43.47**	5.44
PNRI	2005 Jun	0.0	3	70.03	4.35	19.79	1.40	nm		54.99	3.90	62.51	5.15	62.50	2.08	62.50	2.08
		0.5	1	**83.18**	8.93	**25.15**	3.02	nm		69.87	8.39	76.52	10.73	**71.84**	11.06	**71.84**	11.06
		1.0	1	**98.44**	11.07	**23.02**	3.09	nm		63.96	8.58	81.20	12.63	**67.32**	11.45	**67.32**	11.45
		1.5	1	**56.67**	6.15	**17.66**	2.15	nm		49.06	5.97	52.87	7.46	**50.04**	8.00	**50.04**	8.00
		2.0	1	**52.98**	5.79	**14.24**	1.86	nm		39.55	5.16	46.26	6.84	**41.75**	7.37	**41.75**	7.37
PNRI	2006 Jun	0.0	1	**89.82**	9.92	**23.85**	3.13	nm		66.26	8.68	78.04	11.66	**74.71**	12.97	**74.71**	12.97
		0.5	1	**96.14**	11.51	**23.54**	3.56	nm		65.39	9.90	80.77	13.48	**63.07**	11.60	**63.07**	11.60
		1.0	1	**89.31**	10.11	**20.35**	3.39	nm		56.52	9.41	72.91	12.10	**58.54**	10.73	**58.54**	10.73
		1.5	1	**62.81**	7.21	**13.55**	2.13	nm		37.65	5.91	50.23	8.34	**45.78**	9.39	**45.78**	9.39
		2.0	1	**67.75**	8.60	**16.56**	2.65	nm		46.00	7.36	56.88	10.05	**44.25**	8.01	**44.25**	8.01

Eff-Efficiency

BR-Branching ratio

U (k=2)-Expanded relative uncertainty at 95% confidence level

negative AC means blank count is greater than sample count

Appendix H

Photos of some locations of dose rate measurements
inside Plant C and its vicinity

Sampling dates: 15-18 June 2005

Fly ash collection area

Coal yard

Ash pond, quarried portion

Ash pond area

Sampling date: 12-16 December 2005

Fly ash silo

Fly ash cargo truck

Near coal yard area

Flag pole area

Sampling date: 12-16 December 2005 (cont'd)

Ash pond area flooded with water

Residential area across the ash pond

Sugar cane plantation across ash pond C

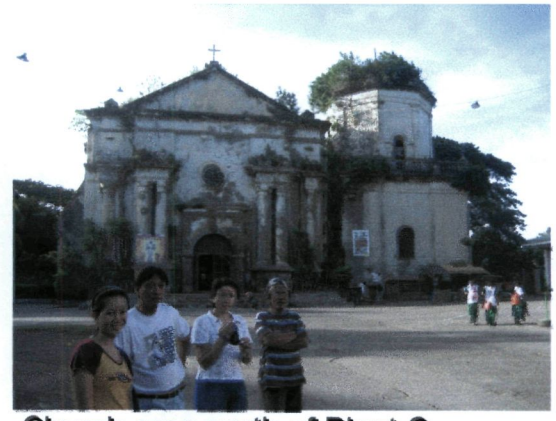
Rice and corn fields northeast of Plant

Sampling dates: 19-23 June 2006

Pasteur area nort of Plant C

Sugar plantation north of Plant C

Ash pond



Church area north of Plant C

Appendix I

Screening levels for discharges into the atmosphere and doses per unit discharge rate of atmospheric release at different effective stack heights

Partial lists of screening levels of radionuclides taken from Tables 43 and 49 of RP 135, Effluent and dose control from European Union NORM industries: Assessment of current situation and proposal for a harmonized Community approach, Radiation Protection 135 (European Commission, 2003)

Screening levels in GBq y^{-1} for discharges into the atmosphere based on a screening level dose criterion of 300 µSv y^{-1} to critical groups

Nuclide or chain segment	Stack 50 m	Critical pathway	Stack 100 m	Critical pathway	Stack 200m	Critical pathway
$^{238}U+$	2.3×10^{3}	I	1.2×10^{4}	I	2.3×10^{4}	I
$^{226}Ra+$	7.3×10^{2}	C	1.6×10^{3}	E	5.4×10^{3}	E
^{232}Th	2.1×10^{2}	I	7.3×10^{2}	E	1.9×10^{3}	I
^{228}Th	1.7×10^{2}	I	9.4×10^{2}	I	1.7×10^{3}	I
$^{228}Ra+$	1.5×10^{3}	C	4.1×10^{3}	C	1.2×10^{4}	C

Doses per unit discharge rate of 1 GBq y^{-1} of atmospheric release at different effective stack heights

Stack height	50 m		100 m		200 m	
Nuclide or chain segment	Sv/y	Critical pathway	Sv/y	Critical pathway	Sv/y	Critical pathway
$^{238}U+$	1.3×10^{-7}	I (95%)	2.5×10^{-8}	I (83%)	1.3×10^{-8}	I (92%)
$^{226}Ra+$	4.1×10^{-7}	I (35%)	1.9×10^{-7}	E (45%)	5.5×10^{-8}	I (39%)
^{232}Th	1.4×10^{-6}	I (73%)	4.1×10^{-7}	E (54%)	1.6×10^{-7}	I (65%)
^{228}Th	1.8×10^{-6}	I (99%)	3.2×10^{-7}	I (99%)	1.8×10^{-7}	I (98%)
$^{228}Ra+$	2.0×10^{-6}	I (55%)	7.3×10^{-8}	C (48%)	2.4×10^{-8}	I (45%)

I = Plume inhalation, C = Consumption of food, E = External radiation

Excerpts from Tables 43 and 49 of RP 135 on Effluent and dose control from European Union NORM industries Assessment of current situation and proposal for a harmonized Community approach, Radiation Protection 135 (European Commission, 2003)

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