Sampling and analysis of environmental materials: QA and uncertainty analysis

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Sources of experience

- Environmental science has expanded dramatically over the last few decades, following concerns over the impacts of human activities
- Some of the earliest work, dating from the ´60s, was particularly focused on fallout from nuclear weapons tests and included studies of Cs-137 on land, in the sea and throughout the food chain
- Radio-Cs studies expanded to include impacts of releases from military and industrial sites (especially involving reprocessing)
- Studies have also followed a number of accidents, including the Windscale fire, Mayak explosion, Goiania Cs source, Chernobyl,…
- UK examples provided previously by Gillian Mackinnon

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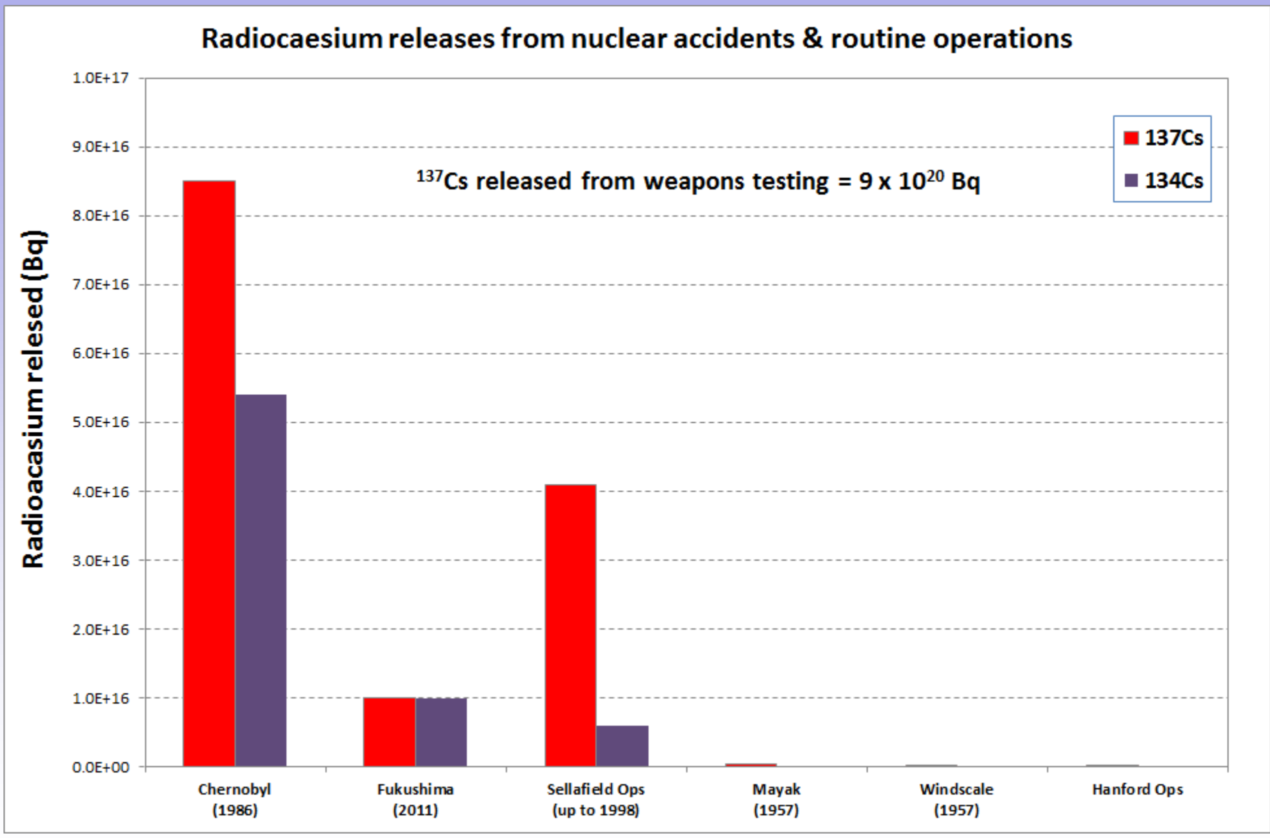

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Sellafield Radionuclide Releases

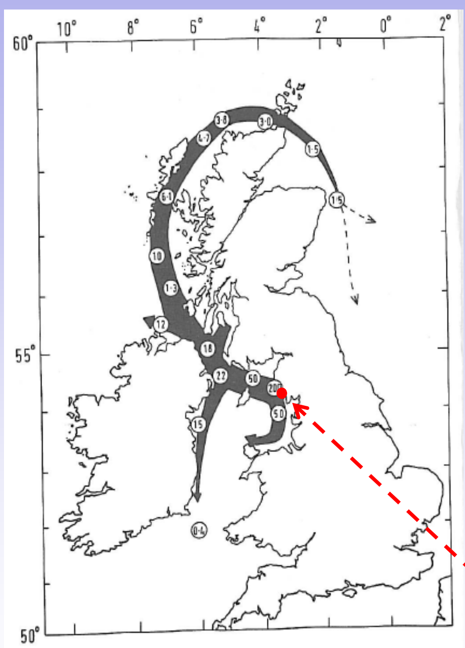

Fig. 1 Concentration of ^{137}Cs (pCi l^{-1}) in UK coastal waters, May/ July 1972 (from Jefferies *et al.*, 1973).

^{3}H	^{134}Cs
^{14}C	^{135}Xe
^{35}S	^{137}Cs
^{41}Ar	^{144}Ce
^{60}Co	^{144}Cr
^{85}Kr	^{144}Pm
^{89}Sr	^{152}Eu
^{90}Sr	^{154}Eu
^{95}Zr	^{210}Po
^{95}Nm	^{237}Np
^{99}Tc	^{238}Pu
^{106}Ru	^{239}Pu
^{110m}Ag	^{240}Pu
^{129}I	^{241}Pu
^{129}Te	^{241}Am
^{129m}Te	^{242}Cm
^{131}I	^{243}Cm
^{132}Te	^{244}Cm
^{133}Xe	

Sellafield & Windscale Operations from 1952

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In-situ measurements

- Regional scale surveys generally provide the starting point for any study – described already in detail by David Sanderson

- May be complemented on a smaller scale by surveys using
  - Total gamma dose measurements (survey meters, backpack, buggy, etc.) as implemented in decontamination pilot projects
  - Gamma camera or other profiling detectors
- Can be extended for other specific purposes, e.g.
  - Downhole probes for measuring profiles
  - Underwater measuring equipment

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Sampling
…should be "state-of-the-art"
…and fully integrated with in-situ measurements

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Sampling Strategy

- Before taking samples the most important thing to know is, what exactly is the question that you are trying to answer!
- The research goals will define the sampling design and the equipment used with which to collect samples
- As discussed later by Ian McKinley, such goals may be best defined within a system model

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Problem definition

- Distribution of RN in the environment is
  - Inherently heterogeneous
  - Inherently dynamic
- How is sampling planned?
- What and when to sample?
- What sampling techniques are used?
- How are samples analysed?
- How are uncertainties quantified?

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Sampling programme practicalities

- There is always an inherent conflict between the desire to take as many samples as possible, distributed in space and time

and

- The constraints set by resources (budget, manpower, equipment)
- There need to be trade offs – either done based on expert opinion or using a formal method (e.g. MAA).
- Again this is best done based on a conceptual model of the entire system studied

Planning a sampling programme

- Identification of key site components
- Assessment of likely heterogeneity (e.g. hot-spots identified by in-situ survey)
- Assessment of timescales of processes and whether they are
  - Gradual
  - Cyclic
  - Influenced by specific events
- Ideally based on a conceptual model of the site

Sampling Design

- Sampling the total population is impossible
- Need to subsample the population using the most efficient method possible in order that your subsamples are representative of the total population
- Sampling locations should not be haphazard or judgemental, but may be constrained by practicality (e.g. accessibility)
- Probability sampling selects samples at random locations using a range of specific sample layouts
  - This allows a range of statistical analyses based on the estimates of variability (uncertainty) about the mean to be used
  - By far the most common type of sampling in soil science

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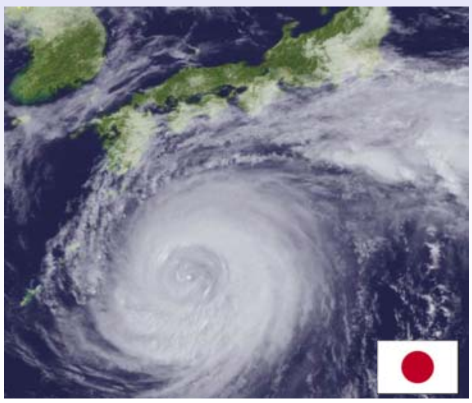
Choosing sampling times

- Should be decided when sites are chosen and could be:
  - One-off
  - Measurements at regular intervals
  - Seasonal / weather-related cyclic measurements
  - Before & after events (e.g. typhoons)
  - Defined by a specific activity (e.g. crop harvest)
  - Random / based on availability of equipment

Storm Events



Integrated sampling plan

- Should document rationale for each sample and its associated analysis
- Ideally understanding captured in system model
- Should be regularly reviewed:
  - Changes in system understanding could result in changes to the location, timing and analyses of future samples

Sampling methods/technology

- Related to defined goals
- Clearly related to requirements for subsequent analysis (size of sample, limits on degree of perturbation allowed,…)
- Constrained by cost, resources,…
- Often trade-off needed between different options

Soil Sample Collection

- The equipment used should both preserve the integrity of the sample and takes the sample as quickly and efficiently as possible
- Scraper plate – well defined sample area but very slow and integrity of sections possibly compromised
- Soil pit – good access to profile but time consuming and highly intrusive
- For radiocaesium profile analysis of soils some type of discrete corer such as a box corer should be used that preserves the integrity of the profile. Fast, cores can be sectioned in the lab

Sediment Sample Collection

- Options: piston corer, gravity corer, grab, diver sample, multi corer using slow penetration gravity device
- Device chosen depends on what the question is
- For benthos studies – Smith McIntyre or van Veen grab samplers are suitable
- However if you want to study the vertical distribution of radiocaesium in a sediment then these are not suitable
- A multi-corer (a variant of the Craib corer) and a slow penetration gravity corer should be used (even a low velocity gravity corer can lose the top 4 cm of sediment)

Handling soil & sediment samples

- Procedures depend on aim, e.g.
  - Bulk Cs content
  - Cs depth profile
  - Sequential extraction to determine association with different mineral / organic phases
- Sampling often causes perturbation (e.g. smearing on side of cores) – sub-sample to avoid such effects
- Soils & sediments are not sterile! Cs behaviour will be influenced by organisms present. To prevent perturbations post-sampling, it is best to keep cool or freeze

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Sampling organics / vegetation / biota

- Sample type depends on aim, which may involve
  - Examination of Cs distribution within a single organism – e.g. single rice plant
  - Average content of Cs within an organism – e.g. bulk sample of rice grains
  - Average over a biosphere compartment – e.g. random grab sample of leaf litter
- For living material, sample timing is very important due to variations in uptake over annual growth cycle
- Coupling may require sampling of many biosphere components to understand Cs fluxes: soil, microbes, plants, insects, animals,…
- Standardised techniques for sampling and sample handling often available – especially for food crops

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Sampling water (1)

- It is often important to distinguish between Cs in true solution, in colloidal phase and associated with suspended solids
  - In any sample these can be distinguished by filtration / ultrafiltration
  - Suspended solids may also be captured in traps

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Sampling water (2)

- Concentrations in true solution generally very low: requires either
  - Direct sampling of a large volume followed by pre-concentration before analysis
  - Selective ion-exchange extraction from large volumes of water
- Filter samples can be directly analysed (for standard geometry) or subject to sequential extraction to determine organic & inorganic components
- Transport in colloidal and, especially, suspended phases may be dominated by individual events (e.g. typhoons), which needs to be considered when deciding when or how to sample

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Sample Containers

- Any material that is in contact with a field sample has the potential to alter the sample via the processes of sorption leaching or dissolution. For example, samples can be contaminated by:
  - zinc from glassware
  - metals from metallic containers, and
  - organic compounds from rubber or plastic materials
- Generally not a problem for Cs, but any associated analysis may need to consider this

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Sampling overview

- Ensure comprehensive records during sampling (photo, video, data-logger)
- Ensure careful labelling to correlate all information
- Where possible include automatic location (GPS) and date stamps
- Include also record of all preparation, handling/transport & storage

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^{129}I in rainwater at Fukushima

Rainwater Samples collected on the roof of the main monitoring building at Fukushima University by Akira Watanabe and Katsuhiko Yamaguchi.

Chemistry prepared at the Technical University of Denmark by Luyuan Zhang

Analysed on the 5 Mv AMS at SUERC by Sheng Xu

Xu et al, ES&T, 2013

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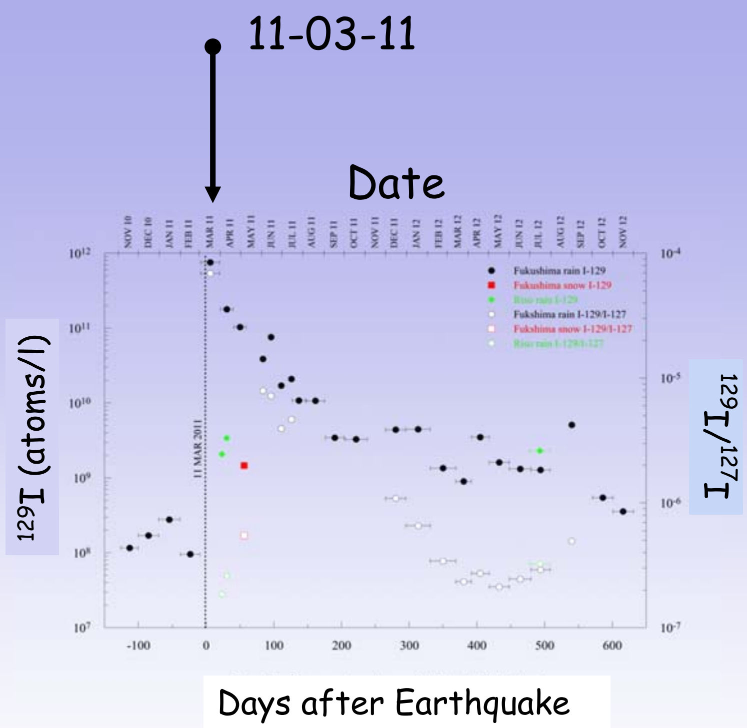

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Analytical methods/technology

- Related to defined goals
- Clearly related to constraints set by sampling (size of sample, degree of perturbation experienced,…)
- Constrained by cost, resources,…
- Often trade-off needed between different options

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Radiocaesium Measurement

- Total content measured by Gamma spectrometry: technique depends on type of sample (likely interference from natural RN) and total radio-Cs content
  - NaI – high efficiency, low resolution
  - HPGe – low efficiency, high resolution
- Distribution of Cs by autoradiography, gamma scanning
- Equipment performance characterised by
  - Shielding / Background
  - Stability / count times
- Throughput can be optimised by using batch counters / automatic sample changers or running low activity samples when staff are not present (nights / weekends)

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Data & Quality Management
…and uncertainty analysis

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Data Management (1)

- The JAEA F-TRACE project and associated remediation work will run for decades and generate huge volumes of information
- Related studies of radiocaesium in the Japanese environment is being undertaken by numerous organisations: e.g. MoE, NIES, Research Institute for Global Change, Kanazawa University, FFPRI, University of Fukushima…..
- Further Fukushima-related work is being carried out by many international organisations
- To put work in context (and test models), relevant work from past Cs contamination events should also be considered

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Data Management (2)

- The value of the work carried out is greatly increased if measurement from different sources can be combined to identify:
  - General trends
  - Inconsistencies
  - Potential for improvement
- This requires assessment of how comparable are the data from all of these organisations? Are they sampling and analysing in the same manner? What is the quality of measurements and the associated uncertainties?
- What is the most efficient way in which to manage all this data?

What is Quality Assurance?

- In analytical work, quality can be defined as the "delivery of reliable information within an agreed span of time, under agreed conditions, at agreed costs, and with the necessary aftercare" (FAO, 1998)
- The agreed conditions include specifications as to data quality objectives (DQOs), which include precision, accuracy, representativeness, completeness, and comparability
- These objectives are directly related to "fitness of use" of the data and they determine the degree of total variability (uncertainty or error) that can be tolerated in the data
- The DQOs ultimately determine the necessary quality control (QC)

Quality Management System

- Implementation of a QM system is the first step in QA
- Set of guidelines for work that is performed repeatedly e.g. soil profile analysis, gamma spectrometry of RNs
- Help provide confidence that the analytical results will satisfy the data quality objectives
- Guarantees that the data is "fit for purpose"
- The end result should be that your data have scientific credibility (stand up to international scrutiny), and thus permits statistical interpretations as well as management decisions to be made
- To assure quality we need to set up a system with a number of checks in place – quality control (QC)

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Quality Control

- All sampling and laboratory activities have one target: the production of quality data that is reliable, consistent, and has a minimum of errors
- To ensure the integrity of QA a system of checks are needed to establish that quality management systems are maintained within prescribed limits providing protection against "out of control" conditions and ensuring that the results are of acceptable quality.
- To achieve this, an appropriate program of QC is needed
- QC includes "the operational techniques and activities that are used to satisfy the quality requirements or DQO s" (FAO 1998)
- Producing quality data is a major enterprise requiring a continuous effort
- Approximately 20% of the total costs of analysis are spent on QA and QC (Carter & Gregorich, 2008)

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Carter & Gregorich, (2008). Soil Sampling and Methods of Analysis. Canadian Society of Soil Science.

What is Uncertainty Analysis

- What is uncertainty?
  - Is a measure of how accurately we know the true value of a measurement
  - Every measurement will have an associated uncertainty or error
- Why is uncertainty analysis important?
  - How significant are differences between measurements
    - On a specific sample?
    - On different samples?

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Example of uncertainty

- The radiocaesium inventory in forest soil before decontamination was 30 kBq m^{-2}, the inventory after decontamination was 25 kBq m^{-2}
- Inventory after is lower BUT is it significantly lower??
- In other words are the values the same or different if we evaluate and propagate all the uncertainties on both of these measurements?
- The two main types of uncertainty here are:
  1. Analytical
  2. Natural variation

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Uncertainties - field to measurement

- Measurement of area or the volume of the sample
- Measurement of weight
- Replicates – measurement of environmental variation
- Counting statistics
  - Gross, Compton – gives uncertainty on the net counts
  - Net counts converted to activity – combine error on N with error on detection efficiency
  - Standards
  - Blanks
  - Background
  - Half-life
- All of these must be combined to provide an overall error (errors added in quadrature)

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Transfer to Fukushima

- There is a vast amount of knowledge on characterisation of radio-Cs mobility in the environment:
  - Some experience can be taken over directly or modified for Fukushima conditions, particularly associated with sampling, sample handling and analysis: this should be formalised in protocols adopted by all involved organisations
  - QA is critical to integration of data from different sources and a general QMS for Japanese teams working in this area could be developed based on experience elsewhere
- Integration of information within a comprehensive database would be of great value
  - JAEA has probably as much experience here as any other organisation
  - Key aspects to be considered are flexibility, expandability and security

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Thanks for Listening!
Any Questions?