



USING RARE EARTH ELEMENTS TO DETERMINE COAL ASH IMPACTS ON BACKGROUND LEVELS OF RADIUM AND THORIUM IN SOIL

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Site Background

- Large Superfund Site (>1,000 properties); industrial, recreational, and residential
- Manufactured gas mantles; imported monazite ore
- Contaminants of concern: Ra-226, Ra-228, Th-230, and Th-232



Site Cleanup Objective

- Excavate soils with total Ra and total Th concentrations 5 pCi/g above background (DCGL)
- Background calculated from samples in residential areas
- Background concentrations; both total Ra and Th ~ 2 pCi/g each



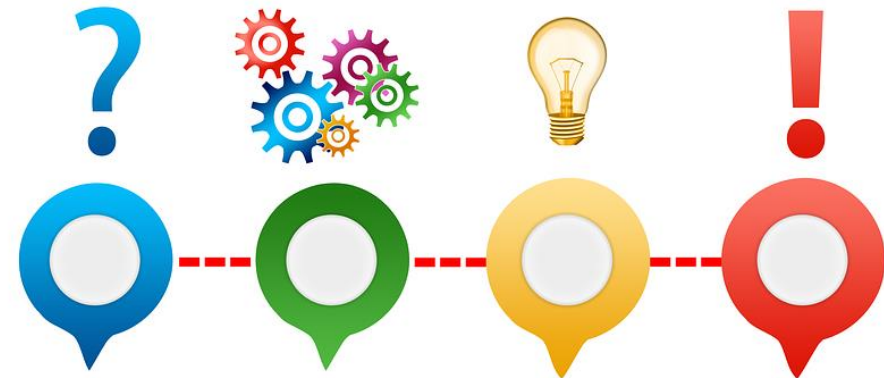
Site Remedial Activities

- 1st properties remediated in residential areas
- As excavation moved to commercial/ industrial areas, historic fill encountered
- Historic fill contains red brick, fly ash, coal ash



Problem

- This site, and many other radiation sites, had processes that generated wastes similar to NORM (fly ash, coal ash, brick, etc.)
- Sites in urban areas also have historic industrial fill with NORM
- NORM can have activity levels near, or above, a site's cleanup goal



How do I differentiate between Site-related contamination and NORM?

Solution

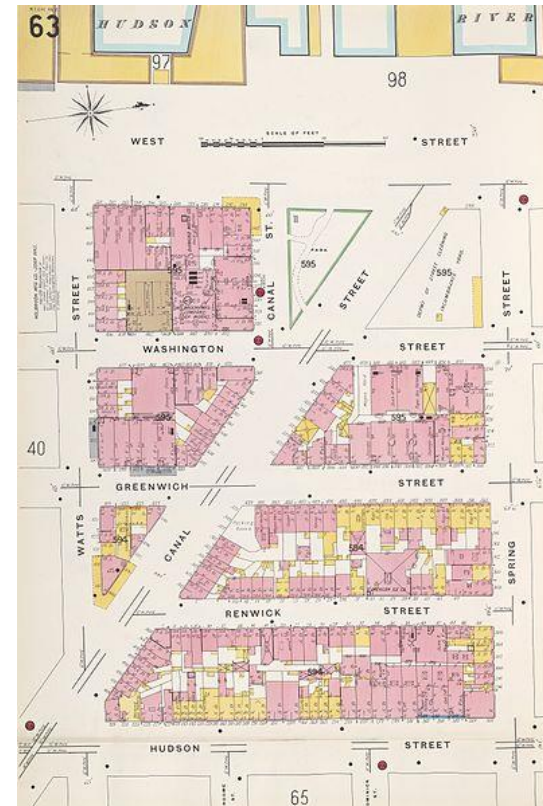
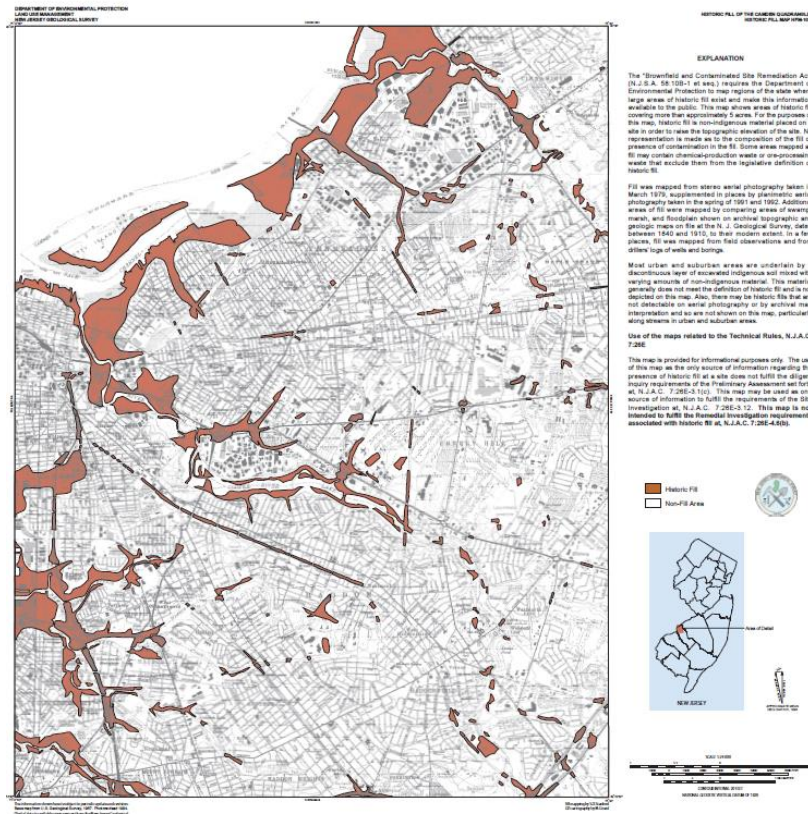
Four evaluations

1. Establish presence/absence of NORM throughout site
2. Determine typical coal ash Ra and Th levels from literature review
3. Review site data to determine if radioactivity levels in historic fill consistent with literature data
4. Establish chemical signatures for Site-related and non-Site related sources using rare earth elements (REE)



Evaluation 1 – Presence/Absence of NORM

Establish presence of historic fill – Development history assessed through historical map review



Evaluation 1 – Presence/Absence of NORM

Establish presence of NORM in historic fill – Boring logs reviewed for brick, granite and coal ash; coal ash predominant NORM

| | Coal | Non-Coal | Undetermined |
|-----------------------|------|----------|--------------|
| Number of borings | 149 | 48 | 51 |
| Percentage of borings | 60% | 19% | 21% |

**Evaluation 1 Outcome:
Historic fill containing coal ash identified across large areas of the Site**

Evaluation 2 – Literature Review

Determine typical coal ash Ra and Th levels from literature review

- IAEA, Technical Report Series No. 419, Extent of Environmental Contamination by NORM and Technological Options for Mitigation, December 2003
- USGS, Radioactive Elements in Coal and Fly Ash: Abundance, Forms, and Environmental Significance, USGS Fact Sheet FS-163-97, October 1997
- Tykva, Richard and Sabol, Joseph, Low-Level Environmental Radioactivity Sources and Evaluation, 1995
- ORNL, Coal Combustion: Nuclear Resource or Danger, Alex Gabbard, Vol. 26, Nos. 3&4, 1993

Evaluation 2 – Literature Review

| Paper | Th in Coal | Th in Fly Ash | Ra in Coal | Ra in Fly Ash |
|-------------------------------|---------------------------|----------------------------------|--------------------------|----------------------------|
| | pCi/g | | | |
| IAEA 2003 | Th-232: 0.10 – 0.57 | Th-230: 1.8 Th-232: 1.0 – 5.7 | Ra-226: 0.2 – 1.6 | Ra-226: 3.0 Ra-228: 2.6 |
| USGS 1997 | Total Th: 0.1 – 0.4 | Total Th: 1 – 4 | Not Given | Not Given |
| Tykva & Sabol 1995 | Th-232: 0.05 – 2.7 | Th: 232: 1.9 | Ra-226: 0.3 | Ra-226: 6.5 Ra-228: 3.5 |
| ORNL 1993 | 0.32 (isotope unk) | 3.2 (isotope unk) | Not Given | Not Given |
| Range from all Sources | Th-232: 0.05 – 2.7 | Total Th: 2.8 – 7.6 | Ra-226: 0.2 – 1.6 | Total Ra: 5.6 - 10 |

Evaluation 2 Outcome:
Max total Ra and total Th concentrations in US coal ash ~8 pCi/g & 10pCi/g

Evaluation 3 – Dataset

Numerous investigations from 2000 - present

- Borehole installation and collection of downhole gamma (DHG) measurements; boring logs completed
- Soil samples collected and analyzed for Ra-226, Ra-228, Th-230, and Th-232



Evaluation 3a - DHG measurements from 119 borings

Evaluation 3b - Samples from 222 borings

Evaluation 3a – Quantitative Site Data Analyses

Field Data Evaluation

1. Boring intervals with elevated DHG measurements identified
2. If no elevated readings, depth with highest DHG measurement identified
3. Intervals with elevated/highest DHG compared to strata containing coal



Evaluation 3a – Quantitative Site Data Analyses

Field Data Evaluation

| Boring type | Total | Co-located with coal ash | Not co-located with coal ash | Co-located with coal ash | Not co-located with coal ash |
|--|--------|--------------------------|------------------------------|--------------------------|------------------------------|
| | Number | | | Percentage | |
| Has elevated DHG readings; elevated readings compared to coal strata | 92 | 85 | 7 | 92% | 8% |
| No elevated DHG readings; max reading compared to coal strata | 27 | 20 | 7 | 74% | 26% |

Evaluation 3a Outcome:
Strong correlation between elevated/maximum DHG and coal-ash containing strata (88% of borings reviewed)

Evaluation 3b – Quantitative Site Data Analyses

Analytical Data Evaluation

If coal ash contributes to elevated radioactivity in historic fill, ROC concentrations should be higher in soil containing coal ash than soil without coal ash

1. Data groups established:
 - a. **Group 1** – All samples containing coal ash with total Ra and Th < 10 pCi/g
 - b. **Group 2** – All samples containing coal ash, regardless of total Ra and Th concentrations
 - c. **Group 3** – All samples without coal with total Ra and Th concentrations < Site cleanup criteria

Evaluation 3b – Quantitative Site Data Analyses

Analytical Data Evaluation

2. Data reduced - following samples removed:
 - a. Samples from borings with material classification of undetermined
 - b. Samples with rejected isotopes
 - c. Outlier sample results
 - d. Duplicative results



Evaluation 3b – Quantitative Site Data Analyses

Analytical Data Evaluation

3. Statistical evaluation:

| Group | Isotope | No. Samples | Min | Max | Mean | Median | 95% UCL |
|---------------------------------------|----------|-------------|-------|-----|------|--------|---------|
| | | | pCi/g | | | | pCi/g |
| 1 – Samples with coal ash; < 10 pCi/g | Total Ra | 74 | 0.70 | 9.6 | 5.2 | 5.4 | 5.6 |
| | Total Th | | 0.54 | 9.6 | 5.2 | 4.9 | 5.6 |
| 2 – Samples with coal ash; > 10 pCi/g | Total Ra | 117 | 0.61 | 41 | 6.2 | 5.5 | 8.4 |
| | Total Th | | 0.44 | 29 | 5.6 | 4.9 | 7.3 |
| 3 – Samples without coal ash | Total Ra | 31 | 0.53 | 6.9 | 3.4 | 3.0 | 4.0 |
| | Total Th | | 0.62 | 6.8 | 3.1 | 3.1 | 3.7 |

**Evaluation 3b Outcome:
Total Ra and Th concentrations higher in soil containing coal ash**

Evaluation 4 – Dataset

Samples collected from two areas and analyzed for REE, Ra-226, Ra-228, Th-230, and Th-232

- 1. Area 1 (Non-Impacted)** – Historic fill not impacted by Site activities that contains coal ash
- 2. Area 2 (Impacted)** – Historic fill impacted by Site activities that contains coal ash



Evaluation 4 – Calculate Ratios

Ratios calculated between REEs and ROCs

1. Th decay chain to REE ratios significantly different (12 to 20X) between impacted and non-impacted samples
2. U Decay Chain:REE ratio difference not as significant (up to 10X)
3. Cerium (Ce), lanthanum (La), neodymium (Nd) most significant difference

Monazite formula - $M(III)PO_4$ where “M” could be cerium, lanthanum, neodymium, or thorium

Evaluation 4 – Calculate Ratios

Data Summary

| Element | Non-Impacted Samples | | | Impacted Samples | | |
|---------|----------------------|------|------|------------------|------|------|
| | Average | Max | Min | Average | Max | Min |
| Ce | 231 | 282 | 121 | 421 | 947 | 66.3 |
| La | 95.7 | 115 | 48.4 | 156 | 350 | 15.5 |
| Nd | 75.2 | 97.0 | 38.0 | 213 | 486 | 23.0 |
| Ra-226 | 2.00 | 3.03 | 1.01 | 213 | 1280 | 2.96 |
| Ra-228 | 2.13 | 3.69 | 0.94 | 547 | 2760 | 17.3 |
| Th-230 | 2.35 | 4.63 | 0.76 | 49.9 | 262 | 1.56 |
| Th-232 | 2.41 | 4.54 | 0.93 | 371 | 1910 | 20.5 |

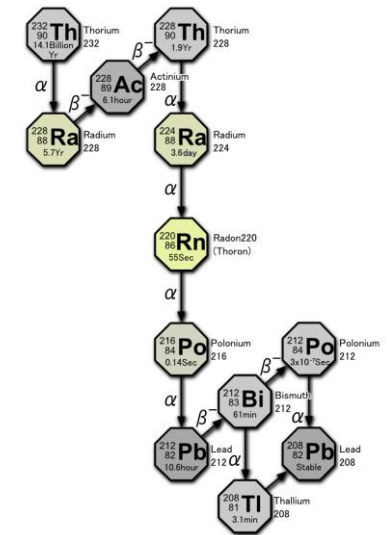
1. REE values are given in mg/kg
2. Ra and Th values are given in pCi/g

Evaluation 4 – Calculate Ratios

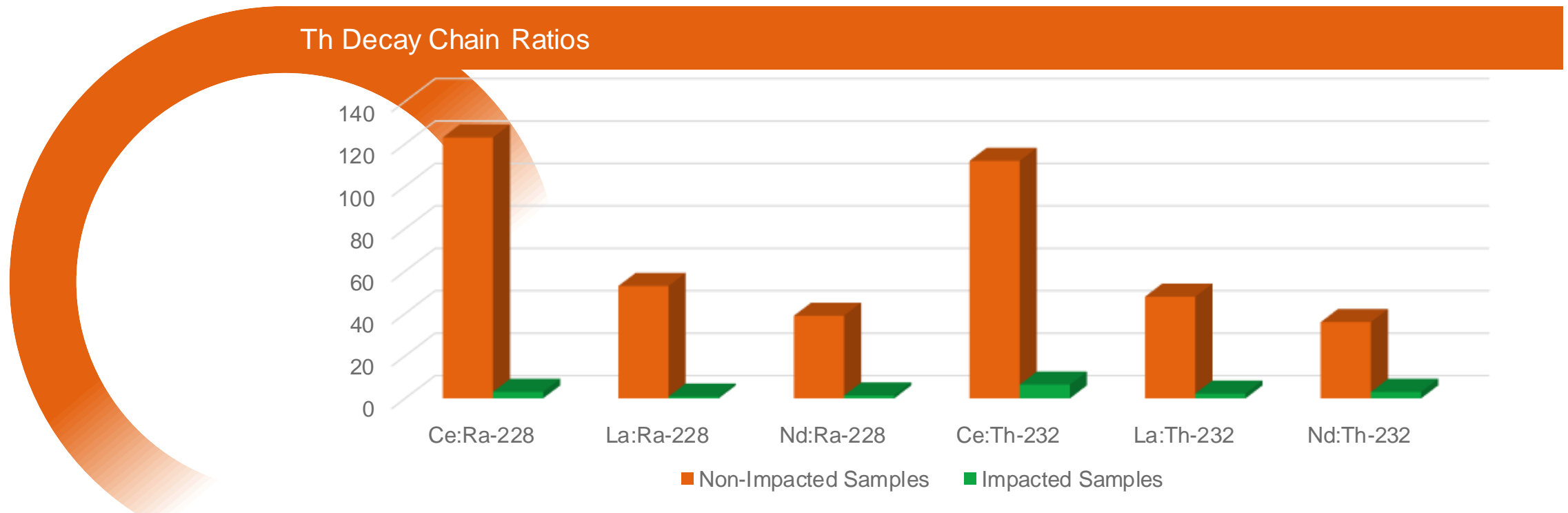
Th Decay Chain Ratios

| REE:Radionuclide Ratios | Non-Impacted Samples | Impacted Samples |
|-------------------------|----------------------|------------------|
| Ce:Ra-228 | 123 | 3.1 |
| Ce:Th-232 | 112 | 6.5 |
| La:Ra-228 | 53 | 0.9 |
| La:Th-232 | 48 | 2.3 |
| Nd:Ra-228 | 39 | 1.4 |
| Nd:Th-232 | 36 | 3.1 |

The average ratios are shown



Evaluation 4 – Establish Chemical Signatures



Evaluation 4 Outcome:
Site-related and non-site-related material can be differentiated using the REE to Ra-228 and Th-232 ratio

Revised Background

- Site-wide background not applicable to coal ash areas – calculated from ~ 100 samples; only 15% contain coal ash
- Revised background for coal-ash containing fill areas determined
 - Concentrations ~ 6 pCi/g each, total Ra and Th
 - ~ 4 pCi/g > than Site-wide background



Impact on Remediation

- ROD criteria the same; cleanup level higher
- Significantly less excavation; focused on Site-related materials
- Practical Consideration – coal ash background may not be appropriate if background corrected mean very negative
 - Upfront planning needed
 - Change from typical construction
 - Not always easy to implement in the field



Conclusions

- REE analysis and ratio determination straightforward, quick, and inexpensive
- Definitive, defensible results obtained
- Minimizes cleanup of non-site related NORM
- Evaluation could result in volume reduction and reduced cost



