A fully automated gamma-ray spectrometer for NORM characterization

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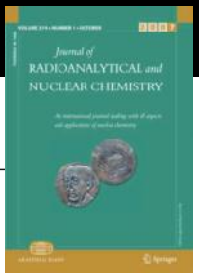
5th Workshop of the EAN$_{Norm}$
December 4th - 6th 2012 Dresden, Germany

Summary

- **NORM residues generation and NORM issue – a global overview**



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The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization

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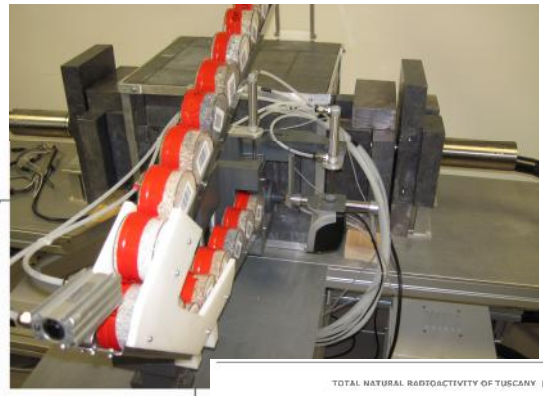
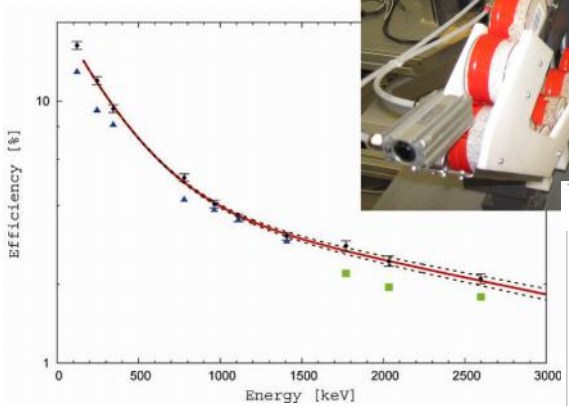
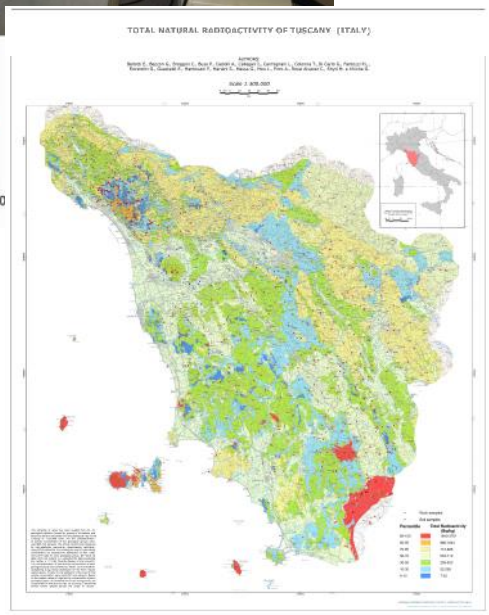
- **MCA_Rad system – a fully automated gamma-ray spectrometer**



- **Efficiency calibration of MCA_Rad system using standard point sources**

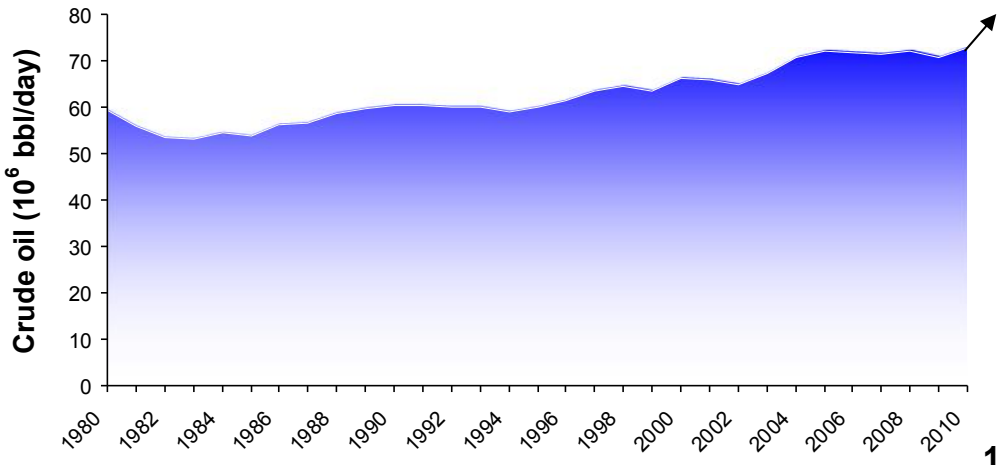


- **Validation of efficiency calibration using certified reference materials**



- **Applications of MCA_Rad system**

Oil and gas industry - residues generation worldwide



- Data from: www.indexmundi.com

25.6 x 10^9 bbl/yr

1 oil barrel (bbl) ~ 160 Liters

scale

sludge

Rough estimation on NORM residues generated globally from oil industry.

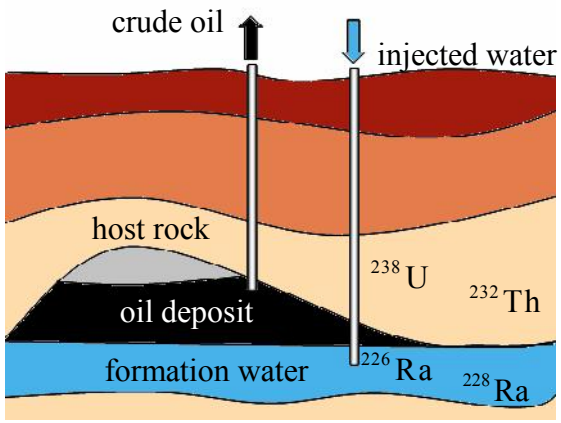
	Generation rate per oil barrel (bbl) produced	Residues estimation (2010)
Produced water	**300 ÷ 900**[(USA)a] **%** (water cut of 75% ÷ 90%[(USA)])	**8 x 10^{10} bbl/yr**
Scale	**3**[b] **%**	**7 x 10^8 t/yr**
Sludge	**0.01**[a] **%**	**3 x 10^6 t/yr**

[a] Source: http://www.epa.gov/rpdweb00/tenorm/oilandgas.html.

[b] Estimated considering that in 2010 in USA were recorded 519569 oil producing wells (Source: http://www.epa.gov/rpdweb00/tenorm/oilandgas.html).

Values expressed as "<" corresponds to the MDA values of the measurement.

NORM issue in oil extraction process



Produced water conc.
0.002 – 1200 Bq/l

Produced water conc.
0.3 – 180 Bq/l

Chemistry

Radium (Ra) is an alkaline earth metal (Ba, Sr, Ca) moderately soluble in water (+2 oxidation state).

The conc. of ^{226}Ra and ^{228}Ra in produced water depend mainly on:

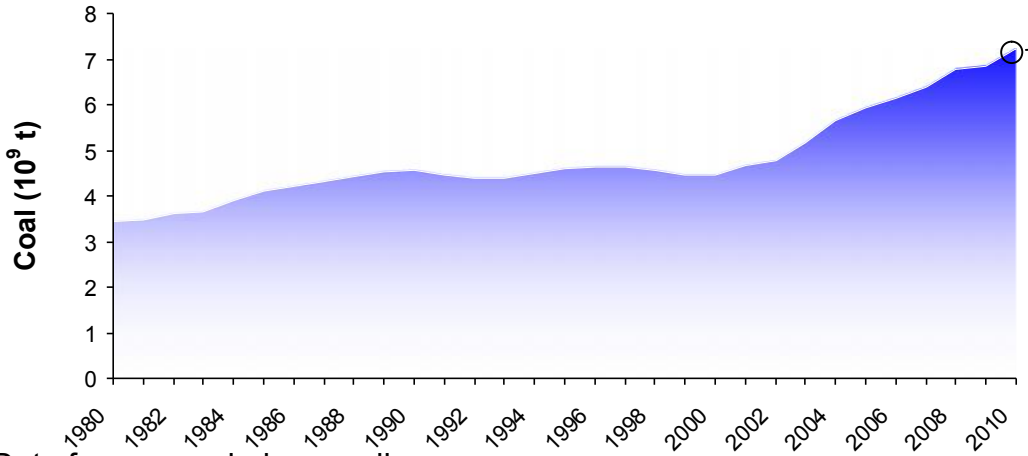
- Insolubility in sulfate and carbonate
- Salinity (cation conc.) of the solution
- Grain size and the total surface area
- Temperature
- U and Th concentration of host rock

Oil field equipments contaminated with scale and scale–bearing sludge:

	^{226}Ra 10^4 (Bq/kg)	^{228}Ra 10^4 (Bq/kg)
Scale	**0.00008 – 1500**	**0.00001 – 280**
Sludge	**0.0005 – 350**	**0.00007 – 205**

* Xhixha et al., 2012. The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization. J. Radioanal. Nuc. Chem. Doi:10.1007/s10967-012-1791-1

Coal combustion - residues generation worldwide



Data from: www.indexmundi.com

According to OECD the global electricity generated from coal combustion at 2010 accounts for **40.5%** (8119 TWh) of the total.

Rough estimation on NORM residues generated from coal combustion (CCP).

	Generation rate during coal combustion*	Residues estimation (2010)
fly-ash	8.4 %	6 x 10^8 t/yr
bottom ash/ boiler slag	3.6 %	2.5 x 10^8 t/yr

The projection on coal consumption for 2035 show an increase tendency of of fly ash generation up to 7.5 x 10^8 t/yr.

*** The % waste/by-product generation was calculated for an average 12% ash containing coal, from which 70% is generated as fly ash and 30% as bottom ash and boiler slag***

- **EU CCP accounts for ~ 10% of global CCP**
- **In 2009, CCP ~ 5.2 x 10^7 tons**

Recycled in construction industry#

- 48% of fly ash
- 45% of bottom ash

* Xhixha et al., 2012. The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization. J. Radioanal. Nuc. Chem. Doi:10.1007/s10967-012-1791-1

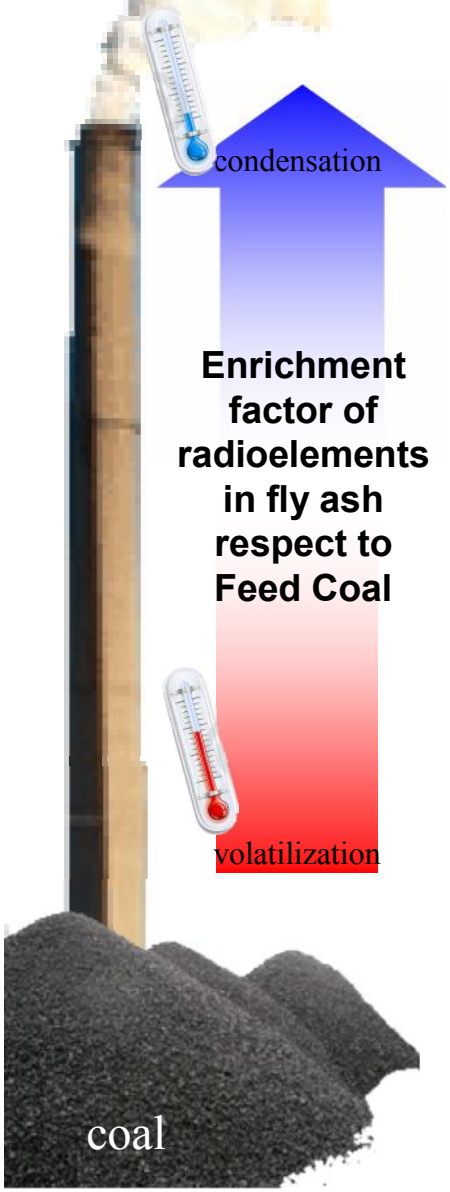
Data from European Coal Combustion Products Association: http://www.ecoba.com/

NORM issue in coal combustion process

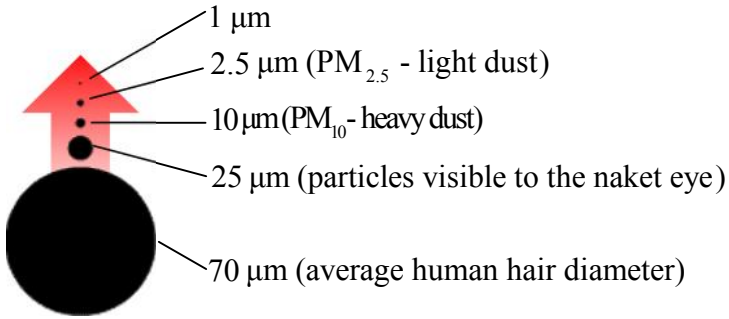
about 2-5% fly ash is released in air

The partitioning between gas and solid is controlled by the volatility and chemistry of the individual elements.

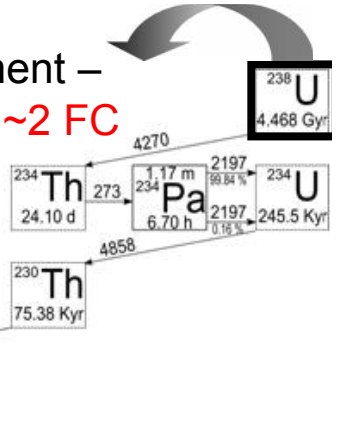
	^{238}U (Bq/kg)	^{232}Th (Bq/kg)
Feed Coal (FC)	10 - 600	10 - 200



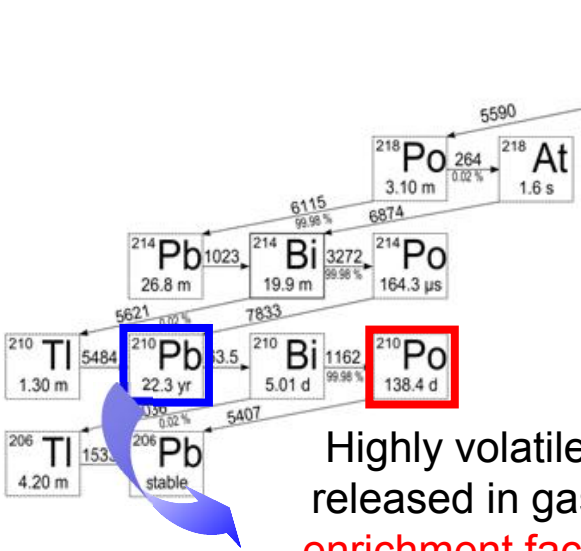
Enrichment factor of radioelements in fly ash respect to Feed Coal



Less volatile element – enrichment factor: ~2 FC



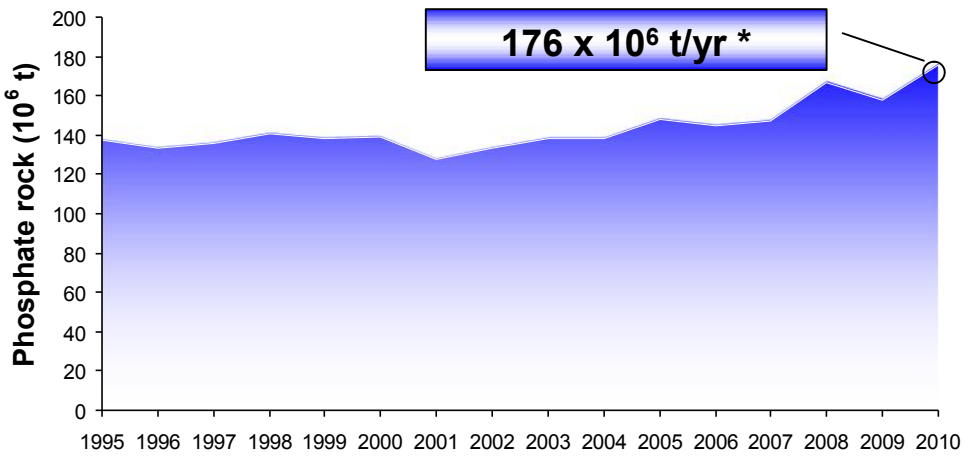
Less volatile element like ^{232}Th- enrichment factor: ~1.5 FC



Highly volatile element released in gas phase – enrichment factor: ~5 FC

^{232}Th, ^{226}Ra and ^{238}U remain in ash matrix and show slight preference for small fly ash particles.

Phosphoric acid production – residues generation



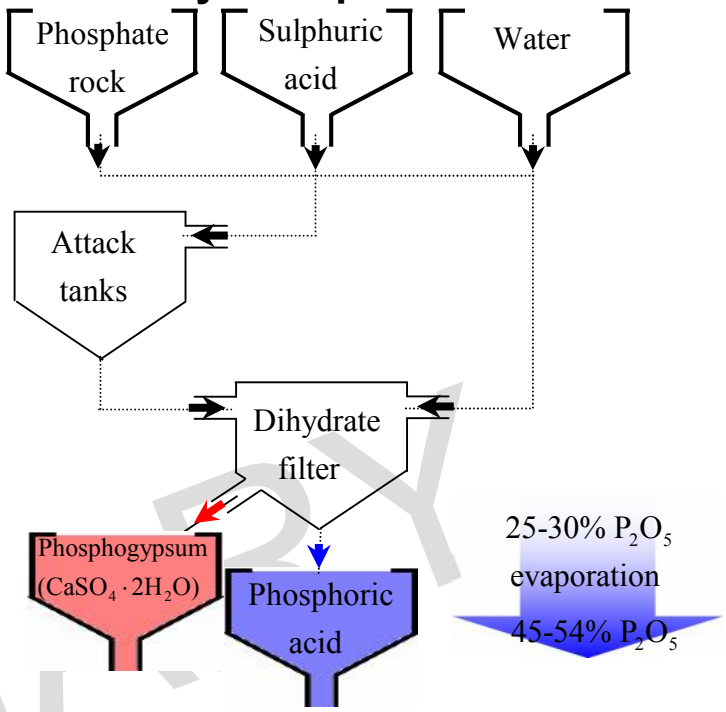
* Data from USGS

Rough estimation on NORM residues generation during dihydrate phosphoric acid production.

Phosphoric acid (2010)	Phosphogypsum
37.5 x 10^6 t	187.5 x 10^6 (t)

~5 times #

Phosphoric acid production – dihydrate process



Approximately **90%** of worldwide phosphoric acid is used in phosphate **fertilizer production industry**.

Phosphogypsum is mainly recycled:

- in agriculture for soil remediation
- in construction industry, in particular in cement production.

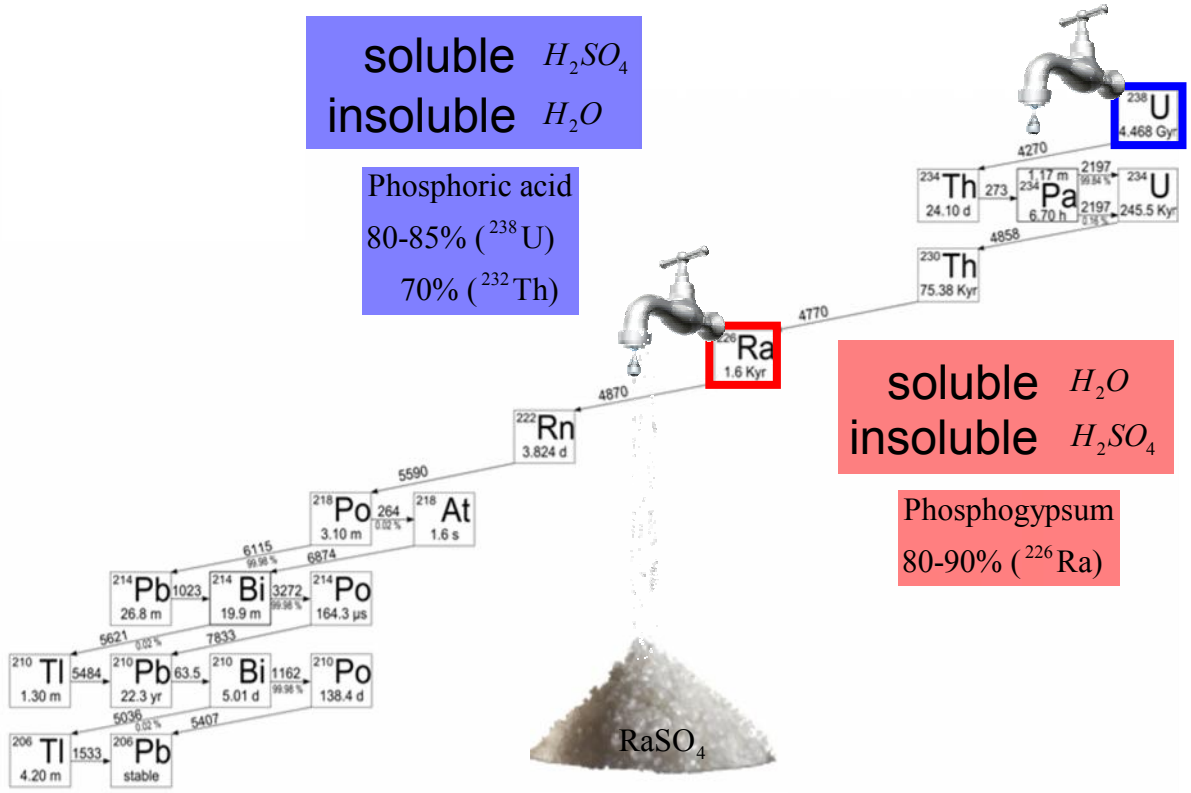
Xhixha et al., 2012. The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization. J. Radioanal. Nuc. Chem. Doi:10.1007/s10967-012-1791-1

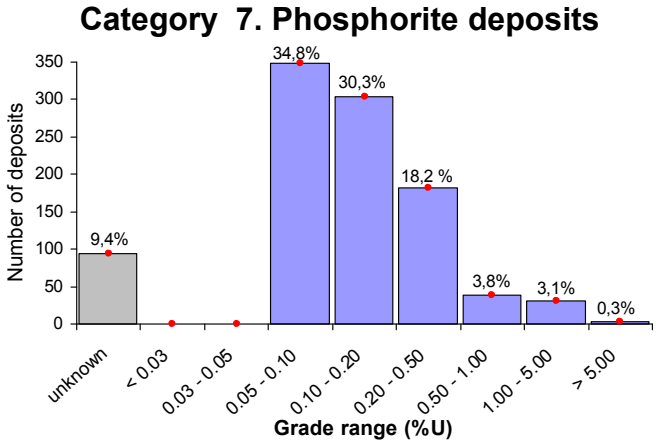
NORM issue in phosphoric acid production

The average content of **^{238}U** in phosphate rocks is often in the range **30-200 µg/g** (0.003-0.020%) max. up to 800-1000 µg/g.

IAEA INFCIS

UDEPO World Distribution of Uranium Deposits



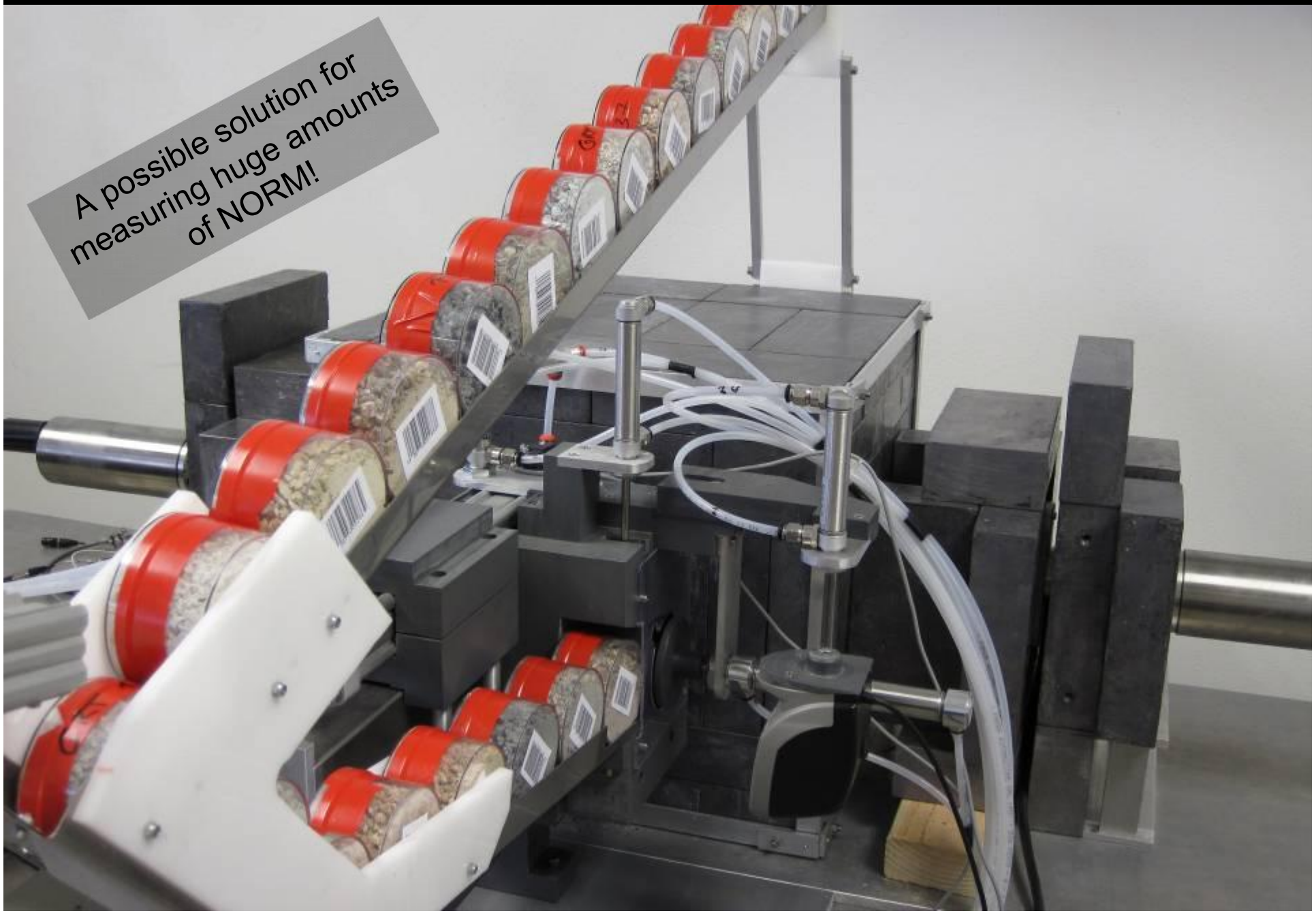


World uranium resources in phosphate rock are estimated at approximately 9 ÷ 22 x 10^6 tons.

The activity concentration of **^{238}U** and **^{226}Ra** in in phosphogypsum are typically found to be respectively in the range **< MDA – 450 Bq/kg*** and **30 – 1350 Bq/kg***.

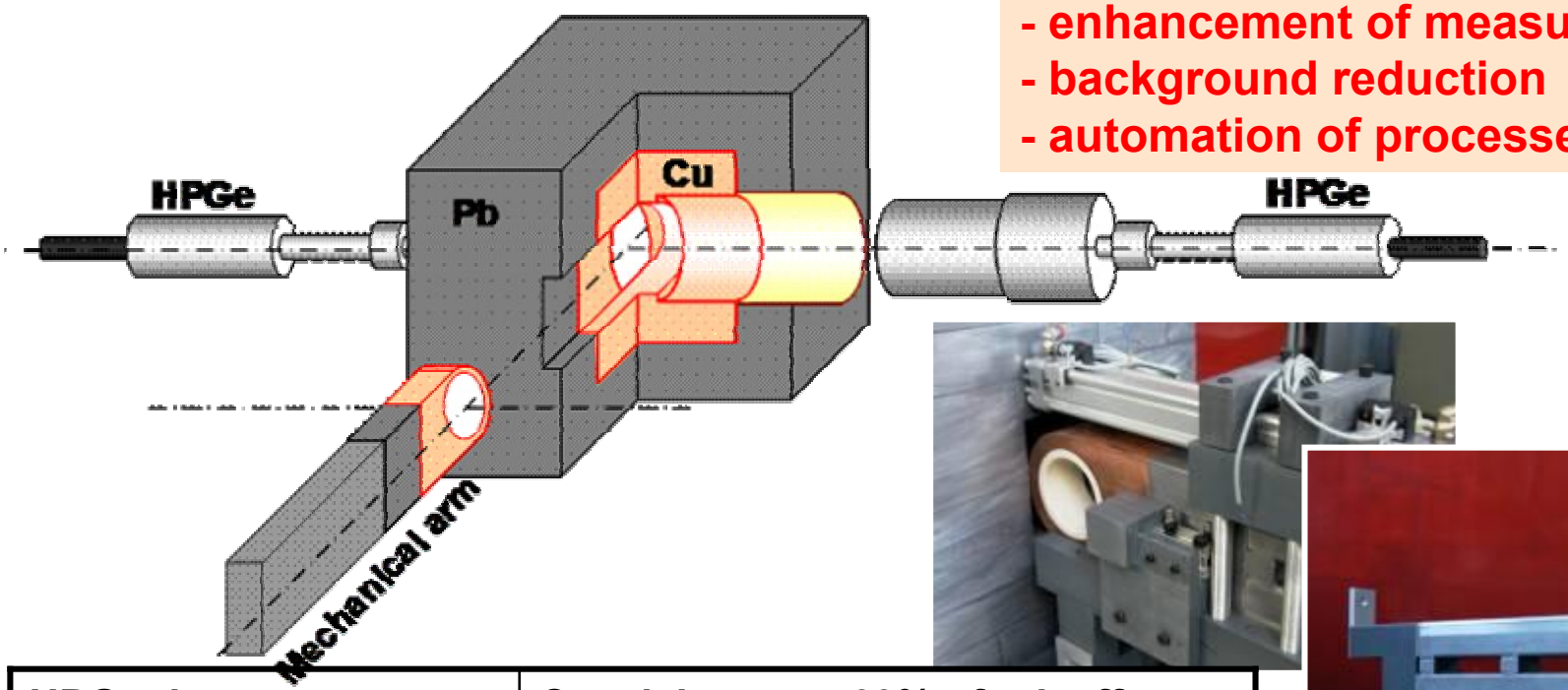
*Xhixha et al., 2012. The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization. J. Radioanal. Nuc. Chem. Doi:10.1007/s10967-012-1791-1

MCA_Rad system – a fully automated gamma spectrometer



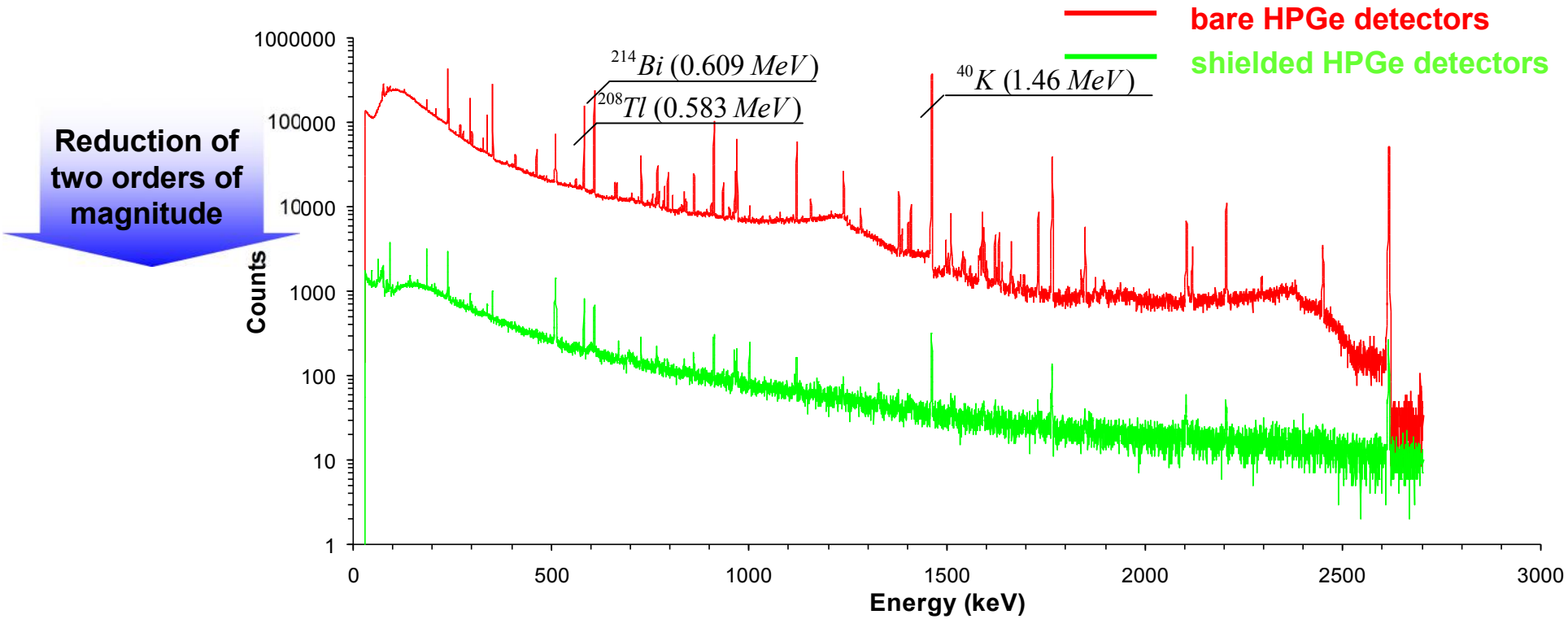
Design and features of MCA_Rad system

Improvements:
- enhancement of measures quality
- background reduction
- automation of processes



HPGe detectors	Coaxial p-type, 60% of rel. eff.
Energetic resolution	1.9% at 1.33 MeV (^{60}Co)
Cooling technology	Electromechanical (~ -190°C)
Shielding composition	10 cm Pb and 5 cm of Cu
Standard acquisition time	1 hour (180 cc sample volume)
Automatic sample manage	24 samples

Background characterization of MCA_Rad system



Estimation of Minimum Detectable Activity (MDA) for a typical 1 hour background spectra.

$$MDA = \frac{3 + 4.65\sqrt{B}}{\varepsilon I_\gamma t}$$

for 95% confidence interval.

Isotope		E (keV)	MDA (Bq)
^{238}U	^{234m}Pa	1001	22.2
	^{214}Pb	352	0.5
	^{214}Bi	609	0.5
^{232}Th	^{228}Ac	911	0.9
	^{212}Pb	239	0.5
	^{208}Tl	583	0.7
^{40}K		1460	5.5

MCA_Rad system: efficiency calibration

Efficiency calibration using standard point sources of complex decay scheme: ^{152}Eu (unc. 1.5%) and ^{56}Co.

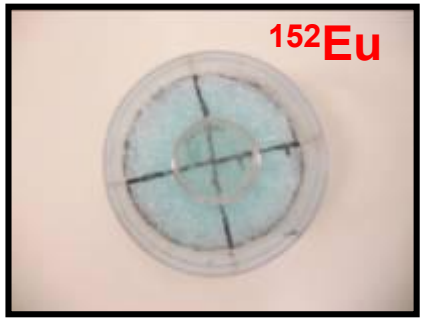
main corrections

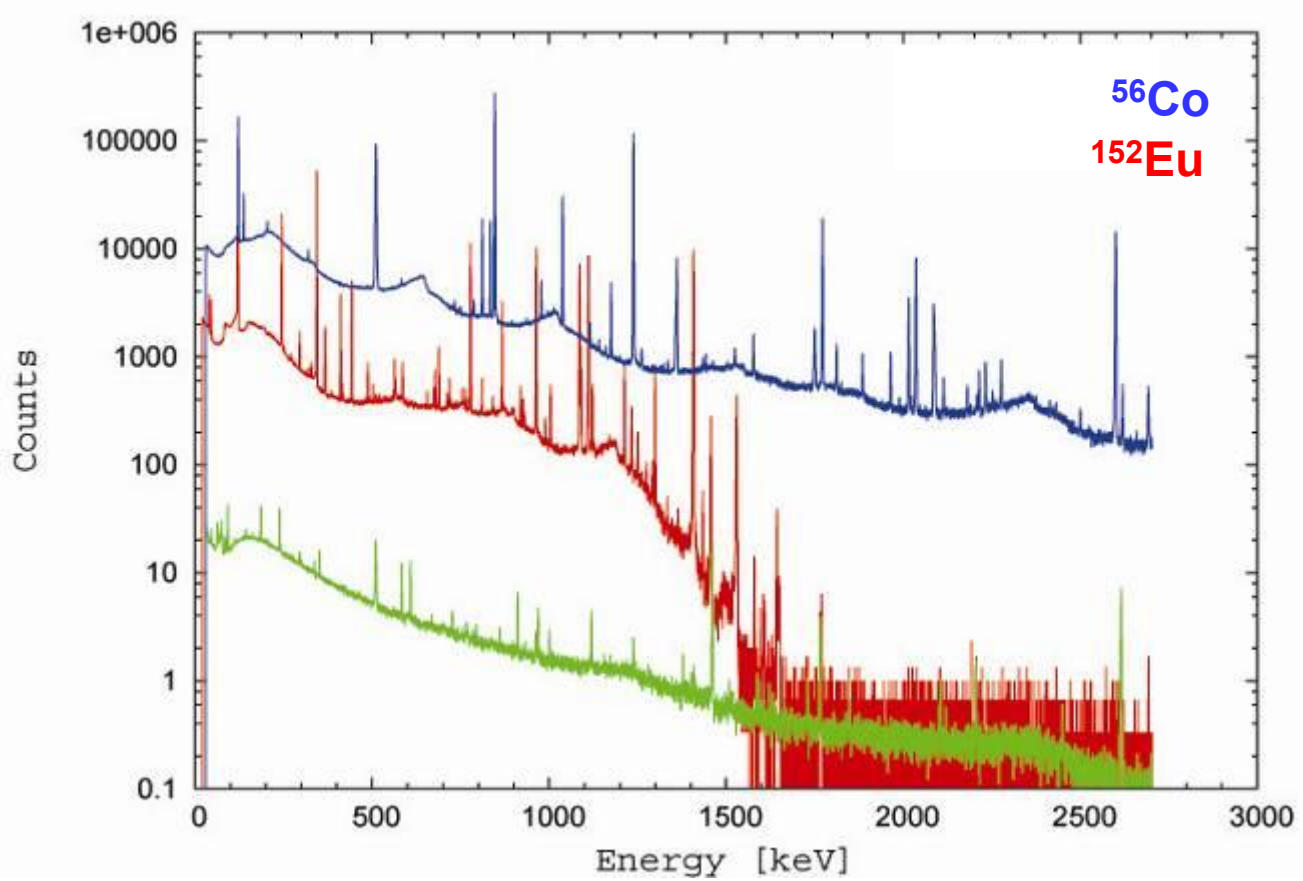
Coincidence summing (C_{CS})

Geometrical (C_G)

Self absorption (C_{SA})

standard point sources



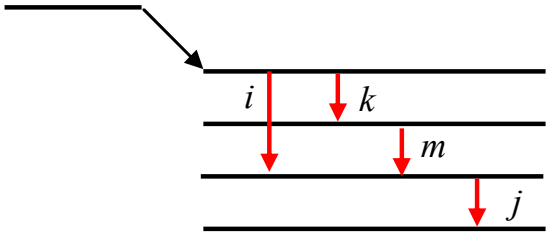


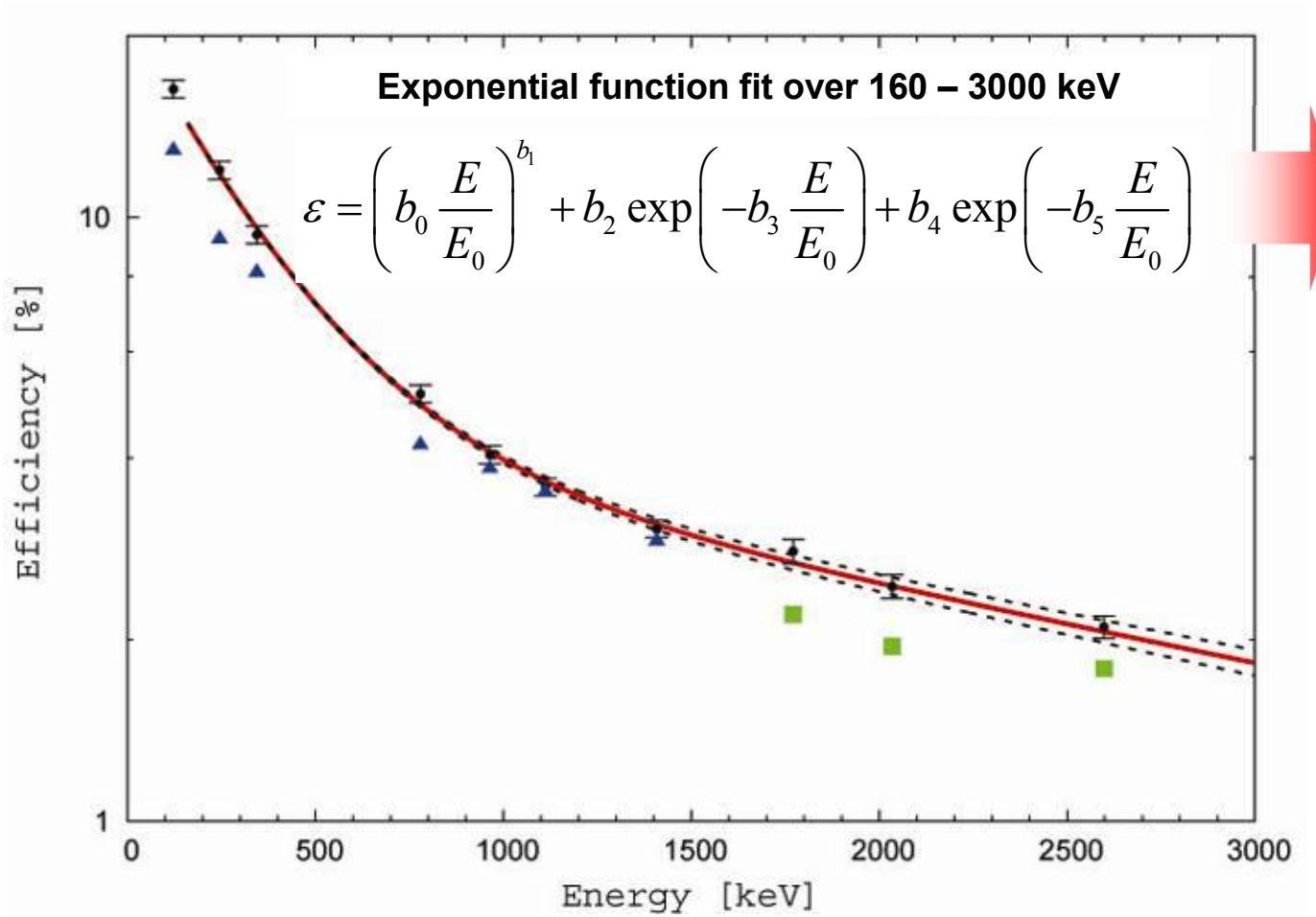
Xhixha et al., 2012. The worldwide NORM production and a fully automated gamma-ray spectrometer for their characterization. J. Radioanal. Nuc. Chem. Doi:10.1007/s10967-012-1791-1

Coincidence summing correction

Coincidence summing correction (C_{CS}) of (i) events takes into account the summing out (j) and summing in (k,m) and effects:

$$C_{CS(i)} = \left[1 - \frac{\sum_j P_{tij} P_i P_j \varepsilon_{tj}}{I_{\gamma i}}\right]\left[1 + \frac{\sum_{k,m} P_{tkm} P_k P_m \varepsilon_k^{app} \varepsilon_m^{app}}{I_{\gamma i} \varepsilon_i^{app}}\right]$$





b_0	1.38
b_1	1.41
b_2	22.97
b_3	5.43
b_4	6.61
b_5	0.44

Before correction

▲ ^{152}Eu

■ ^{56}Co

After correction

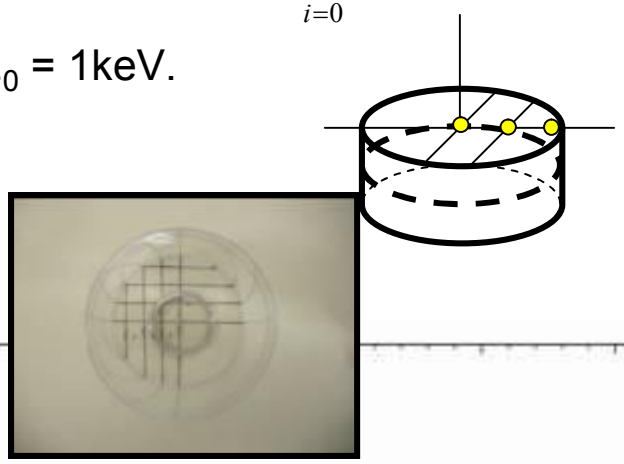
● ^{152}Eu, ^{56}Co

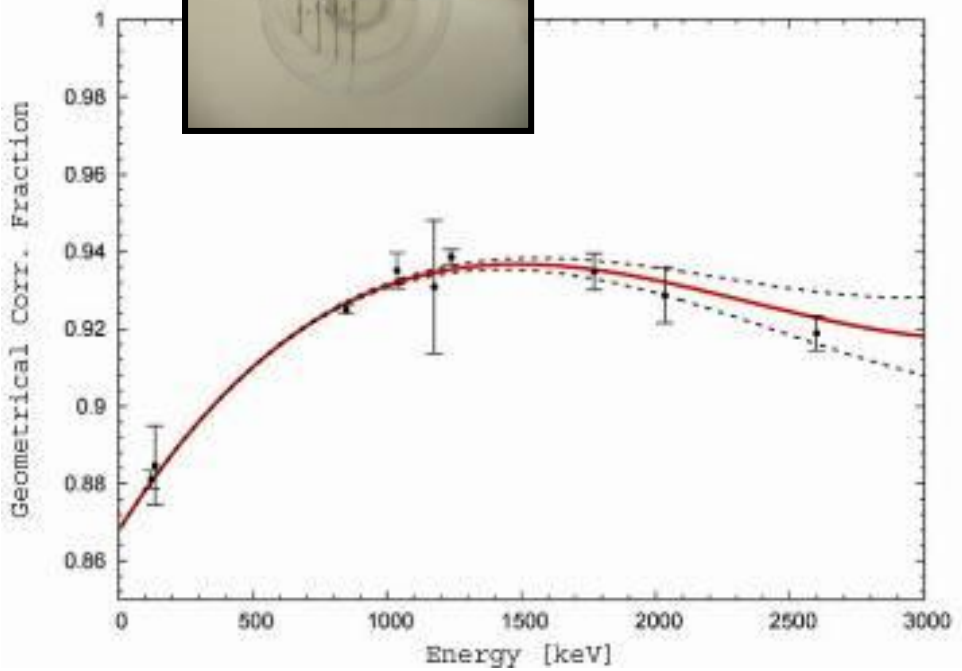
Geometry and self absorption correction

Geometrical correction (C_G): moving the standard point source in three positions (for three planes) we calculate the C_G for different energies (E_i) fitting the expression.

$$C_G = \sum_{i=0}^{3} a_i (E_i / E_0)^i$$

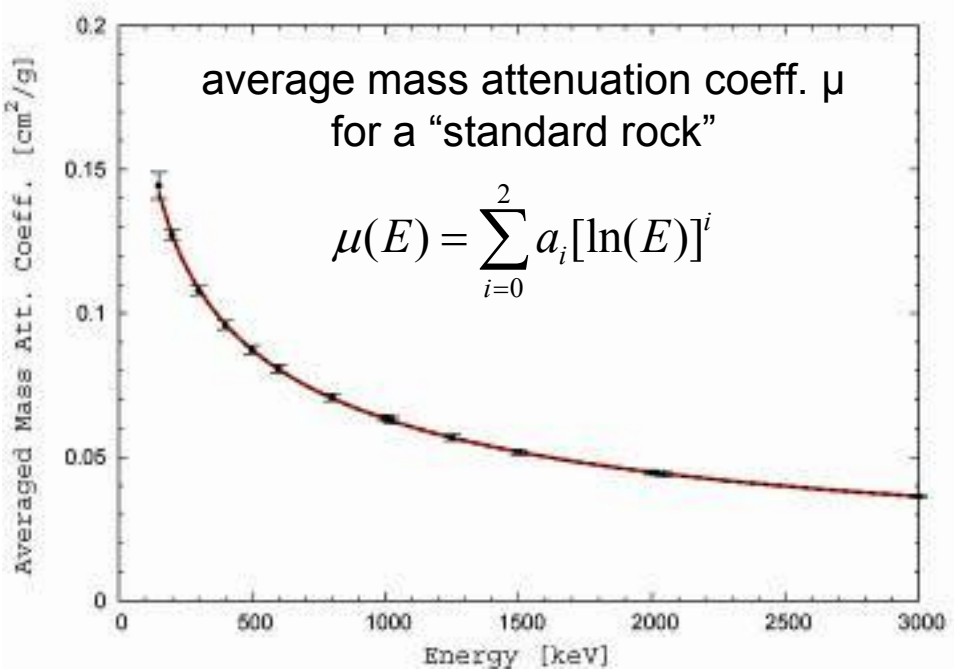
where E_0 = 1keV.





Self absorption correction (C_{SA}): averaging the mass attenuation coeff. μ for a "standard rock" with density ρ, we calculated the C_{SA} for the sample thickness t = 4.5 cm using the simplified approach:

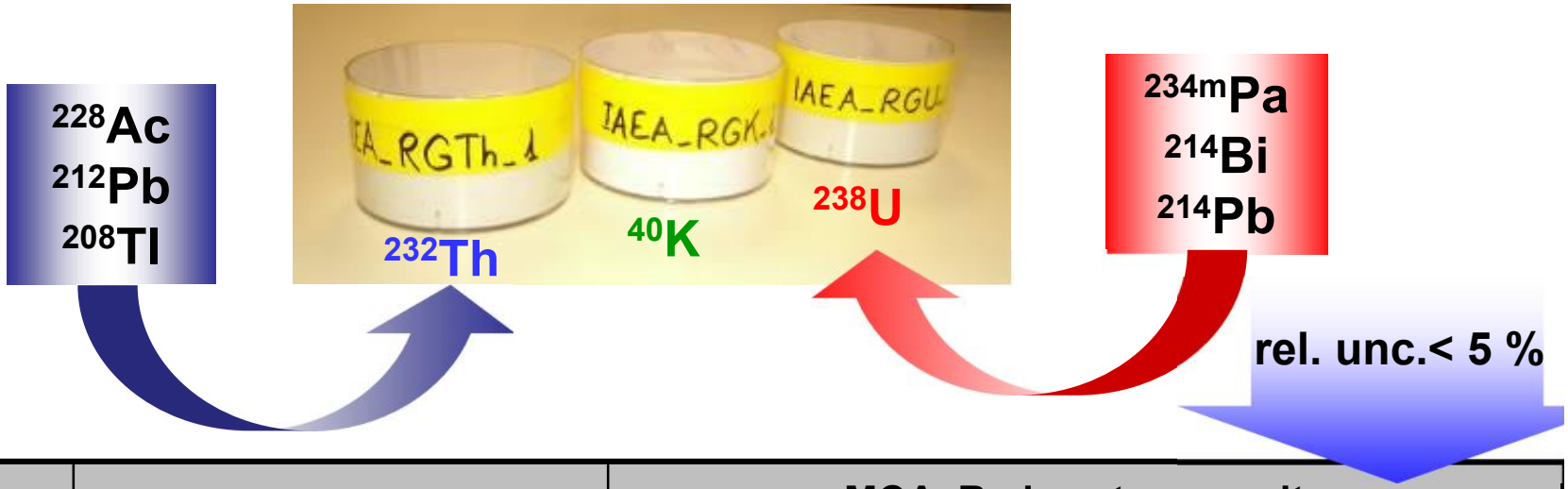
$$C_{SA} = \frac{1 - e^{-(\mu_s \rho_s - \mu_{ref} \rho_{ref})t}}{(\mu_s \rho_s - \mu_{ref} \rho_{ref})t}$$



For different rock forming minerals the average μ is estimated with a standard deviation of less than 2% (200 – 3000 keV).

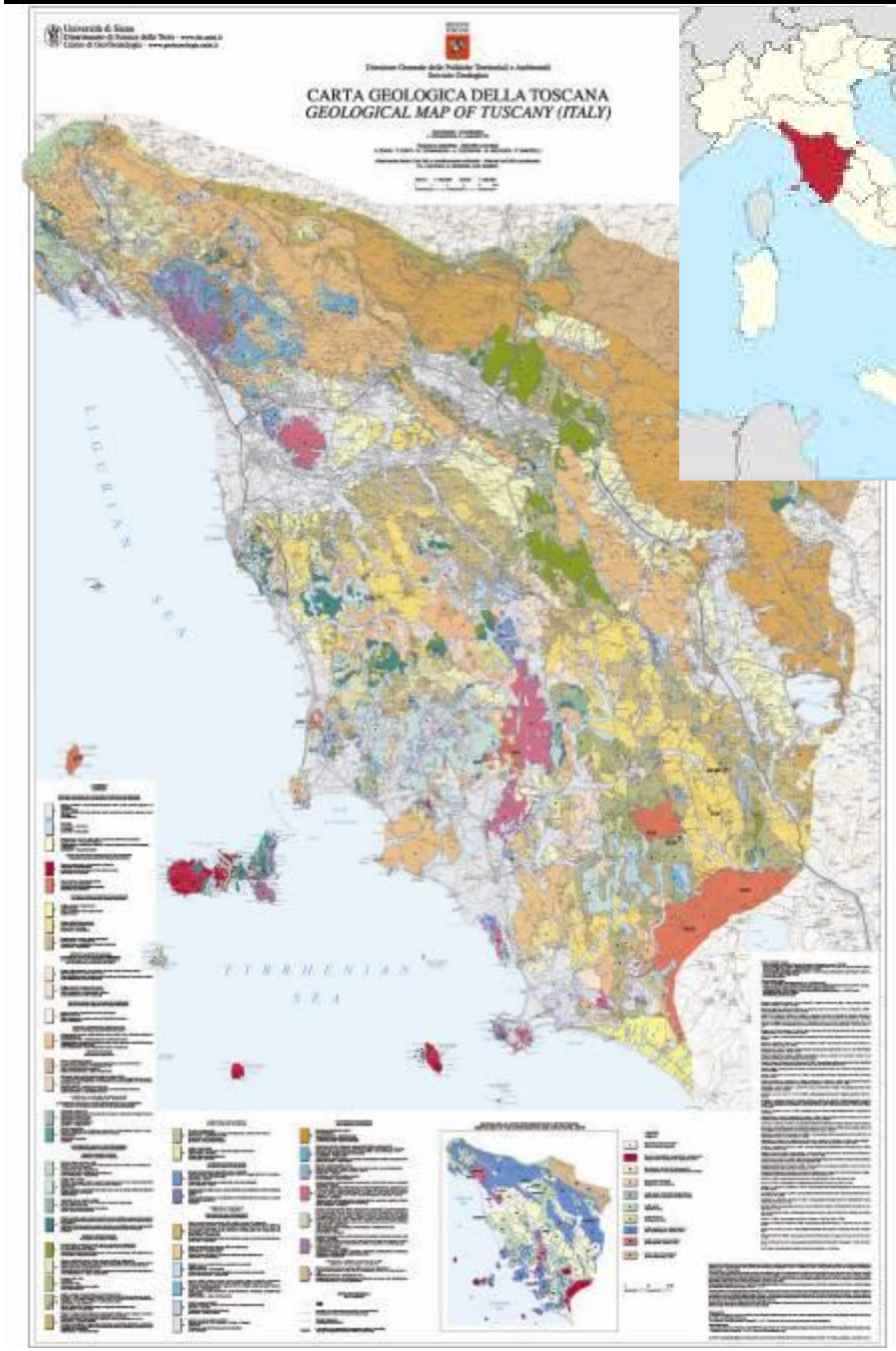
Validation test using certified IAEA ref. materials

Certified IAEA reference materials (in secular equilibrium).



	Data certified by IAEA	MCA_Rad system results		
Ref. material	**A (Bq/kg)**	**Isotope**	**Energy (keV)**	**A (Bq/kg)**
IAEA_RGU_1	**4940 ± 40**	^{234m}Pa	1001	**4875 ± 87**
		^{214}Bi	609	**4872 ± 73**
		^{214}Pb	352	**4773 ± 72**
IAEA_RGTh_1	**3250 ± 90**	^{228}Ac	911	**3092 ± 47**
		^{212}Pb	239	**3246 ± 49**
		^{208}Tl	583	**3342 ± 50**
IAEA_RGK_1	**14000 ± 400**	^{40}K	1460	**14274 ± 241**

Map of radioactivity content of Tuscany territory



During 2009-2011 we realized the first survey of natural radioactivity in Tucany Region (Italy).

The sampling strategy was based on the radioactivity characterization of 43 geological groups identified in the geological map of Tuscany at scale 1:250,000.

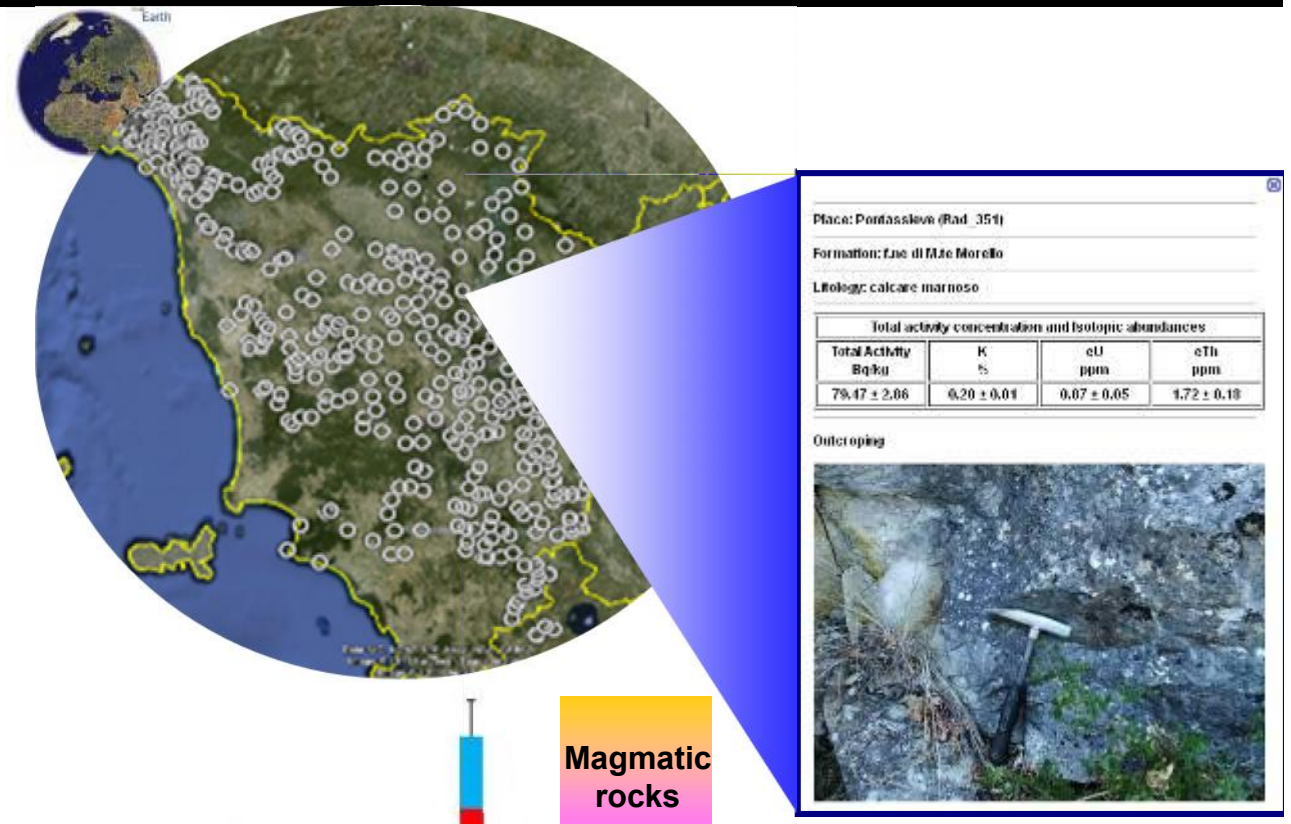
- Total samples: **1913**
  - Rock samples: **865**
  - Soil samples: **1048**
- Sampling days: **92**
- Mean sample distribution **~12** km^2

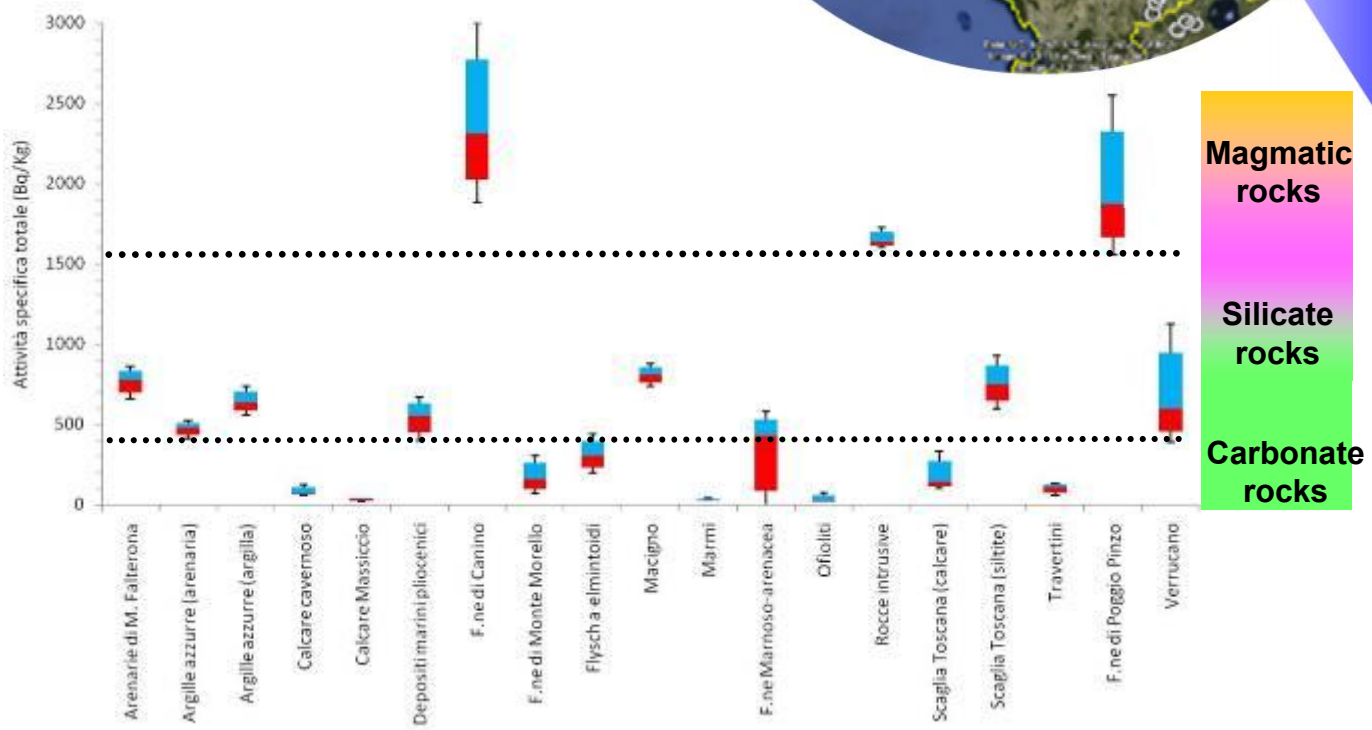
First result – webgis database based on GoogleEarth®

Database:

Rock samples: 865
- Location coordiantes
- Geological description
- Radioactivity concentration
- Outcrop photo

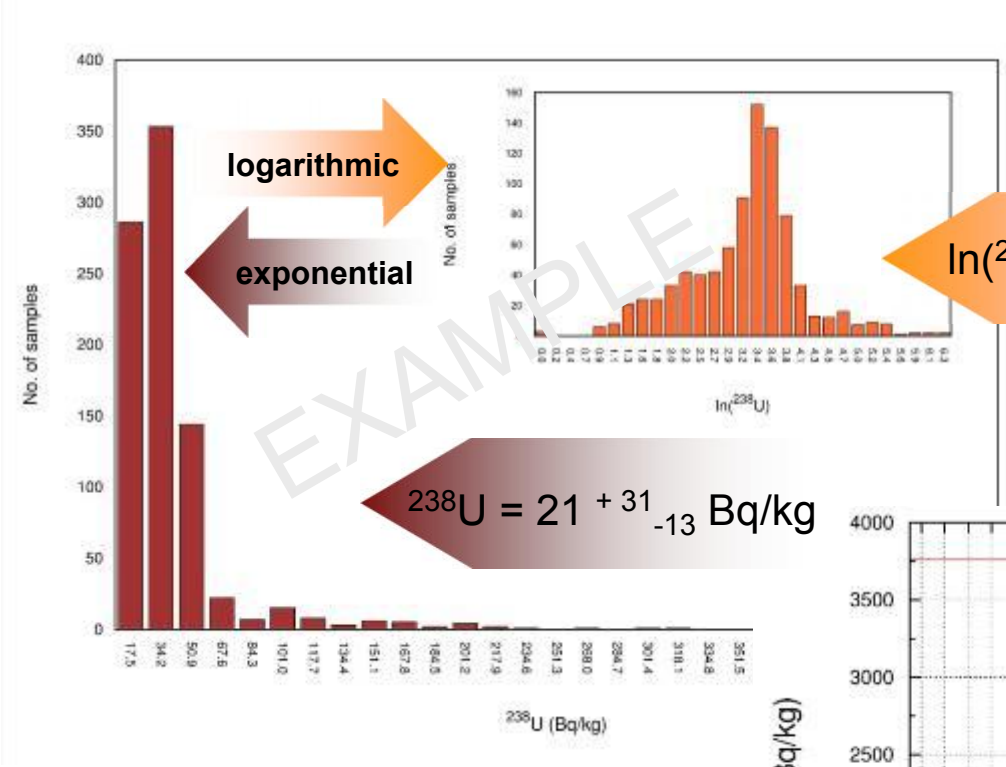
Soil samples: 1048
- Location coordinates
- Geopedology description
- Radioactivity concentration





Approximately 50% of rock deposits were characterized for their radioactivity content based on a statistics of more than 10 samples.

Mapping the natural radioactivity – statistical analysis



Based on high statistics (865 rocks samples) we characterized 43 geological groups (1:250,000) by considering log-normal distributions

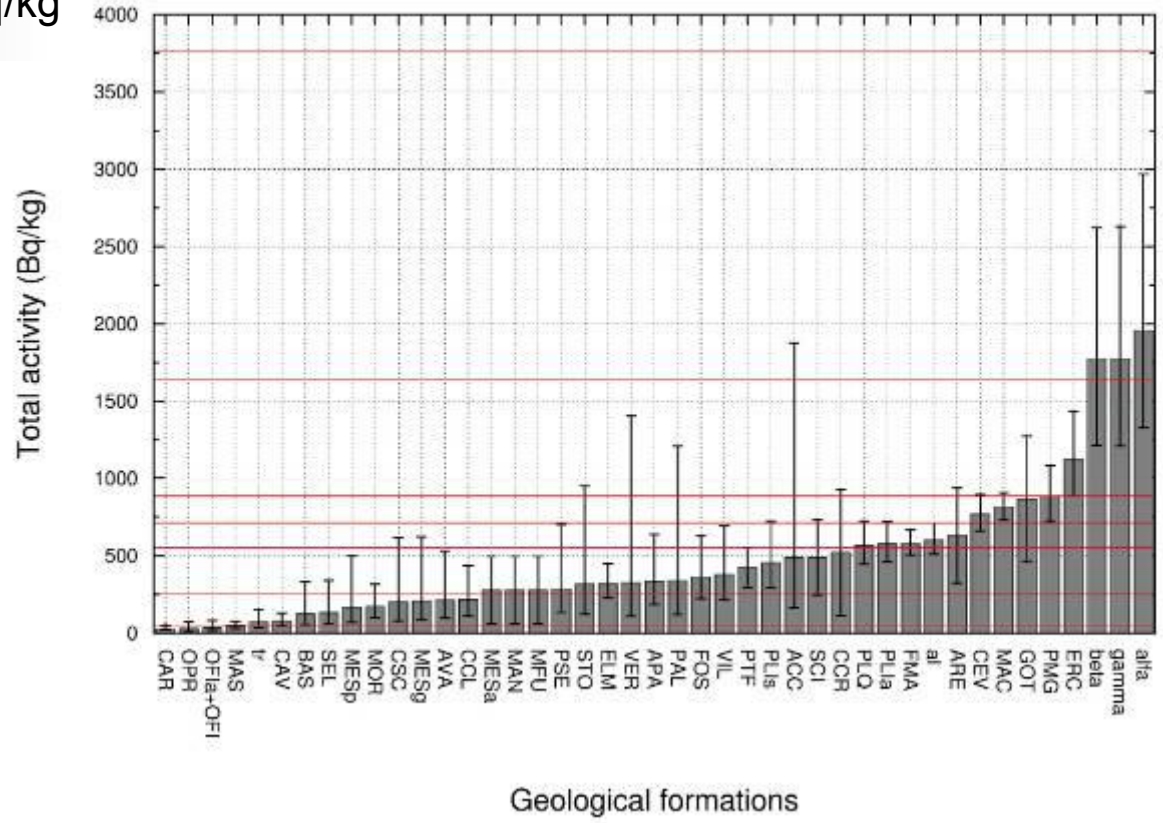
$\ln(^{238}U) = 3 \pm 0.9$

Note that considering a Gaussian distribution loose information on distribution tails:

$^{238}U = 32 \pm 42$ Bq/kg

$^{238}U = 21\ ^{+31}_{-13}$ Bq/kg

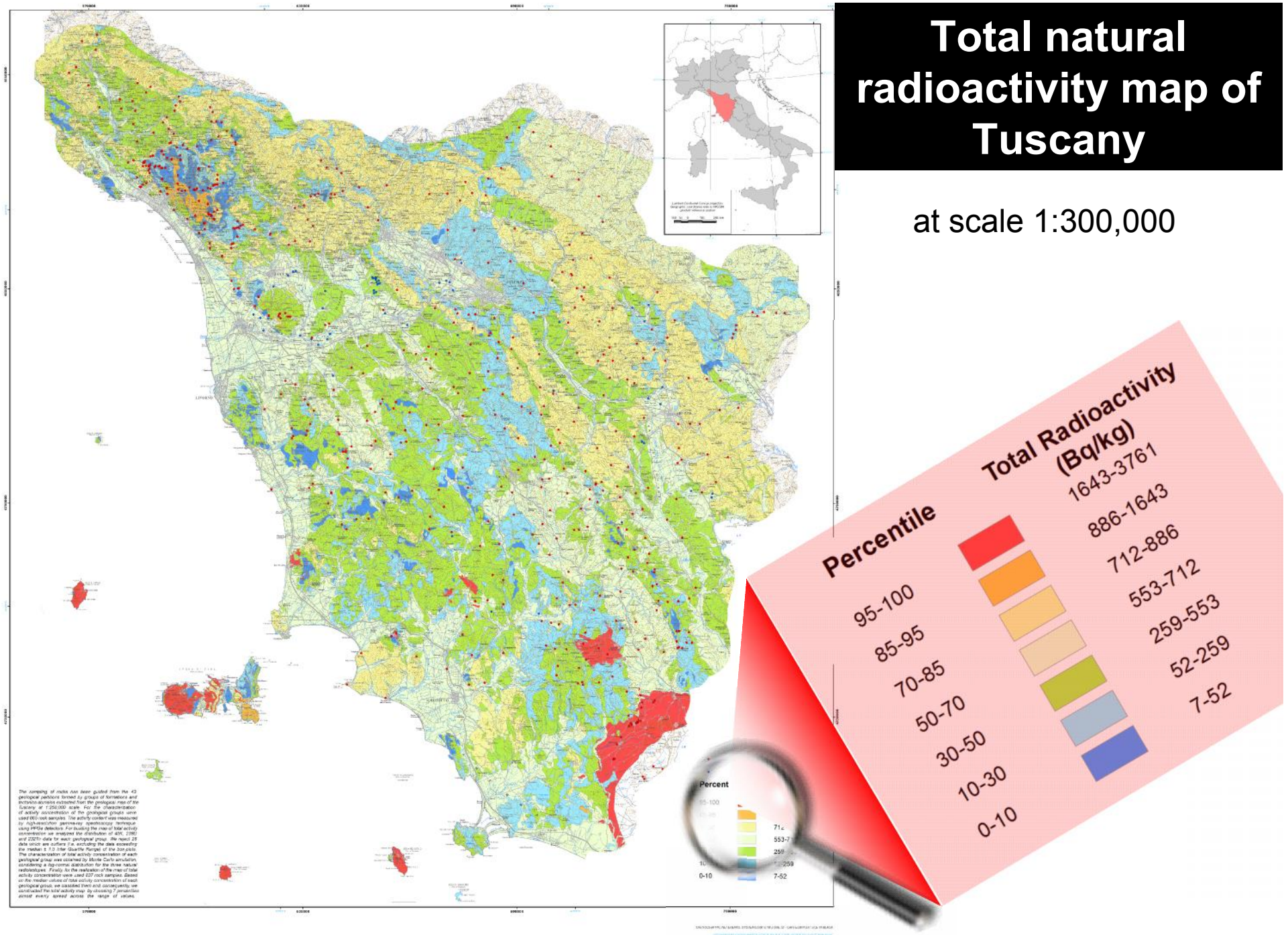
The total natural radioactivity map was represented as the geological classification based on data percentiles chosen on order statistics: 10%, 30%, 50%, 70%, 85%, 95% and 100%.*



***Callegari et al., 2012. Total natural radioactivity map of Tuscany (Italy). Submitted to J. Maps.**

Total natural radioactivity map of Tuscany

at scale 1:300,000

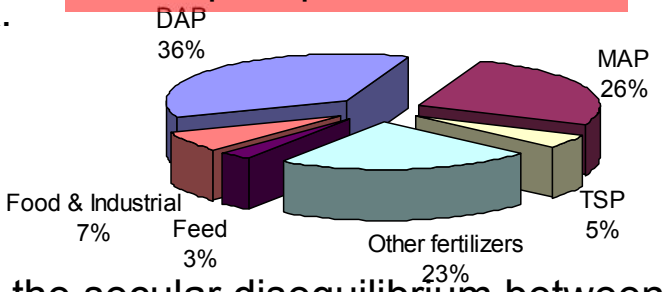


Callegari et al., 2012. Total natural radioactivity map of Tuscany (Italy). Submitted to J. Maps.

Measurements on fertilizers using MCA-Rad system

Fertilizers are generally labeled with the macronutrients N, P, K.
DAP is diammonium phosphate (NP);
MAP is monoammonium phosphate (NP) and
TSP is triple supper phosphate (P).

World phosphoric acid uses



By measuring 1h different fertilizers it was possible to observe the secular disequilibrium between ^{238}U (measured using ^{234m}Pa) and ^{226}Ra (measured using ^{214}Bi).

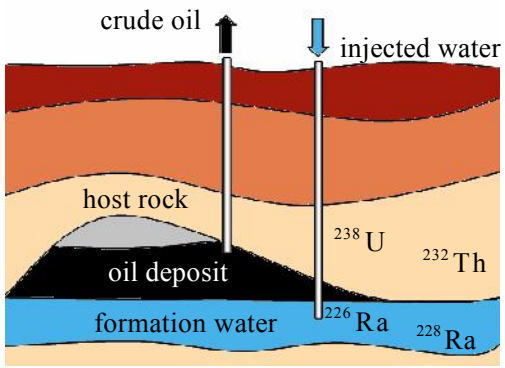
Fertilizer type	Country	Nr. samples	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{238}U (Bq/kg)	^{232}Th (Bq/kg)
NK (13-0-46)	Israel	1	12557 ± 77	<3	n/a	<4
NCa (15-0-0)	South Africa	1	<4	6 ± 1	<115	<2
NPK (12-**12**-17) granular	Belgium Italy	3	4098 ± 199	**80 ± 56**	**595 ± 184**	14 ± 9
NPK (5-**15**-30) granular	Italy	1	7646 ± 63	**253 ± 5**	**<522**	20 ± 5
NPK (20-**20**-20) crystalline	Belgium Italy	3	5388 ± 493	**<2**	**<469**	<4
MAP (11-**48**-0)	n/a	2	35 ± 9	**627 ± 22**	**918 ± 62**	13 ± 4
DAP (18-**46**-0)	Italy	2	146 ± 140	**79 ± 77**	**850 ± 70**	44 ± 6

Values expressed as "<" corresponds to the MDA values of the measurement.

Conclusions

Huge amount of NORM residues are generated globally, and need characterization for:

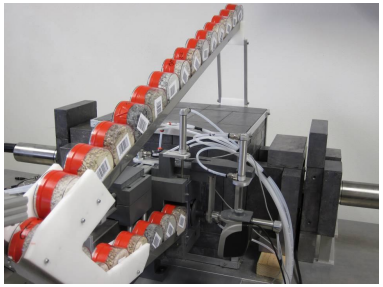
- **public and worker health protection,**
- **storage**
- **transport**
- **recycling**



The complexity of the chemical and industrial processes together with the natural variability of radioactivity doesn't permit to generalize the NORM issue.

We realized the MCA_Rad system, which has the following characteristics:

- **manage autonomously up to 24 samples,**
- **measure low sample quantity, maximum up to 180 cc,**
- **accurate efficiency calibration, validated less than 5%.**



More than 1000 measurements are successfully performed by the MCA_Rad system, testifying the readiness of this instrument.