TRITIUM and the ENVIRONMENT

SOURCES

MEASUREMENT

and TRANSFER

Ph GUETAT, CEA

Thanks for their help to C Douche, JC Hubinois, N. Baglan, D Galeriu, Ph. Davis, W Raskob
SOURCES 1

- \(1 \text{ g} = 0.358 \text{ PBq}\)

**Natural:**
- 1300 PBq, 3.5 kg at equilibrium
- 72 PBq/an, 200 g/a

**Atmospheric nuclear tests**
- 190 000 PBq north, 420 kg
- 50 000 Pbq south, 140 kg
  \[\text{remains 40 kg 2007}\]

**Reprocessing Plants**

\[
0.4 \text{ PBq.}(GW.a)^{-1} = 1 \text{ g.}(GW.a)^{-1} \quad \text{as liquid release}
\]

- La Hague - sea 10 PBq.an\(^{-1}\), 30g - air 0.07
- Sellafield - sea 2 to 3 PBq.an\(^{-1}\), 8g - air 0.6 to 0.2
SOURCES 2

\[ 1g = 0.358 \text{ PBq} \]

- **Fission reactors releases** (TBq.a\(^{-1}\). GW\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GCR</strong></td>
<td>4</td>
<td>200-300</td>
</tr>
<tr>
<td><strong>HWR</strong></td>
<td>100-1000</td>
<td>100-500 (= 1g)</td>
</tr>
</tbody>
</table>

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SOURCES 3 - 1g = 0.358 PBq

• **Industrial and Small users**
  - Amersham 0.5 PBq.a⁻¹ before 2000 0.1 PBq.a⁻¹
  - R&D biology – labelled compounds: french stock 0.5 PBq 1g
    - Small amounts,
    - Incinerators; surface disposal - with¹⁴C
  - Tritium lighting devices
  - other paintings 0.1-0.5 TBq/device (1 mg/device)

• **Future users**
  - Laser (ie: LMJ) few tritium gas (mg.a⁻¹)
  - Fusion reactors, use of: JET 20g - ITER 1.5 kg.an⁻¹
• **Waste and waste disposals**
  - Sea dumping 1967-1982 : 20 PBq 60g
  - In France very small amounts in surface disposal
    • CSM  9 PBq  30 g
    • CSFMA < 4 PBq <10 g
    • CSTFA VLLW (ANDRA) low acceptance criteria.
  - Graphite : small outgassing  (• 10^{-7} a^{-1}?)
    subsurface
    20 000 t  -  5 PBq (2007)
  - Hulls & nozzles : 20 TBq / t
    small outgassing (< 10^{-6} a^{-1})
    type B
  - CEA tritium waste : 5PBq after treatment + storage
  - Rods B_4C, sodium cold trap… storage treatment
AUTHORIZED RELEASE TRITIUM [gramme]

- 358 TBq
- 4 PBq
- 4 TBq
- g/a

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Production of tritiated releases and waste in the future

– Depending on:
  - Conception of process
  - Treatments of air and waste
In Tritium buildings

• Avoid dilution
  – Limit volumes of air
  – Limit water vapor in air => dry air

• Limitation of leaks

• Detritiation of air - recycling

• Waste management a major source of Tritium release

• Detritiation of very low activity water not reasonable
Tritiated Solid waste treatment on VALDUC

- Process in GloveBox
  - Tritium Building
  - Dismantling
  - Maintenance
- Confine
  - FE200
- Cutting
- Melting furnace

2nd barrier
- Organics
  - Metallics
  - Detritiation Unit
- Orgamics Oven process
  - Treatment by vapor
  - Reduced outgassing
- HTO
- Ingot

<50 MBq/D.drum
- MLW
- Glow Box
- <2MBq/D.drum
- LLW
TRITIUM RELEASE Ci/Year Fct (Temp. °C) : MA Waste Storage

\[
y = 358.48e^{0.0762x}
\]

\[
R^2 = 0.9646
\]
Container for tritiated waste

Å Reversibility
Ç Confining
Ε Internal atmosphere Analysis

Drum 200 L

![Elastomer joint](image1) 10^{-3} \, \text{Pa.m}^3/\text{s}  
60 \, \text{€}

![Elastomer joint](image2) 10^{-5} \, \text{Pa.m}^3/\text{s}  
1400 \, \text{€}

![Welded joint](image3) 10^{-9} \, \text{Pa.m}^3/\text{s}  
\text{•} 1500 \, \text{€}

EPICEA

FE200

![Metal joint](image4) 10^{-7} \, \text{Pa.m}^3/\text{s}  
5000 \, \text{€}

12200 \, \text{€}

NB. initial costs of the drum

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Prospective cumulated volumes & Tritium activity of waste in France

1 - Small amounts of tritiated waste
2 – Program law N° 2006-739 28th juin 2006 - storage solutions…

Graph showing cumulative volumes and tritium activity from 2000 to 2050.
CONCLUSIONS for SOURCES

- **Natural** Tritium production is higher than man-made release.
- **Atmospheric nuclear test** multiplied by 100 at world scale and more.
- **Reprocessing plants** = main sources (sea).
- **Heavy water reactor** produces much more Tritium (D-T) than PWR, and PWR (boron) more than BWR (ternary fission). T production increases.

**Industrial use**:
- AMERSHAM: specific transfer for dissolved Organic Compounds in estuary environment
- Lighting devices: in US landfills, many places >20000 pCi/L

**Waste**:
- Tritium in many types of waste: activity and outgassing
- Very few in surface disposal in France.
- Air tight containers are expensive.

**Fusion use**: The use increases but no fundamental change for release what outgassing for waste?
Measurement
1 - introduction

• Preparation of sample depending on the physicochemical form

  – Gas : HT  HTO other
  – Liquide (Water) : pure or not (distillation)
  – Solid : T₂ HT HTO OBT (E OBT and NE OBT)
    • Bio
    • Metal
    • Powder - hydrides
2 - Principles - What is measured?

- Calorimetry: 0.1 mg
- Ionization chamber: 0.5 MBq/d
- Mass Spectrometry
- Raman Spectrometry
- Chromatography (gas phase 1 to 10 ppm, 10 mn)
- Scintillation:
  - Scintillating medium
  - photons
  - liquid Scintillation: 10 Bq/L
  - solid Scintillation: 10 ppm
- Activated charcoal
- UV excitation
- Permeation in column
- Mass H D T He
- T
- 3He
- e−
3 - Objectives of measurements

- **Inventories**:  
  - Calorimetry  
  - solid Scintillation

- **Releases**: *alarm or precision*  
  - Ionization chamber  
  - liquid Scintillation

- **Isotopy, impurities**:  
  - Mass spectrometry  
  - Gas chromatography  
  - Raman spectrometry

- **Waste**: *outgassing or inventory*  
  - ionization chamber,  
  - He3  
  - Surface contamination, wipe test + scintillation

- **Environment**:  
  - Liquid scintillation, electolytic enrichment
4 - Liquid scintillation

- **Principle**: A scintillating cocktail transforms \( (e^-) \) in photons, use of gauging curves to determine efficiency of counting before tritium activity calculation.

- **Detection levels**:
  - **Survey**: 10 Bq.L\(^{-1}\) 2 hours for measurement
  - **Very low level**: 1 Bq.L\(^{-1}\) NE OBT (1,5 day/sample).

- **Reference water**: A<0,2 Bq.L\(^{-1}\)

- **Pure Water**: no salt, no color, no other nuclides - or distillation

- **Contamination problems**
  - Controls for measure, distillation, lyophilisation, burning
  - Radon, C14…
  - Chemiluminescence
  - Static electricity
4.1 - Chemical Forms and sampling for tritium measurement in air

- Gas: tritiated water vapor HTO; hydrogen gas (HT) and tritiated methane.
  - sampling:
    - Active pump + bubbling
Organically bound tritium: definition

Example of the cellulose molecule

2 categories of hydrogen

- Bound to **O, N or S**: weakly bound high capacity of exchange with H or T of environment = **exchangeable** organic tritium.

- Bound to **C**: strong covalent bound, small capacity of exchange with H or T of environment. **Non Exchangeable** organically bound tritium.
4-3 solid sample Preparation for measurement

Sample → combustion → Total tritium Measurement

Lyophilisation → Free water → HTO Measurement

Dry matter → combustion → total organically bound tritium Measurement

Wash → lyophilisation → Pure 2nd free water → E OBT

Combustion + distillation of water of combustion → Dry matter → NE OBT
5 - Procorad intercomparisons

Procorad 1996 pollution

Procorad 2007
**Ionisation Chamber**
confining during 30 minutes

- tritium out-gasing GCC
  - LD = 0.5 MBq/Day/Drum

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**Method He3**
confining during some hours

- Total activity
  - LD = some GBq/drum
Conclusions for measurement

• Measurement apparatus for large inventories and large volumes to improve

• Easy to measure at a low level but need to have a good preparation

• Preparation takes time for solid material (case of incident ?)

• Not Easy to reach ANDRA’s requirements for disposal
• LEVELS in ENVIRONMENT
10 – activities of rain and surface waters in the past

Effet des essais nucléaires atmosphériques

In 1963 in Vienna (Austria):
150 Bq.L\(^{-1}\) in rain

In 1991 in Vienna (Austria):
2 Bq.L\(^{-1}\) in rain

1 U.T.
(Tritium Unit)
= 0.118 Bq.L\(^{-1}\)


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11. Distribution: sea and oceans

Repartition of T:
- 87% in oceans,
- 12% in continental waters,
- 1% in the atmosphere (HT and HTO)

Evolution of tritium activity versus depth:

<table>
<thead>
<tr>
<th>Profondeur (m)</th>
<th>Activité tritium (U.T.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1000</td>
<td>1.0</td>
</tr>
<tr>
<td>-2000</td>
<td></td>
</tr>
<tr>
<td>-3000</td>
<td></td>
</tr>
</tbody>
</table>


Atlantic (surface, 1998): ≈ 0.1 Bq.L⁻¹

chanel (surface, 1994): ≈ 0.3 Bq.L⁻¹

C (-1000 m, 1998): 0.005 ± 0.001 Bq.L⁻¹
• Tritium transfer in environment
  – Continuous release
  – Accidental release

TRS 364
Mechanisms and time scale for equilibrium

Inhalation + transcutaneous : few mn- h
Air-vegetable contamination HTO : few h - days
Air-vegetable OBT : few weeks
Soil (to reach equilibrium with air) : few months
  HTO and OBT in vegetable from soil water : in equilibrium
  Vegetable HTO in equilibrium with soil water within 2 days

Animal products : more or less in equilibration with fodder – Grass : few weeks of delay
A global IDEA of the tritium (HTO) pseudo equilibrium

« \( X\% = \text{order of magnitude of water concentration ratio} \) »

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**AIR**

- Transpiration absorption
- Rain 20%
- Evaporation
- Deposition

**SOIL**

- Leaching
- 30% deposition

**Vegetable water**

- 50% absorption
- 70% deposition

**Organic matter**

- 30% absorption
- 45% deposition

**Animals**

- 75% absorption
- 45% deposition

Dry matter content: 90% to 5%
HT transfer compared to HTO transfer

AIR

No air-leaves transfer

Veg water  Organic matter

Animals

No deposition by Rain

SOIL

Dry deposition (10 times lower)

HTO

microorganisms

No deposition by Rain

HTO transfer compared to HTO transfer
HTO vs. HT Predicted Dose

10g = 370 TBq/y; chronic; DCART
\[ \chi/Q = 1 \times 10^{-6} \text{ s.m}^{-3} \]
\[ \text{total} = 9 \mu\text{Sv} \]

For similar source terms, an HT release has a 1-10% dose impact compared with HTO.
## Concentration and mass balance

### Water equivalent factor

<table>
<thead>
<tr>
<th>Fresh weight = dry weight + water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 kg</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Protein</th>
<th>7 % H =&gt; 63% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>12 % H =&gt; 108%</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>6 % H =&gt; 54%</td>
</tr>
</tbody>
</table>

\[ \text{Weq} \cdot 50\% - 60\% \]
Final assessment for dose assessment

\[ C_{\text{total}}^{\text{plant.fw}} = [K_{\text{air}} + K_{\text{soil}}] \cdot [K_{\text{OBT}} + K_{\text{HTO}}] \cdot C_{\text{air.w}} \]

\[ C_{\text{total}}^{\text{plant.fw}} = [H_{r_{\text{air}}} + 0.3(1 - H_{r_{\text{air}}})] \cdot [(1 - H_{\text{plant}}) \cdot W_{eq} \cdot D_p] + H_{\text{plant}} \cdot C_{\text{air.w}} \]

\[ C_{\text{total}}^{\text{plant.fw}} = [H_{\text{air}} + 0.3(1 - H_{\text{air}})] C_{\text{air.w}} \cdot [(1 - H_{\text{pl}}) \cdot 0.3 + H_{\text{pl}}] \]

\[ C_{\text{green veg}} = (0.7_{\text{air}} + 0.09_{\text{soil}}) \cdot (0.06_{\text{obt}} + 0.8_{\text{HTO}}) \cdot C_{\text{air.w}} \]

\[ C_{\text{grain cereal}} = (0.7_{\text{air}} + 0.09_{\text{soil}}) \cdot (0.24_{\text{obt}} + 0.2_{\text{HTO}}) \cdot C_{\text{air.w}} \]
Conclusions for normal releases


- For HTO:
  - At each step of the transfer chain, dilution occurs
  - Vegetable Ingestion is clearly dominant
  - Direct Air-plant pathway dominant

- A HT release has a 1-10 % dose impact compared with HTO
  - Exposure comes then from HTO converted in soil

- Tritiated water of plant follows air concentration and so is not stable
  - OBT integrates air concentration
• ACCIDENTAL RELEASE
• ACUTE RELEASE
• Dynamic models
The different mechanisms involved in plants contamination: acute release

- **AIR**: Incorporation rate
- **HTO**: Storage
- **SOIL**: Decrease slope
- **1st Crop**: Deposition
- **next Crop**: Harvest

**Processes**:
- **Veg water** → **Organic matter**
- **SOIL** → **Veg water** → **Organic matter**
Tritiated particulates – dust & metallic hydrides

- Captation and deposition depending on particles’ size
Total impact of a 10g HTO release at 1km: effect of the weather

Do we know enough about Tritium impact?

Strong influence of atmospheric diffusion conditions

Some conditions where optimization is required

- OK for fine sunny day
- Factor 10 for rain
- > Factor 10 for night

10 g of HTO = the frontier.
optimization limited to few km

10 g of HTO = the frontier.
optimization limited to few km
Vegetable Ingestion 
main pathway

Garden veg or cereal 

With rain no change.

At night, still food.
Diurnal and seasonal effects on ingestion dose after an accidental tritium release calculated with RODTRIT)

Dose is given in arbitrary units (a.u.). The plants and animals were exposed to a constant HTO air concentration for one hour.
Relative importance of mechanisms

• Presently not enough certitude about acute release.

• Strong Rain may increase quite a lot the soil pathway, (but not the total exposure) ?

• Even with a strong rain (15mm), air pathway remains dominant in IAEA-EMRAS exercise.

• OBT generally dominant because of cereals – is that realistic ?

• Dose has to be integrated over one agricultural season because of soil pathway.
Question about scenario : case of wheat

• Ingestion of wheat is a specific problem for tritium:
  – The effect of cereals is reinforced by the storage and one year of consumption.

• What is covered by the name Cereals?
  – 260g of cereals: flour, Bread, rice, corn-flakes…
  – Question of dry or wet weight.
    • 260g/d of flour û 430 g/d of bread
  – The use of a single point in the wind axe is possible for a garden but has to be changed at least to a surface of a field for industrial food productions. That has a strong effect at short distance.
  – Sensible pathway only for few weeks per year.
Example of uncertainties for night assessment

Concentration of HTO in tissue water of leafy vegetables following the night-time release, 1-24 h.

Note: Results for UPRTRI/A and UFOTRI are identical and therefore symbols are superimposed on graph.
Agricultural data to develop (sojabean example)

Influence of date of contamination on OBT concentration in different parts of the plant at harvest

Incorporation rate (h⁻¹)

- Flowers at -90 days before harvest July 7th
- May 22th
- Sawing 136 days before harvest October

Time between contamination and harvest (days)
Regulation: Reference level for food limitation after accident

(calculated for 1 mSv in 1 year after accident 10% local and 650 kg/y)

$10^7$ to define area concerned the 1st day

$10^6$ to precise area in the following days

(After 2 days equilibrium reached with soil water)

$10^4$ of Codex alimentarius far too low

(activity of leaf vegetable at 1 hour after accident)

(activity of leaf vegetable at 2 days after accident)

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Conclusions for environment : R&D

• Tritium does not concentrate in food chain

About models
• Variability remains very large in case of accident especially in rain and night cases.
• Modification needed for wheat modelization - realistic approach

About experimental Data
• Translocation of organic matter from leaves to edible part of the vegetable.
• Case of the night for experimental data.
• What about Tritiated particulates ?

About modelers
• The present Tritium scientific community is very small,
• has to synthesize what is absolutely needed in models for acute release.
• This community could disappear from EU in the few next years.
Conclusions for regulation?

- what level for food trade?

- $10^4$ Bq/kg is not the right level and is really too low

- Not Consistent with the 10 mSv ICRP level for optimization of interventions (>2 orders of magnitude)
- Not Consistent with codex alimentarius principles 1 mSv + 10% of a huge consumption + level decreasing after an accident + assessment for 1 year.
- Not Consistent with $10^4$ Bq/L for WHO drinkable water in normal conditions. (0,1mSv-100%)

- Transport

4 Bq/cm² is not reasonable for Tritium

- Drinkable water:

  WHO should be kept as reference $10^4$ Bq/L. keep 100 Bq/L as an investigation value but not a definition of drinkable limit. (Cf USA)
Environmental Regulation or reference data

- $10^9$ Bq.kg$^{-1}$ - European directive radioprotection 1996
- $10^5$ Bq.kg$^{-1}$ - IAEA clearance level for waste
- $10^5$ Bq.kg$^{-1}$ - Canada OBT food trade value after accident
- $10^4$ Bq.kg$^{-1}$ - Codex alimentarius proposal after accident
- $10^4$ Bq.L$^{-1}$ - WHO for drinkable water
- $740$ Bq.L$^{-1}$ - USA reference value for watertable 20000 pCi.L$^{-1}$
- $100$ Bq.L$^{-1}$ - EU for distribution water control
- $10$ to $10000$ Bq.L$^{-1}$ - normal T activity in the vicinity of a plant
- $10$ Bq.L$^{-1}$ - reference value for ANDRA storm rain basin
- $1$ to $10$ Bq.L$^{-1}$ - normal tritium activity of water
- $4$ Bq.cm$^{-2}$ - beta value for transport
Thank you for your attention