

出國報告（類別：實習）

赴日本福島國際研究教育機構
(F-REI)等相關單位進行「放射性核種
分析」訓練

服務機關：核能安全委員會輻射偵測中心

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摘要

本中心為提升我國放射性化學分析技術，赴日本相關實驗室實習，透過見習與經驗交流，了解日本對於環境中微量之放射性核種分析技術，以利精進我國在放射性核種之分析能力。本次實習造訪福島教育研究機構（Fukushima Institute for Research, Education and Innovation, F-REI）及日本原子能研究開發機構（Japan Atomic Energy Agency, JAEA）學習以質譜儀分析銥-90 及鎳-99 之方法。另由於福島第一核電廠氚排放事件，本次實習也前往福島大學環境放射能研究所(Institute for Environmental Radioactivity at Fukushima University, IER)瞭解海水中氚的濃縮技術。

此外，本次實習實驗室皆長期致力於環境中放射性核種分析及含量調查，具有豐富的環境取樣經驗及成熟的分析技術，本次實習借鏡日本在微量放射性核種的分析經驗，有助於精進我國在放射性核種的分析能力，並提供設備更新規劃之參考。

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壹、 目的

環境中含有微量的放射性核種，依其釋放能量之形式，分為阿伐核種、貝他核種及加馬核種，其中部分核種為純貝他或純阿伐核種，此類核種由於所釋放粒子之特性，以放射分析方式進行量測與定量較為困難，故屬於難測核種。因此，國際上逐漸嘗試以質譜法進行難測核種分析技術之研究開發。

由於質譜法的量測訊號是與原子的數目成正比，較適合用於長半衰期的放射性核種分析，因半衰期長的核種具有較低的比活度、衰減的速度慢，在相同的活度下，半衰期長的核種濃度較高而有較多的原子數，使得質譜法較易測得。這類型的放射性核種，相較於放射分析法的偵測極限，質譜法的偵測極限可能更低且快速。

為瞭解質譜法在放射性核種分析之應用及分析操作流程，本次實習造訪福島教育研究機構（Fukushima Institute for Research, Education and Innovation, F-REI）及日本原子能研究開發機構（Japan Atomic Energy Agency, JAEA）學習以質譜儀分析銥-90 及鎳-99 之方法，除前述核種外，福島教育研究機構也建立海水中放射性銫之分析方法，並執行福島縣周圍海水之量測。

此外，由於福島第一核電廠氙排放事件，本次實習也前往福島大學環境放射能研究所(Institute for Environmental Radioactivity at Fukushima University, IER)瞭解海水中氙的電解濃縮技術及福島縣周圍海水及海生物氙含量之變化。

本中心長期執行臺灣環境輻射監測及調查作業，考量鄰近國家核子科技的開發與應用及臺灣核電廠的除役作業等，環境輻射監測之放射性核種可能有所改變。因此，希望藉由本次實習瞭解日本在難測核種之分析技術，並精進本中心之分析能力，及相關設備購置規劃之參考。

貳、 行程

本次實習自 113 年 11 月 5 日至 9 日，實習時間如下表 1。

表 1 實習時間表

日期	行程	地點
2024.11.5	去程：高雄機場 → 成田機場 → 福島市	
2024.11.6	熱電離質譜法鋇-90 分析訓練	福島國際教育研究機構 (F-REI)
2024.11.7	氚電解濃縮分析訓練	福島大學環境放射能研究所(IER)
2024.11.8	感應耦合電漿質譜法鎔-99 分析訓練	日本原子力研究開發機構 (JAEA) 東海研究中心
2024.11.9	回程：東京 → 成田機場 → 桃園機場 → 高雄	

參、 實習紀要

本次主要實習項目為了解以質譜法分析鋇-90 及鎳-99 等相關核種之技術、海水中放射性銫分析技術及氬電解濃縮分析技術。

一、 熱電離質譜法鋇-90 分析訓練

熱電離質譜儀(Thermal Ionization Mass Spectrometry, 簡稱 TI-MS, 圖 1), 是以加熱的方式使樣品中的原子離子化, 溫度可由室溫升高至攝氏 2300 度, 可藉由控制溫度將樣品中的特定原子離子化, 形成離子束。離子束經過磁場後依不同質量分離, 進入偵檢器, 此類質譜儀具有多個收集檢測器, 可同時分析多個同位素。熱電離質譜儀主要分為 3 個區域(圖 2), 樣品離子化區、磁場質量分離區及質量分析計測區。樣品離子化區的真空度為小於 10^{-8} mbar, 磁場質量分離區及質量分析計測區的真空度則需低於 10^{-16} mbar。低真空度可避免樣品與氣體的化學或碰撞反應, 以提高儀器的靈敏度。因外, 熱電離質譜儀是目前精密度及準確度最高的同位素分析儀器, 屬於一級標準儀器, 常用於地球化學、地質年代鑑定等研究, 也因儀器之高精密度及準確度, 故對於操作人員的技術要求非常高。

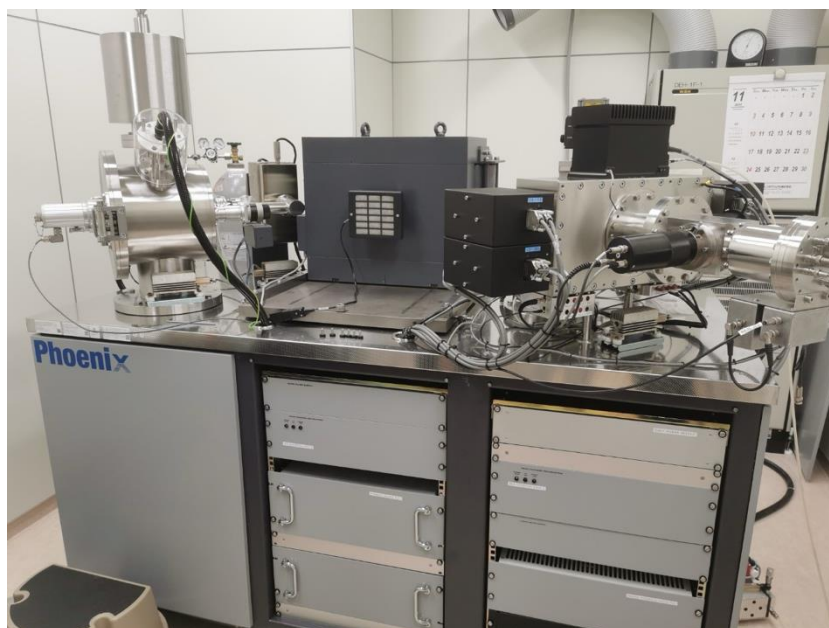


圖 1. Phoenix X62 熱電離質譜儀

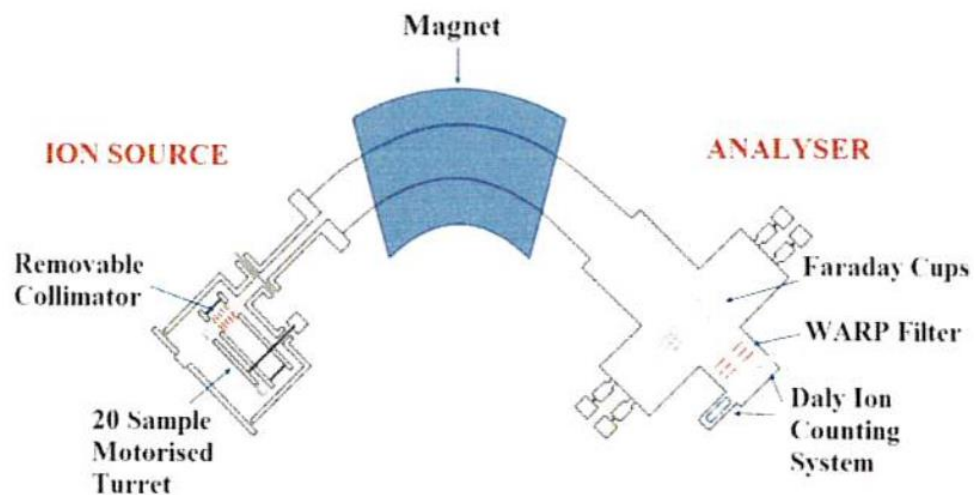


圖 2. 熱電離質譜儀簡圖

熱電離質譜儀離子化方式是藉由控制電流加熱金屬，並控制溫度至待測原子離子化之溫度，其所需之金屬純度需大於 99.999%，一般會使用銠 (Rhenium, Re) 或是鉭 (Tantalum, Ta) 金屬做成的燈絲作為加熱樣品的載體。在樣品執行分析前，需要將銠或是鉭燈絲焊接在樣品座 (Bead block, 圖 3、4) 上，焊接完成的樣品座需要使用除汙 (degas) 設備 (圖 5) 在高真空及 4.5 安培的電流下進行 1 小時的除汙處理來去除金屬燈絲上的不純物及干擾物，前處理後的金屬燈絲建議放置幾天形成氧化層，可避免在上樣品時，樣品溶液滑出金屬燈絲。經處理的燈絲可放於乾燥箱備用。

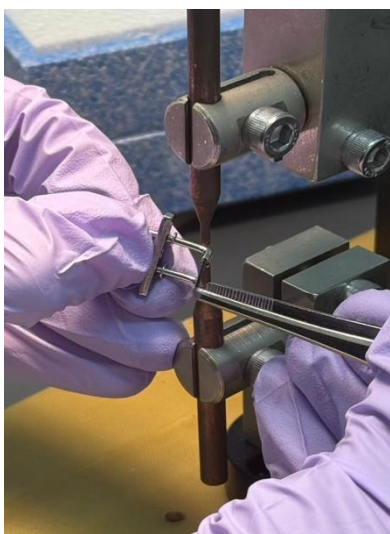


圖 3. 焊接金屬燈絲

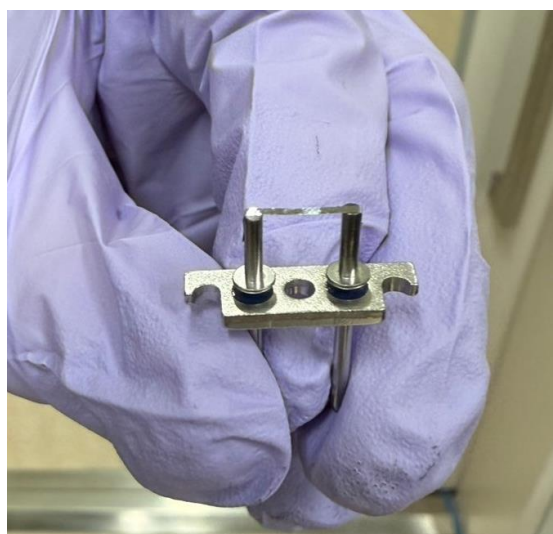


圖 4. 完成焊接的樣品座



圖 5. 樣品座除汙的設備。樣品座安裝於左圖的架子上，加蓋後如右圖並抽真空。

樣品上機步驟如表 2，將金屬燈絲座插在樣品板（圖 6），為避免樣品在乾燥附著的過程中揮發，需要先在金屬燈絲上滴入五氟化鉬（ TaF_5 ）並以 0.5 安培的電流使其乾燥，再以微量吸管取純化後的樣品點在金屬燈絲上，並以 0.5 安培的電流使其乾燥（去除酸液）附著於金屬燈絲上。將含有樣品的金屬燈絲座置於樣品轉塔盤（turret plate，圖 7）上，一座轉塔盤有 20 個樣品區。轉塔盤放入樣品離子化區後，開始抽真空並等待真空度下降，通常會需要 6~8 小時才能達到分析要求的真空度（ $<10^{-8}$ mbar）。

表 2. 樣品上機步驟

編號	步驟	備註
1	燈絲除汙（degassing）	至少 4.5 安培 1 小時（上樣前步驟）
2	燈絲氧化	靜置數日形成氧化層（上樣前步驟）
3	燈絲活化	滴上五氟化鉬並以 0.5 安培加熱蒸乾
4	上樣	滴入樣品並以 0.5 安培加熱蒸乾
5	酸蒸發	蒸乾時，使用的電流必須小於 2 安培，且燈絲不能發光

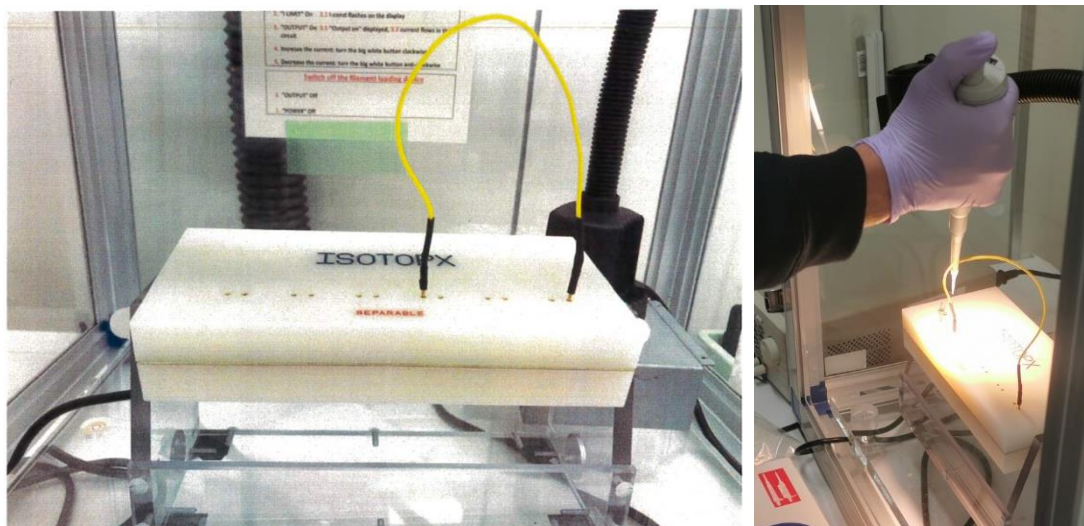


圖 6. 樣品板 (Sample loading station)

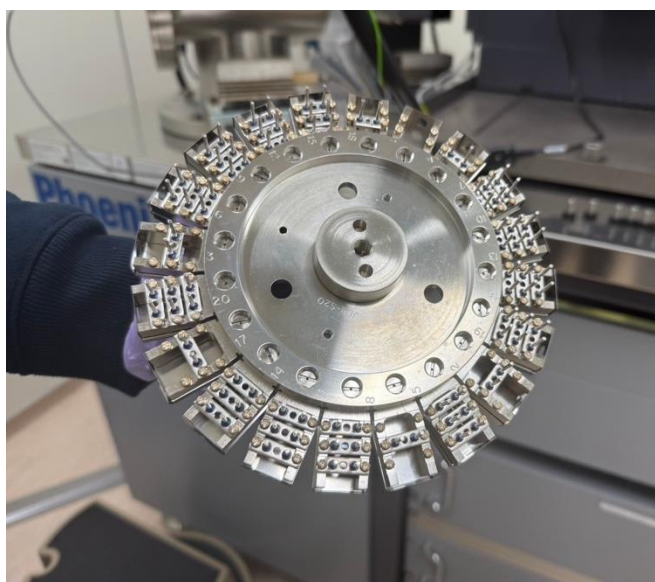


圖 7. 樣品轉塔盤 (Turret plate)

熱電離質譜儀質量分析計測區為具有多個收集檢測器 (Multi- collector) 並配有數個法拉第杯 (Faraday cups) 以及一個戴利離子計數器 (Daly ion counting detector), 圖 8。多個收集檢測器可同時收集分析同一元素的同位素, 法拉第杯可精準偵測進入偵檢器的離子數量, 戴利離子計數器包含二次發射極 (dynode) 及光電倍增管 (Photomultiplier tube), 可將含量極低的同位素訊號放大並偵測。此外, 在戴利離子計數器前設有過濾器 (Warp Filter) 可將離子能量小於 8,000 伏的其他離子去除, 以降低背景雜訊。

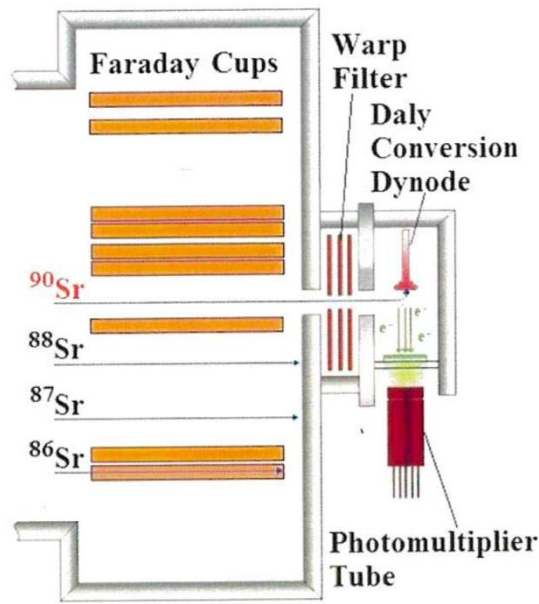


圖 8. 偵檢器示意圖

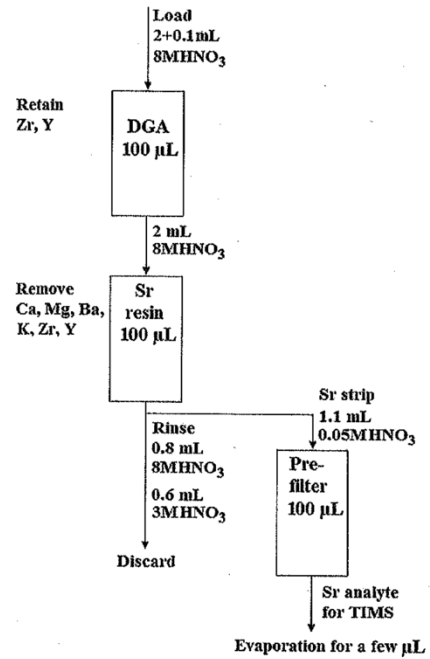


圖 9. 樣品前處理流程

本次實習之福島教育研究機構之熱電離質譜儀主要應用於銨-90 檢測及樣品中銨同位素比值分析，檢測樣品包含土壤、自來水、牛奶及奶粉等。樣品前處理的過程如下（圖 9）：

1. 樣品消化：取 1 毫升的牛奶進行微波消化（圖 10）或以攝氏 600-700 度進行灰化（圖 11），再以 2 毫升 8M 硝酸溶解。
2. 銨分離純化：分別取 100µl DGA 樹脂及 100µl Sr 樹脂填入長 42mm、直徑 5mm 的管柱中。DGA 樹脂可將鋯(Zr)及鈮(Y)留在管柱中，而 Sr 樹脂分別以 0.8 毫升 3M 硝酸及 0.6 毫升 8M 硝酸流洗，可將樣品中鈣(Ca)、鎂(Mg)、鋇(Ba)、鉀(K)、鋯(Zr)及鈮(Y)洗出，再以 1.1 毫升 0.05M 的硝酸將銨洗脫，洗脫液再經 100µl prefilter 樹脂去除有機質。最後加熱洗脫液蒸發至數個微升 (µl)。
3. 熱電離質譜儀分析：取 1µl 純化後的洗脫液，依前述上機步驟進行銨同位素分析。由於銨-90 的離子化溫度較高，在攝氏 1,400 度以上，且銨-90 與銨-88 比值會先進行分析。基於同位素分餾效應，即質量較輕的同位素會先被蒸發，導致銨-87 與銨-86 的比值會受影響而偏移或改變，使銨-87 與

銻-86 比值分析時的準確度會下降，故須以環境中銻-86 與銻-88 的比值進行校正。



圖 10.微波消化系統



圖 11. 灰化設備

以熱電離質譜法分析銻-90 的偵測極限 (Detection Limit, DL) 與樣品中穩定銻-88 含量有關，當樣品中銻-88 含量高時，銻-88 的訊號的拖尾 (Peak tail) 會成為銻-90 的訊號，使銻-90 的偵測極限提高 (圖 12)。當銻-90 與銻-88 的比值在 2.1×10^{-10} 時，銻-90 的偵測極限約為 0.88 毫貝克 (0.17×10^{-15} 克)。另，此方法也以標準參考物質 (IRMM-426 藍莓及 NIST-4353 湖底沉積物) 進行分析，以確認其於定量上之準確性，圖 13。

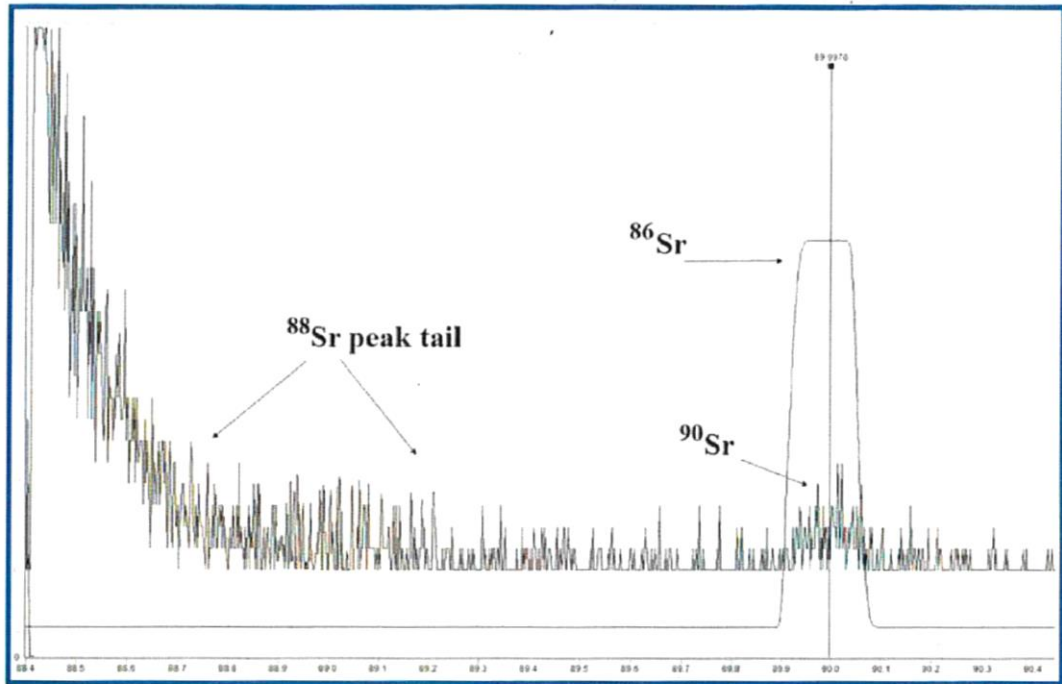


圖 12. 銥-90 分析時，銥-88 的訊號拖尾 (銥-90 與銥-88 比值為 1.44×10^{-9})

表面電離型質量分析計を用いた ストロンチウム-90 (^{90}Sr) の新たな分析法

Novel method for measurement of ^{90}Sr in environmental samples using thermal ionization mass spectrometry

はじめに

- ^{90}Sr は、放射性CsやPuと同じように人工的に生成された放射性核種です。1950-60年代の大気圏内核兵器実験や原子力施設事故などにより環境中に放出され、降下物、土壌や水に存在している。
- 従来の放射線計測法による ^{90}Sr 分析法に比べ、この質量分析計を用いることで、従来の約1/10程度の少量の試料で、試料処理から定量までの所要時間が1日以内と迅速に精密よく測定できる方法を確立した。
- ^{90}Sr のデータをより多く蓄積し、放射性Cs以外の放射性核種も含まれた環境への影響や被ばく線量をより的確に評価することに役立つと期待される。

方法

- 本研究では表面電離型質量分析装置 (TIMS) として、英国Isotope社のTIMS (型番Phoenix XG2) を用いた。
- このTIMSには、フラアデーカップ検出器が9つデューリー・イオンカウンティング検出器1つ搭載されています。
- ^{90}Sr と ^{86}Sr をそれぞれのフラアデーカップ検出器で、 ^{90}Sr をデューリー・イオンカウンティング検出器で同時に測定することに成功しました。

1. 環境試料の前処理
試料 (0.1g, 2.0g) を準備

2. 試料の定量化
1. 酸化性をフッ素酸に換換
2. 酸化性をフッ素酸に換換

3. Srの化学分離と精製
1. Srの化学分離と精製

3. 検出器毎に分離
表1. ^{90}Sr 測定における試料量と所要時間の比較

試料量 (μg)	所要時間 (分)	検出器	検出器タイプ
10	2.0	1	IC
10	2.0	2	IC
10	2.0	3	IC
10	2.0	4	IC
10	2.0	5	IC
10	2.0	6	IC
10	2.0	7	IC
10	2.0	8	IC
10	2.0	9	IC
10	2.0	10	IC
10	2.0	11	IC
10	2.0	12	IC
10	2.0	13	IC
10	2.0	14	IC
10	2.0	15	IC
10	2.0	16	IC
10	2.0	17	IC
10	2.0	18	IC
10	2.0	19	IC
10	2.0	20	IC
10	2.0	21	IC
10	2.0	22	IC
10	2.0	23	IC
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10	2.0	26	IC
10	2.0	27	IC
10	2.0	28	IC
10	2.0	29	IC
10	2.0	30	IC
10	2.0	31	IC
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10	2.0	33	IC
10	2.0	34	IC
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10	2.0	36	IC
10	2.0	37	IC
10	2.0	38	IC
10	2.0	39	IC
10	2.0	40	IC
10	2.0	41	IC
10	2.0	42	IC
10	2.0	43	IC
10	2.0	44	IC
10	2.0	45	IC
10	2.0	46	IC
10	2.0	47	IC
10	2.0	48	IC
10	2.0	49	IC
10	2.0	50	IC

表2 ストロンチウム同位体

同位体	由来	存在	半減期	崩壊
^{84}Sr	天然	0.56 %	安定	-
^{86}Sr	天然	9.86 %	安定	-
^{87}Sr	天然	7.0 %	安定	-
^{88}Sr	天然	82.58 %	安定	-
^{89}Sr	人工	-	50.5 日	β^-
^{90}Sr	人工	-	28.8 年	β^-

表3 質量数に対するSr同位体ごとのカウント数の比較

表4 従来のLSC法とTIMS分析法による定量結果の比較

標準参照物質による ^{90}Sr の分析精度チェックについて

- ワイルドベリー (IRMM-426) 1gと基底増殖物(NIST-4354) 0.5gの標準参照物質を用いてTIMSによる ^{90}Sr の定量を実施した。
- ワイルドベリー中の安定Sr濃度と ^{90}Sr 濃度は、認証値が $5.1 \mu\text{g/g} \pm 1.24 \pm 24 \text{Bq/kg}$ に対して、実測値は $4.5 \pm 0.6 \mu\text{g/g} \pm 1.27 \pm 7 \text{Bq/kg}$ でした。
- 基底増殖物の安定Sr濃度と ^{90}Sr 濃度は、認証値が $1.37 \mu\text{g/g} \pm 51.2 \pm 11.8 \text{Bq/kg}$ に対して、実測値は $1.5 \pm 0.3 \mu\text{g/g} \pm 53.3 \pm 4.9 \text{Bq/kg}$ でした。

標準参照物質による ^{90}Sr の分析精度チェックについて

- 迅速かつ正確な測定が困難な環境試料中のストロンチウム90(^{90}Sr)の分析法が開発された。
- 質量分析法を用いることにより、少量の試料で、かつ測定までにかかる時間の大幅な短縮と高精度化に成功した。
- 環境中の ^{90}Sr のデータをより多く蓄積し、福島環境への影響や被ばく線量のより的確な評価に役立つことが期待される。

References
1. Kawanishi, M., Sakano, M., Aono, T. (2019) Zirconium decontamination factor test on DCA and Sr resin for ^{90}Sr analysis using organic acid decontamination. J. Radioanal. Nucl. Chem. 114, 1313-1344.
2. Kawanishi, M., Sakano, M. (2019) Method for ^{90}Sr Analysis in Environmental Samples Using Thermal Ionization Mass Spectrometry with Only Ion-Counting System. Anal. Chem. 91, 2960-2969.

圖 13. 參考物質定量分析之成果海報

福島教育研究機構除有熱電離質譜儀外，也設有其他類型之質譜儀等，包含多接收器感應耦合電漿質譜儀（MC-ICP-MS，廠牌：Nu Plasma3，圖 14）感應耦合電漿質譜儀（ICP-MS/MS，廠牌：Agilent 8800，圖 15）以及感應耦合電漿原子發射光譜儀（ICP-OES，廠牌：Hitachi PS7800，圖 16）等，用於各種樣品中穩定元素的分析等。

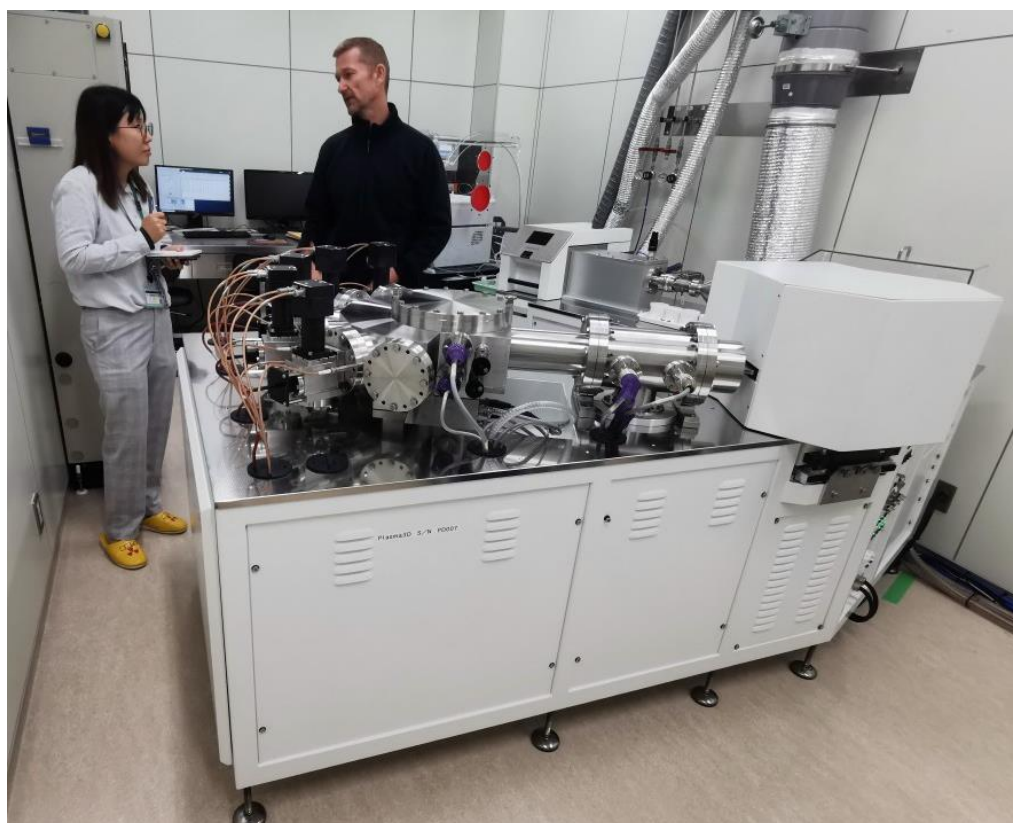


圖 14. 接收器感應耦合電漿質譜儀（MC-ICP-MS）



圖 15. 感應耦合電漿質譜儀

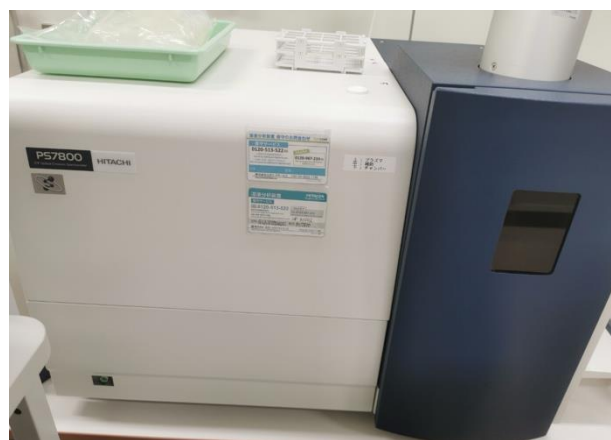


圖 16. 感應耦合電漿原子發射光譜儀

二、氚電解濃縮分析訓練

氚是氫的放射性同位素，可放出低能量（18.3 keV）的β粒子而衰變為氦原子，半衰期為 12.3 年，氚是天然的放射性核種也是人為的放射性核種，人為產生的氚主要源自於核電廠中壓水式及重水式核反應器，以及核子意外事故等。當氚原子進入環境中的水循環時，主要以 HTO 的形式存在，由於海水中氚的含量相當低，故無法直接以液態閃爍計數器直接測量。根據文獻顯示，氚水（HTO）的解離電位較水（H₂O）稍高（表 3），因此可利用水電解方式，將樣品水中的氚離子還原形成氫氣排出，來濃縮樣品中的氚。

表 3. 攝氏 25 度下，氚同位素的解離電位（可逆反應）

氚同位素水	解離電壓
H ₂ O	1.230
HDO	1.248
HTO	1.250
D ₂ O	1.263
DTO	1.271
T ₂ O	1.277

目前國際上應用於氚濃縮之電解方法主要有鹼式電解法(Alkaline Electrolysis)及固態高分子膜電解法(Polymer Electrolyte Membrane, PEM or Solid-Polymer Electrolysis, SPE)。

鹼式電解法用於環境水樣氚之濃縮已行之有年，此方法通常使用固定體積（250 至 500 毫升）電解槽彼此串聯並放置在能控制溫度(~5°C) 的容器中，電解槽中使用成對的金屬電極進行電解，目前日本分析中心（Japan Chemical Analysis Center, JCAC）也是採用此方法，圖 17。2016 年 B. Kumar 等人設計另一種電解槽可電解大體積的水樣，發表於 Applied Radiation and Isotopes 期刊上並進行商品化（日本化研公司），日本 JAEA Miharu 機構是採用此方法，圖 18。

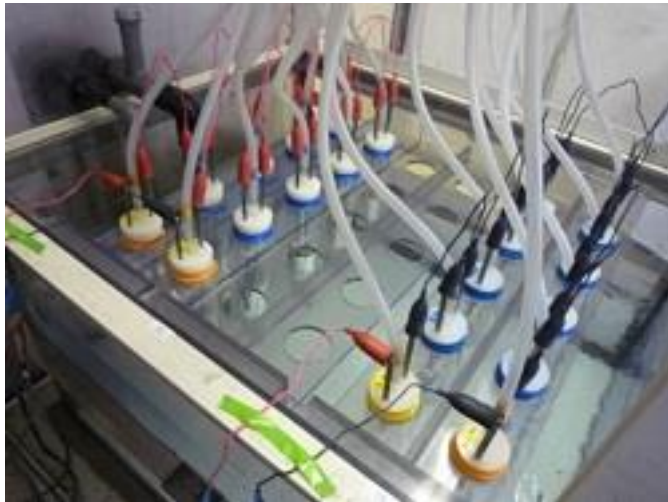


圖 17. 鹼式電解設備 (JCAC)



圖 18. 鹼式電解設備 (JAEA)

由於環境水樣中含有之各種離子，在電解過程中易附著於電極上，因此在電解前需蒸餾純化樣品，但純水的電阻高不易電解，因此需要在樣品中添加鹼液，一般會添加過氧化鈉 (Na_2O_2) 作為電解質。JCAC 的鹼式電解設備可將 500 毫升的水樣進行濃縮，但每次濃縮後的體積無法固定。工作電流最大可達 20 安培，電解濃縮所需的時間為 2 周左右，一次可濃縮 8 個樣品，但由於每個電解槽採串連方式，因此頭尾兩端的電解槽必須使用標準品，用於計算本次電解的回收率，一般約為 70% 左右。

近年來國際上越來越多實驗室使用固態高分子膜電解法進行水樣中氫之電解濃縮，由於固體高分子膜是一種良好的離子導體，因此在電解的過程中無需額外加入電解質。此外，這種固體高分子膜對於氫離子具有良好的通透性，因此可將電解產生的氫氣及氧氣分離，使分析過程更安全。目前日本、中國及韓國均有開發此類商品化的設備，圖 19。

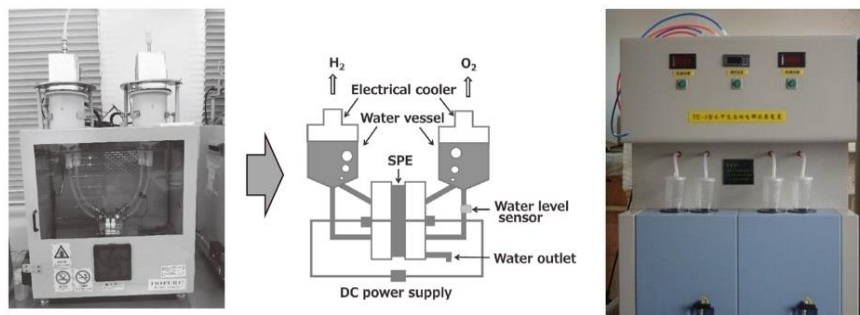


圖 19. 固態高分子膜電解設備 (左：日本，右：中國)

本次實習之福島大學環境放射能研究所使用的是固態高分子膜電解設備（廠牌：DeNora，型號：TRIPURE[®]，圖 20）進行海水樣品中氚的濃縮，此套設備可將 800~1000 毫升的樣品濃縮至 50 毫升左右，濃縮所需時間為 3 天左右，電解分為 2 階段，其電流分別為 50 安培及 20 安培。樣品體積濃縮約 15 倍，氚活度濃縮約 8.59 倍，電解回收率約 50% 左右。由於水與氚水的解離電壓差異小，當電解使用電流較大時將影響氚的回收率，故樣品體積的濃縮倍數大於氚活度的濃縮倍數，氚的最小可測活度為 0.05 貝克/升。

綜上，本報告彙整日本相關實驗室所採用之電解設備資料如下表 4。



圖 20. 福島大學環境放射能研究所的氚電解濃縮設備

表 4. 電解設備資料表

	TRIPURE [®]	日本化研	JCAC 自組
電解類型	固態高分子膜	鹼式	鹼式
體積	1000 毫升濃縮至 60 毫升	2000 毫升濃縮至 100 毫升	500 毫升濃縮至 50 毫升
工作電流	50 安培, 20 安培	20 安培	20 安培
電解時間	3 天/件	2 周/8 件	2 周/8 件
氚回收率	50%	80~90%	70~80%
氚濃縮倍率	8.59	16	7~8
備註	無法出口台灣	可出口台灣	需個別訂購零件自組 (自組零件詳附錄)

三、感應電漿耦合質譜法銻-99 分析訓練

銻-99 為純貝他的放射性核種，其半衰期為 213,000 年，銻-99 主要來源為核燃料的再處理、核醫藥物的使用及核電廠除役等。鑑於銻-99 的長半衰期，傳統的放射分析法(如:液態閃爍偵檢器)所需要的計測時間較長且相較於質譜法而言，其偵測極限也較高。根據文獻顯示，液態閃爍偵檢器的偵測極限約為 10^{-10} ~ 10^{-11} 克 (約 6~60 毫貝克)，而感應耦合電漿質譜儀的偵測極限約為 10^{-12} ~ 10^{-13} 克 (約 0.06~0.6 毫貝克)。

感應耦合電漿質譜儀(Inductively Coupled Plasma Mass Spectrometer, ICP-MS)主要是以溫度 6000K 到 10000K 電漿使樣品中的待測物離子化形成離子束進入質量分析器分析，目前最常見的質量分析器為四極柱分析器，藉由四根電極產生隨時間變化的電場，使特定質量的離子通過，而其他離子則將被偏轉抽離，與四極柱碰撞後而移除，以進行特定質量的定量分析。

日本原子能研究開發機構(Japan Atomic Energy Agency, JAEA)使用的是四極柱串聯的感應耦合電漿質譜儀 (Multi-Quadrupole Inductively Coupled Plasma Mass Spectrometer)(廠牌:PerkinElmer 型號:NexION 5000, 圖 21)。四極柱串聯感應耦合電漿質譜儀的 Q2 碰撞腔有 3 種模式，可用來降低其他共存離子之干擾。

(一) 反應 (Dynamic Reaction Cell, DRC) 模式：透過四個氣體通道同時選擇最多四種反應氣體，如氨氣、氧氣、氫氣、二氧化碳、甲烷等反應性氣體注入腔中，與分析物或干擾離子產生可預測的化學反應，形成分子形式離子態，再依據分析物的需要選擇質量，以獲得準確的結果和更低的偵測極限。

(二) 碰撞 (Kinetic Energy Discrimination, KED) 模式：碰撞腔相容於多種碰撞氣體，可消除未知的光譜多原子干擾。在此模式下，可以惰性氣體 (例如氫氣) 或輕微反應性氣體混合物注入碰撞腔中，與穿過碰撞腔的離子碰撞。由於許多干擾多原子離子往往具有比分析物

離子更大的直徑(碰撞截面),因此它們將比分析物遭受更多的碰撞。這些額外的碰撞意味著干擾離子會損失更多的動能,因此會透過動能差異(KED)被去除。儘管在此模式下某些元素的靈敏度可能會顯著下降,但對於通常存在多原子干擾的元素,它比標準模式提供更好的偵測極限。

(三) 標準模式(不添加氣體):通常用於沒有干擾或同重素和少量多原子干擾的元素。



圖 21. 感應耦合電漿質譜儀(廠牌:PerkinElmer 型號:NexION 5000)

一般使用感應耦合電漿質譜儀分析樣品中鎘-99時,由於質譜法是以質荷比為分離條件,故分析時可能會有同重素或相同質荷比的分子產生訊號干擾。此外,環境中存在穩定的鈦-99(^{99}Ru , 豐度約 12.6%)和鉬-98(^{98}Mo , 豐度為 24.3%),鉬-98(^{98}Mo)會和設備內的氫氣生成質量為 99 的 $^{98}\text{Mo}^1\text{H}$,使得無法準確定量鎘-99,如圖 22。因此,在樣品前處理時盡可能的將樣品中的鈦-99 及鉬-98 移除,以避免成為質譜分析的干擾訊號。

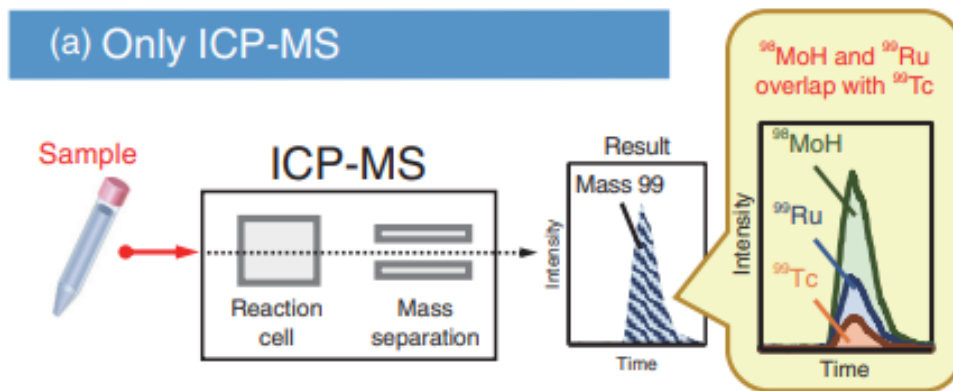


圖 22. 同位素訊號重疊干擾示意圖

由於海水中鈦-99 含量是鎢-99 的 400 倍，而鉬-98 含量是鎢-99 的 1.6×10^9 倍，因此 JAEA 設計多階段分離系統進行分析，此系統由流動注入分析 (Flow Injection Analysis, FIA) 搭配固相萃取管柱 (solid-phase extraction, SPE) 純化後直接進入四極柱串聯的感應耦合電漿質譜儀，如圖 23。固相萃取管柱中裝填選擇性樹脂(TK201)，可初步移除硝酸萃取液中的 ^{99}Ru 及 ^{98}Mo ，使其濃度分別有效降低至 1/4000 和 1/3000，再利用四極柱串聯的感應耦合電漿質譜儀碰撞腔 (Q2) 的反應模式，在碰撞腔中注入氧氣使得干擾物質 $^{98}\text{Mo}^1\text{H}^+$ 氧化為 $^{98}\text{Mo}^{16}\text{O}^+$ 及 $^{98}\text{Mo}^{16}\text{O}_2^+$ 而被移除，這種多階段分離系統可提高解析度，使之能夠分析鎢-99 與鉬-98 比值為 10^{-8} 的樣品。JAEA 以此方法分析海水參考物質 (驗證值為 159-250 mBq/L)，所得到的數值 (200.1 ± 9.6 mBq/L) 與驗證值一致，此外此方法分析 50 毫升樣品所需的時間為 30 分鐘，偵測極限(Minimum Detectable Amount, MDA)為 5.9 mBq/L。

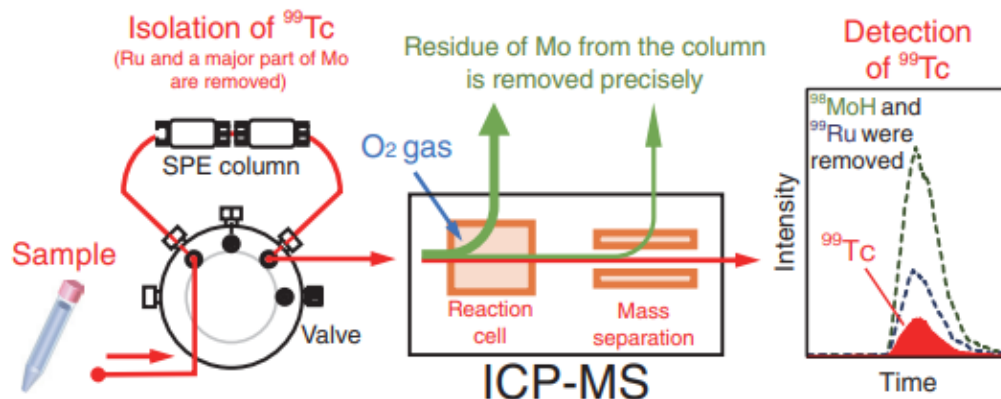


圖 23. 多階段分離系統

另因海水中之含量極低，文獻指出海水中鎔-99 的背景活度在 0.01 到 0.1 毫貝克/升之間，因此若需分析海水中鎔-99 背景活度，則需先將大量海水樣品進行濃縮。利用鎔-99 在水中以過鎔酸根(TcO_7^-)離子存在，以強陰離子交換樹脂進行鎔-99 的濃縮。JAEA 選擇使用 300 克 AG1-X8 陰離子交換樹脂來吸附 200 公升海水中的鎔-99，再將 300 克樹脂以攝氏 400 度進行灰化並以 50 毫升的硝酸萃取，硝酸萃取液後續以多階段分離系統進行分析，JAEA 表示目前此方法尚在測試階段。

綜上，四極柱串聯的感應耦合電漿質譜儀可有效移除樣品中共存離子，降低儀器偵測極限及獲得精準的分析結果，除應用於鎔-99 分析外，還可用於碘-129、銨-90、鐵-55、銻-241/錒-241 等放射性核種的分析。

四、加馬核種分析系統

(一) 日本福島國際研究教育機構(F-REI)之加馬核種分析系統：

- 1 海水中銫-137 之放射化學純化方法採磷鉬酸胺(AMP)共沉澱法，並收集沉澱物(銫)如圖 24 所示，其方法與本中心相同。
- 2 純鍍偵檢器以 CANBERRA 廠牌為主，而分析軟體為日本自行開發。
- 3 標準樣品包括 2 種幾何形狀，採用計測容器、極薄針型容器進行效率校正後，將待測樣品包括生物試樣、海水及沉積物等，置放於計測腔內進行量測。



圖 24. 日本福島國際研究教育機構之加馬核種分析系統

(二) 福島大學環境放射能研究所之加馬核種分析系統：

- 1 福島大學之加馬核種分析系統包含鉛屏蔽同軸純鍺偵檢器及自動化進樣系統，主要應用於環境試樣中各種加馬核種之定量分析。
- 2 純鍺偵檢器以 CANBERRA 廠牌為主，而分析軟體則為日本自行開發，搭配自動化進樣系統，可減少人工置換樣品時間如圖 25。
- 3 標準樣品配合不同幾何高度進行效率校正後，將待測樣品置放於計測腔內進行量測。



圖 25. 福島大學環境放射能研究所之加馬核種分析系統

肆、心得與建議

本次赴日本福島教育研究機構、福島大學及日本原子能研究開發機構實習，了解日本應用質譜儀分析放射性核種的方法、氙的電解濃縮技術及加馬核種分析系統。

日本福島教育研究機構以熱電離質譜儀分析環境試樣中的銨-90，可大幅縮短分析時間，一批次 18 件樣品只需要 30 小時，單件樣品則為 16 小時左右，而其偵測極限為 0.88 毫貝克。惟熱電離質譜儀屬精密儀器設備造價高，不易維護且維護成本高，此外，TI-MS 對分析人員的技術要求也較為嚴格。另外日本原子能研究開發機構則是使用感應耦合電漿質譜儀分析環境試樣中的放射性核種（包含銨-90、鎘-99 及碘-129），由於此類核種在環境中含量較低，故以放射分析方法測量，所需樣品量大且分析時間更長。因此，針對長半衰期的難測核種，以感應耦合電漿質譜儀進行分析更為簡便及快速。

由於福島氙水排放事件，本次也針對日本相關實驗室在氙的電解濃縮技術進行訓練及交流，福島大學所用電解設備可將 800~1000 毫升的樣品濃縮至 50 毫升左右，濃縮所需時間為 3 天左右，樣品體積濃縮約 15 倍，氙活度濃縮約 8.59 倍，故可測得福島周邊海水中氙的活度，並掌握氙水排放對海洋的影響。

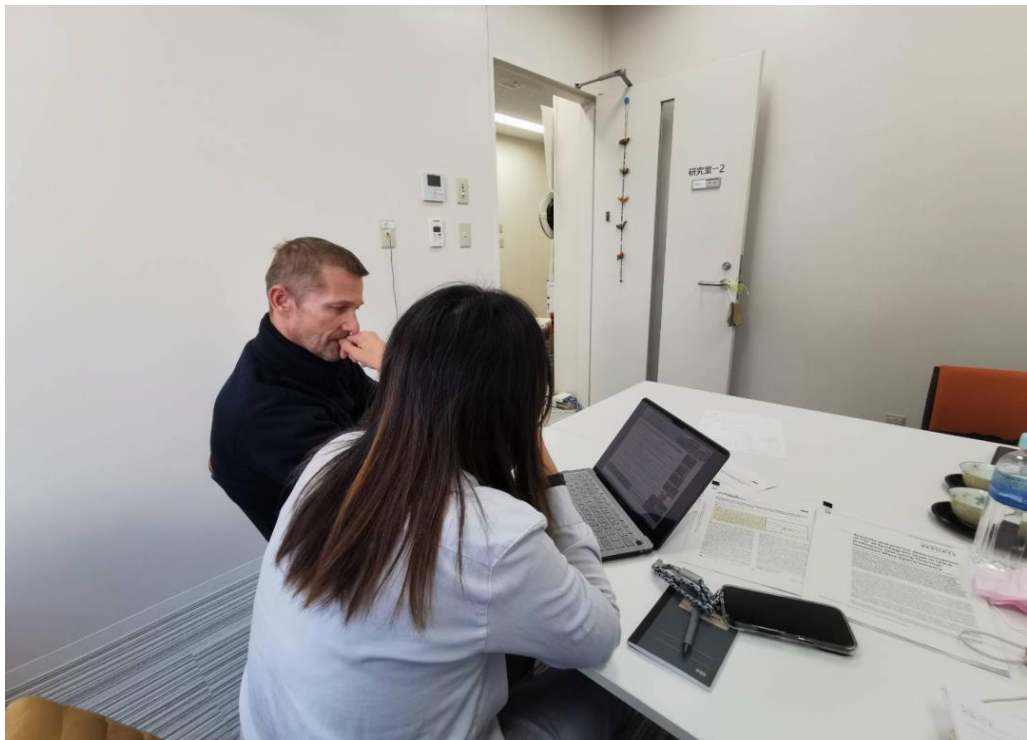
日本加馬核種分析實驗室採用國際常見 CANBERRA 純鍺偵檢器和自動化進樣系統，其系統不僅提高量測效率，亦降低人為操作過程中的不確定度。此外，能譜分析軟體及標準幾何驗證等程序，有助於提升分析結果之準確性。

綜上，透過本次之見習及經驗交流，了解日本在應用質譜儀長半衰期難測核種的分析方法、氙的電解濃縮方法及加馬核種分析等，提供本中心在放射性核種分析技術精進之方向，並提出建議事項如下：

- 一、因應福島核廢水預計排放時程達 30 年及海水中氙含量較低，應建立氙濃縮系統，以更好掌握台灣周邊海域氙含量的變化。

- 二、除放射性核種氬外，海水中其他核種如鎔-99、碘-129 等，建議本中心可參考日本鎔-99 分析方法，採用感應耦合電漿質譜儀技術，提升對長半衰期人工核種的檢測能力。
- 三、此外，加馬核種分析亦可考量採購自動化進樣系統，減少人力負擔並提高量測效率。

伍、 附錄



與日本福島國際研究教育機構 F-REI 放射生態學組

組長 青野 辰雄博士、KAVASI Norbert 研究員進行技術討論



於日本福島國際研究教育機構合照

(左一 Dr.KAVASI Norbert 研究員 右一 青野 辰雄博士)



於福島大學環境放射能研究所分析棟合照

(右一 高田 兵衛 副教授)



與日本原子能研究開發機構松枝誠博士、柳澤華代博士


討論實驗室技術能力

陸、 参考資料

1. Kavasi N, Sahoo SK. 2019. Method for ^{90}Sr analysis in environmental samples using thermal ionization mass spectrometry with daly ion-counting system. *Analytical Chemistry*. 91(4):2964-2969.
2. Kavasi N, Sahoo SK, Arae H, Aono T, Palacz Z. 2019. Accurate and precise determination of ^{90}Sr at femtogram level in iaea proficiency test using thermal ionization mass spectrometry. *Scientific Reports*. 9(1):16532.
3. Kavasi N, Sahoo SK. 2024. Measurement of ^{90}Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in japanese cow milk sample using thermal ionization mass spectrometry. *Food Chemistry*. 434:137421.
4. Isotopx Inc. Phoenix brochure.
<https://www.isotopx.com/wp-content/uploads/2022/11/Phoenix-brochure-Nov-2022-compressed.pdf>
5. 刘佳煜, 李华, 秦来来, 等. 固体聚合物氙电解浓缩系统的性能研究[J]. *核技术*, 2018,41(4):040502 DOI : 10.11889/j.0253-3219.2018.hjs.41.040502
6. 日本原子力規制廳 放射性測量系列 No.9 氙分析方法 (2023 年 10 月改訂)
7. Rapid Analysis for Long Half-Life ^{99}Tc —ICP-MS Analysis with Solid-Phase Extraction and Gas-Phase Reaction
https://rdreview.jaea.go.jp/review_en/2022/e2022_1_13.html
8. Matsueda, 2021, Online Solid-Phase Extraction—Inductively Coupled Plasma—Quadrupole Mass Spectrometry with Oxygen Dynamic Reaction for Quantification of Technetium-99
9. 福島大學環境放射能研究所研究設備
<https://www.ier.fukushima-u.ac.jp/about/facility#link-03>
10. 「イオン交換樹脂を用いた水道水放射能モニタリング前処理法の開発と応用に関する研究」実績報告書
https://tarachineiwiki.org/wpcms/wp-content/uploads/shiryou_20220200_1.pdf
11. 「環境放射能モニタリングのための水中の放射性セシウムの前処理法・分析法」技術資料
https://unit.aist.go.jp/georesenv/information/20150917/TechRep_Cs_Monitoring_Water.pdf



柒、 補充資料


1. 福島事故後的劑量評估及訂定食品管制限值等相關資料（青野辰雄博士提供）

Session 1. Measurement and Ecosystem after Fukushima Accident 

Dynamics of radionuclides in the marine environment and dose assessment in consideration of future studies


Tatsuo Aono
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 ISTC/STCU Technical Working Group Meeting on the environmental assessment for long term monitoring and remediation in and around Fukushima
MEXT Special Meeting Room No.1, Tokyo, December 11-12, 2012 


Session 1. Measurement and Ecosystem after Fukushima Accident 

Topics



1. Dynamics of radionuclides in the marine environment
2. Dose assessment in consideration of future studies




Before March 11th, 2011



Present (imagination)



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Dynamics of radionuclides in the marine environment and dose assessment in consideration of future studies

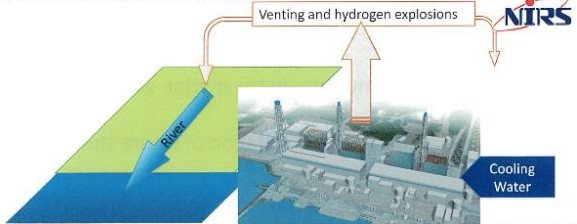
1. Dynamics of radionuclides in the marine environment

1-1. Release and dispersion of Radionuclides(RN) from FD1NPP

- What RN released?
- How much is the released RN amount?
- How did RN dispersed ?

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• After the earthquake on March 11, 2011, the blackout caused the reactor cooling system down of FD1NPP.

• Large amount of water to cool the fuel rods was supplied and this procedure increased the amount of water contaminated with radionuclides and the contaminated water leaked onto the land and into the ocean.

• An important long term concern arising from the FNPP-AC is radioactivity-contaminated water and its effects on the marine environment and marine resource.

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Effects of released radionuclides by venting and hydrogen explosions

Detected nuclides (mainly)
I-131, Cs-134, Cs-136, Cs-137, Te-129, Te-129m, Ag-110m

(Not detected : Ru-103, Ru-106, Ce-141, Ce-144)

Unit: MBq/km²·month

Radioactivity of fallout in the prefecture (MEXT)

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Map of Cs-134+Cs-137 deposition and contamination of Japanese soil due to the Fukushima nuclear accident

Fig. Direction and transit time of plume (Chino, 2012)

✓ No information of deposition in ocean
✓ Estimated fallout to land : 20~30%

http://radioactivity.mext.go.jp/ja/contents/7000/6213/view.htm

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Location around the facilities in Fukushima Dai-ichi Nuclear Power Plant

- Monitoring of seawater near FD1NPP had started from March 22, 2011, as large volume of water had been used to cooling of the NPP.
- Radionuclides were detected in seawater, and then monitoring area was expanded in the Pacific.
- High contaminated water was leaked from the pit of FD1NPP No.2 (in the end of March, 2011).

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Observed ¹³⁷Cs concentration in D1NPP

Two major release pathways by analyzing observed ¹³¹I/¹³⁷Cs activity ratios, direct release and atmospheric deposition. The direct release started from 26 March, 2011.

The total amount of ¹³⁷Cs originating from direct released was estimated to be 3.5 ± 0.7 PBq.

Tsumune, et al., J.E.R. 111, 100-108, 2012.

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Dynamics of radionuclides in the marine environment and dose assessment in consideration of future studies



1. Dynamics of radionuclides in the marine environment

1-2. Temporal and spatial distribution of RN

- Seawater
- Sediments
- Marine biota

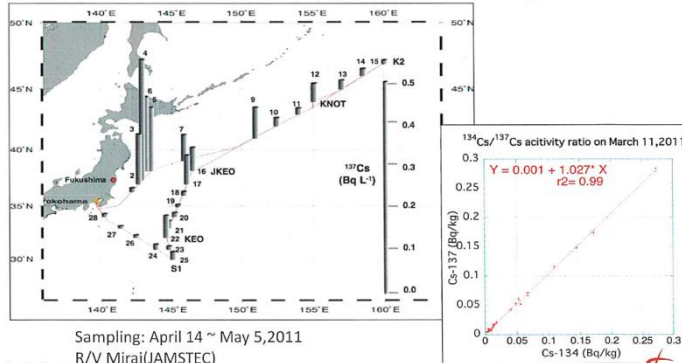
1-3. Remediation in the marine environment

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Session 1. Measurement and Ecosystem after Fukushima Accident

Dispersion of artificial ¹³⁴Cs and ¹³⁷Cs in the western North Pacific one month after the Fukushima accident.

(Honda, Aono, Aoyama, et al., 2011, Geochmeical J., 2011 accept)



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Session 1. Meas

JCOPE2 (Cesium137) 2011/04/14-2011/04/26

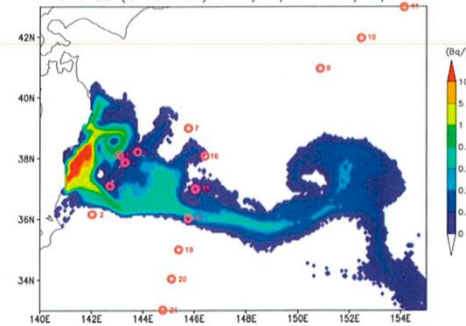


Figure 2 Simulated horizontal distribution of ¹³⁷Cs in surface waters of the western North Pacific during 14-26 April 2011 (Honda, Aono, Aoyama, et al., 2011, Geochmeical J., 2011)

Result shows numerical simulation with particle tracking model based JCOPE2.

The high Cs observed at #3-6 and #16-17 can be explained by dispersion of water discharged directly into the ocean from the FNPP.



(Honda, Aono, Aoyama, et al., 2011, Geochmeical J., 2011)

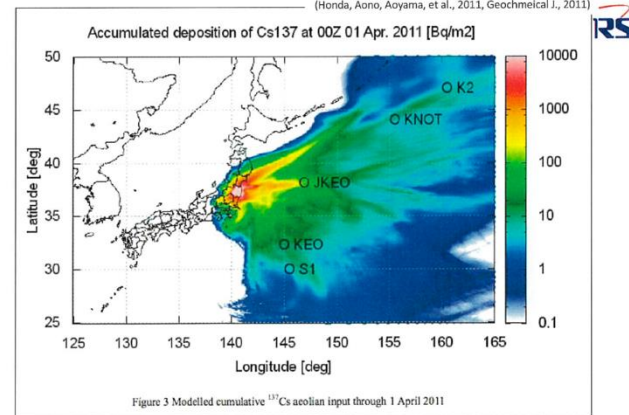
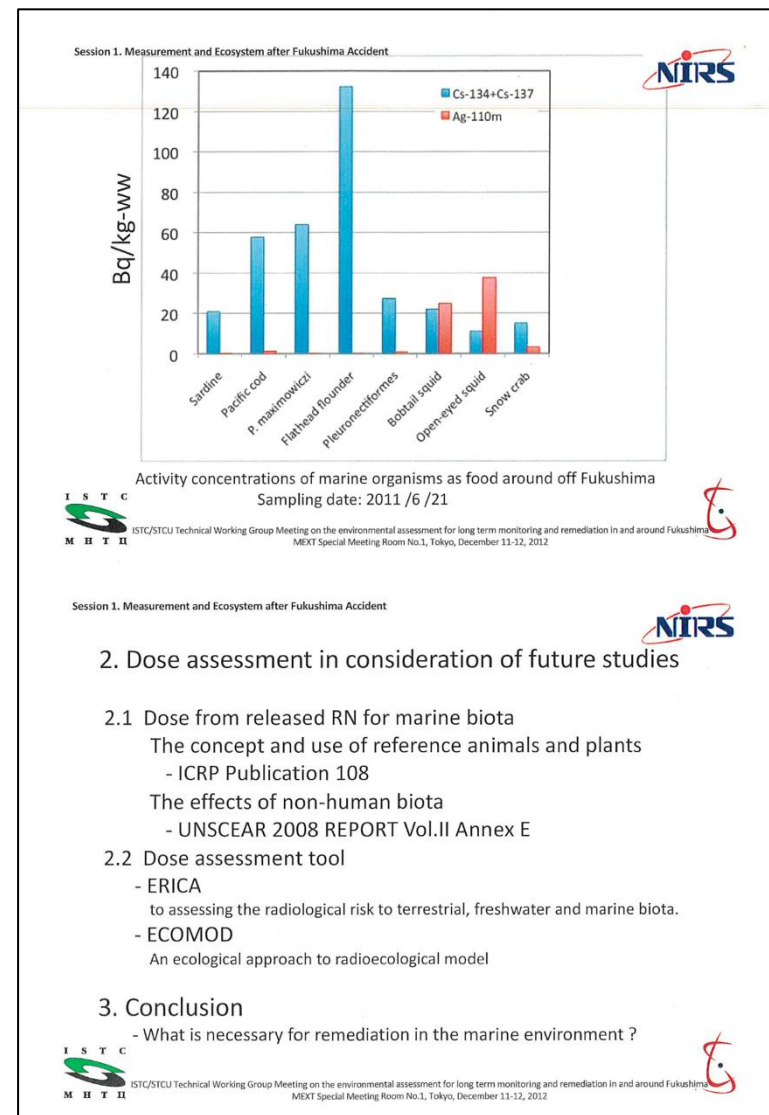
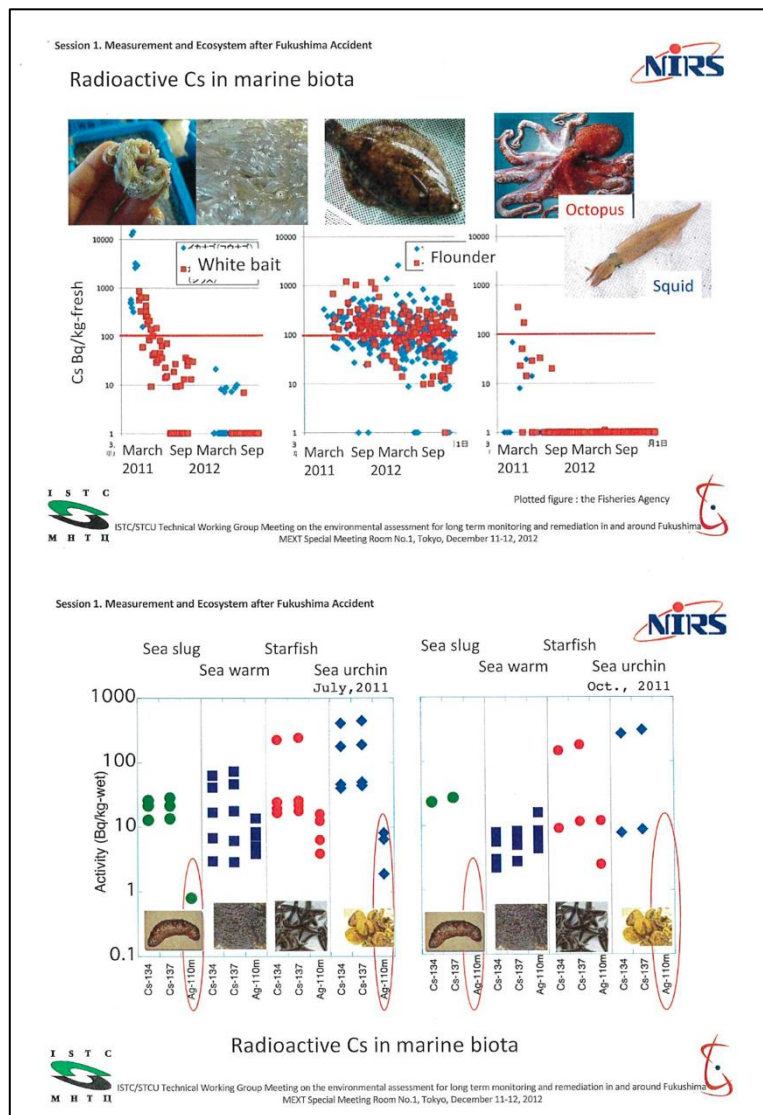


Figure 3 Modelled cumulative ¹³⁷Cs aeolian input through 1 April 2011

Radionuclides were transported to distant locations to the north-east by another mechanism.

A numerical simulation of the aeolian depositions flux indicated, and Cs emitted from FNPP would have been deposited over a wide area of the western North Pacific.





Derived Consideration Reference Levels (mGy/d) for Reference Plants and Animals (ICRP: Pub. 108)

Dose rate (mGy/d)	0.01	0.1	1	10	100	1000
Deer						
Rat						
Duck						
Frog						
Trout						
Flatfish						
Bee						
Crab						
Earthworm						
Pine tree						
Wild grass						
Brown seaweed						



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© ICRP Pub.66

Adult effective dose coefficient Cs-137
Ingestion 1.3×10^{-5} mSv/Bq Inhalation 3.9×10^{-5} mSv/Bq

For example, Fat greenling (Hexagrammos otakii) was 30,000 Bq-Cs/kg
 $30,000 \text{ Bq/kg} \times 1.3 \times 10^{-5} \text{ mSv/Bq} = 0.3 \text{ mSv/kg}$



© ICRP Pub.108

Flatfish
< 0.1 Gy/Day : no effects
0.1 - 1 Gy/Day : possible death
30 Gy : Death rate ~ 50%

© UNSCEAR 2008

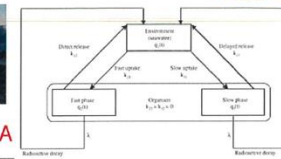
Scale factor to marine biota from seawater
 $4.3 \times 10^{-4} (\mu\text{Sv/Day}) / (\text{Bq/m}^3)$

Seawater $\sim 1 \text{ Bq/m}^3$: 0.43 nSv

Sediment max $150,000 \text{ Bq/m}^3$: 65 $\mu\text{Sv/Day}$

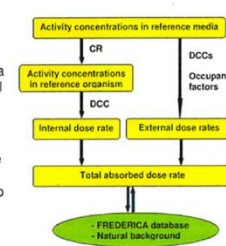


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Underlying approach to EIA in ERICA

- Transfer in the environment
- Estimates of dose to biota from internal and external distributions of radionuclides
- Establish the significance of the dose rates the organisms are exposed to

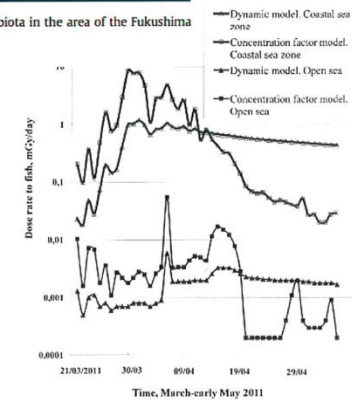


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- ECOMOD An ecological approach to radioecological model

Dynamics of radiation exposure to marine biota in the area of the Fukushima NPP in March–May 2011

I.I. Kryshev, A.I. Kryshev, T.G. Sazykina



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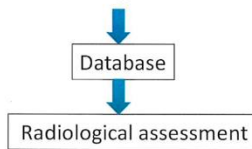


Conclusion

Remediation in the marine environment

- Seawater : same level
- Sediment : high level
- Marine biota : intricate pattern

The monitoring continues.....



The monitoring locations of the coastal area around Japan

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Благодарю вас за внимание.

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The response and activity for TEPCO Fukushima Daiichi NPP Accident Part III (current movement in Japan)

3-1 Regulation for food contamination in Japan

Topics

1. Emergency disaster control measures
2. Provisional regulation values
3. New standard limits

Tatsuo Aono
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March 23, 2012 1

To provide against emergencies

(1) Act on Special Measures Concerning Nuclear Emergency Preparedness

- ✓ A declaration of a nuclear emergency situation pertaining to the area of the relevant prefecture has been issued, collecting information regarding the relevant nuclear disaster
- ✓ Establishment of a Nuclear Emergency Response Headquarters in Cabinet office (Administrative Chief: Prime Minister)



(2) Regulatory guide: Emergency Preparedness for Nuclear Facility

(the Nuclear Safety Commission

(NSC))

- ✓ This guide was created in 1981, has been revised after the accidents of nuclear facilities.
- ✓ Chapter 5: 5-3 Index to Radiation Protection (revised in 1998)
The provisional regulatory level for radioactive materials in

foods

2

Chronology-2011

March 12-March 15	Hydrogen explosions at unit 1 and 3, the large sounds occurred at unit 2 and fire broke out at Unit 4.
March 16 -17	Food and drinking water monitoring were started.
March 17	The provisional regulatory level was set for radioactive materials in foods with reference to the index levels designated by the Nuclear Safety Commission (NSC).
March 21	Leaf vegetables and milk exceeding the guideline values for iodine-131 were confirmed and under the restriction in Fukushima, Ibaraki, Gunma and Tochigi prefecture. Iodine-131, Cs-134 and Cs-137 were observed in seawater around off Fukushima and Ibaraki.
April 8	Fish (Japanese sand lance, <i>Ammodytoidei Personatus</i>) exceeding the guideline values for iodine-131(4,000 Bq/kg) were confirmed and under the restriction in Fukushima and Ibaraki prefecture.

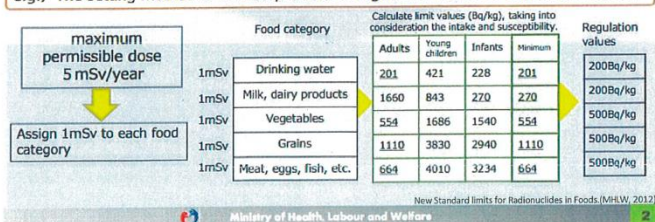
The concept of Current Provisional regulation Values

The current provisional regulation values were established based on the concept shown below, in line with "index relating to the restriction of food intake" derived by the Nuclear Safety Commission under assumption of nuclear power plant accidents.

- 1) Set the annual maximum permissible dose from radioactive cesium in foods as 5mSv and assign to each food category.
- 2) Assuming that people continue to consume contaminated foods for a long time, derive regulatory values, based on the intakes according to food categories, so that the permissible dose is not exceeded.

Note: Apply the lowest levels - which are obtained by taking into consideration the intake and susceptibility of the groups of adults, young children, and infants - to all age groups.

e.g.) The setting method of current provisional regulation values for radioactive cesium



Category and intake



Table Intake of category in case of radioactive iodine (kg or L)

Category	Adults	Young children	Infants
Drinking water	1.65	1.0	0.71
Milk, Dairy products	0.2	0.5	0.6
Vegetables (except Root and Potato)	0.4	0.17	0.07

Table Intake of category in case of radionuclide (kg or L)

Category	Adults	Young children	Infants
Drinking water	1.65	1.0	0.71
Milk, Dairy products	0.2	0.5	0.6
Vegetables	0.6	0.25	0.105
Rice	0.3	0.11	0.055
Meat, Fish, Egg etc.	0.5	0.105	0.05
Total diet (except water)	1.6	0.965	0.81

Derived Intervention Level and regulation values

Category	Derived Intervention Level of I-131 (Bq/kg)				Regulation values
	Adults	Young children	Infants	Minimum	
Drinking water	1,270	424	322	322	300
Milk, Dairy products	10,500	849	382	382	300
Vegetables (except Root and Potato)	5,220	2,500	3,280	2,500	2,000

Category	Derived Intervention Level of Cs-134+137				Regulation values
	Adults	Young children	Infants	Minimum	
Drinking water	201	421	228	201	200
Milk, Dairy products	1660	843	270	270	200
Vegetables	554	1686	1540	554	500
Rice	1110	3830	2940	1110	500
Meat, Fish, Egg etc.	664	4010	3234	664	500

The activity ratio of Sr/ Cs

Soil	I-131	Cs-134	Cs-137	Sr-89	Sr-90	Sr-90/Cs-137	Sr/Cs
	Bq/kg-dry weight						
Point A	9.40E+04	5.00E+05	5.00E+05	2.80E+03	4.80E+02	0.001	0.003
Point B	2.00E+04	3.80E+04	4.00E+04	1.90E+03	3.40E+02	0.009	0.029
Point C	9.10E+04	1.10E+05	1.10E+06	1.70E+03	3.00E+02	0.0003	0.002

Seawater	I-131	Cs-134	Cs-137	Sr-89	Sr-90	Sr/Cs	Sr/Cs
	Bq/kg						
Point A	9.60E-03	6.30E-02	6.80E-02	2.40E-03	4.40E-04	0.006	0.022
Point B	4.80E-03	6.30E-02	5.70E-02	1.90E-03	3.40E-04	0.006	0.019
Point C	4.60E-03	3.40E-02	4.00E-02	2.80E-04	1.20E-05	0.0003	0.004
Point D	4.40E-03	3.00E-02	4.30E-02	1.40E-03	2.40E-04	0.006	0.022

When the concept of regulation value is assumed that the activity ratio of Sr/Cs is 0.1, the ratio are less than 0.1 shown in the monitoring.

Current provisional regulation values

Category	Iodine	Cesium	Uranium	Plutonium (alpha nuclides)
	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)
Drinking water	300	200	20	1
Milk, Dairy products	300	200	20	1
Vegetables	2,000			
Rice	-	500	100	10
Meat, Fish, Egg etc.	Only Fish 2,000			
Baby foods	-	-	-	1

This value in fish products is used residual one third of 50mSv and set up on April 8, 2011

• Water supply (1/2)

Regarding the measures taken against radioactive materials in tap water related to the nuclear power plant accident, the heads of departments in charge of water supply administration in each Prefectural Government and water supply utilities were notified of the following:

1. To refrain from drinking water, in case the level of radioactive materials in tap water exceeds the index level (radioactive iodine: 300 Bq/kg, and radioactive cesium: 200 Bq/kg) and having infants intake tap water, including giving them formula milk dissolved by tap water, in case the level of radioactive iodine in tap water exceeds 100 Bq/kg.
2. The tap water poses no problem for domestic use without any concern.
3. It is not intended to restrict drinking water in case you have no access to alternative drinking water. (March 19 and 21)

9

• Water supply (2/2)

- April 4, 2011 As for the index levels on radioactive materials in tap water, the following were publicly announced and notified to water supply utilities:
1) the maintenance of the present index levels for the time being,
2) the monitoring policy on radioactive materials in tap water, and 3) the ideas of judging the need of and cancelling the intake limit based on survey results.
- May 26, 2011 The Meeting to Consider Countermeasures on Radioactive Materials in Tap Water (2nd meeting) was held to consider the mechanism on the impact of radioactive materials in tap water, measures to reduce radioactive materials in tap water, and the mid-and-long-term efforts made based on the results of monitoring surveys.
- Oct. 12, 2011 The "Manual on the Radiation Measurement of Tap Water" was compiled, and MHLW notified all prefectures and water supply utilities to make use of it as a reference when conducting radioactive measurements on tap water and raw water. (October 12)
- Feb. 28, 2012 The survey results on radioactive materials within tap water were publicly announced and the results of the most recently conducted surveys: Among 2,164 data obtained from February 10 to 17, 0 case exceeded the index level.

10

• Food

The Damage Situation of and Measures Taken Against the Great East Japan Earthquake —114th Announcement
Ministry of Health, Labour, and Welfare (MHLW)

- April 4, 2011 In the light of the Nuclear Emergency Response Headquarters' concepts on the establishment and cancellation of the restrictions on the shipment and intake of foods, an announcement was made on Prefectural Governments' monitoring plans, decided in consultation with the relevant ministries, together with the handling of the provisional regulatory levels of radioactive materials within foods.
- April 6, 2011 The Food Safety Committee was asked for evaluation of the health effects on foods related to radioactive iodine in fishery products.
- April 8, 2011 The Task Force on the Countermeasures against Radioactive Materials, the Food Safety Commission, the Pharmaceutical Affairs and Food Sanitation Council, was set up and compiled provisional remarks on the handling of provisional regulatory levels related to radioactive iodine in fishery products.
- April 28, 2011 Relevant prefectures were notified of the MHLW's report on the status of formulation and implementation of survey plans on radioactive materials within foods and tap water, compiled based on the relevant prefectures' reports.

11

■ Establishment of New Standard limits for Radionuclides in Food

1. Concept of Review

- Based on current scientific knowledge, commodities that meet current provisional regulation values are considered to be safe, and in fact food safety is basically secured. However, to achieve further food safety and consumer confidence, Japan is planning to reduce maximum permissible dose from 5mSv/year to 1mSv/year.
- Establish the four categories of "Drinking water", "Infant foods" and "Milk", which are deemed to need special consideration, and "General foods" for other foods.

2. New standard limits

(Date of enforcement: April 1, 2012) Transitional measure applies to some commodities.)

○ Provisional regulation values for radioactive cesium¹

Category	Limit
Drinking water	200
Milk, dairy products	200
Vegetables	500
Grains	
Meat, eggs, fish, etc.	

○ New standard limits for radioactive cesium²

Category	Limit
Drinking water	10
Milk	50
General Foods	100
Infant Foods	50

(Unit: Bq/kg)

NOTE: 1 These values take into account the contribution of radioactive strontium

2 These limits take into account the contribution of radioactive strontium, plutonium etc.



Ministry of Health, Labour and Welfare New Standard limits for Radionuclides in Foods (MHLW, 2012)

3

■ The concept of radionuclides to be regulated (1)

● Radionuclides

Targets to be regulated are all radionuclides which were placed on the trial calculation list of the Nuclear and Industrial Safety Agency as substances emitted by the Fukushima nuclear power plant accident, and whose half-life is over 1 year.

Note: Standard limits are not established for radioactive Iodine, which has a short half-life and has been no longer detected, and the for Uranium, whose level is the almost the same in the nuclear power plant site as in the nature environment.

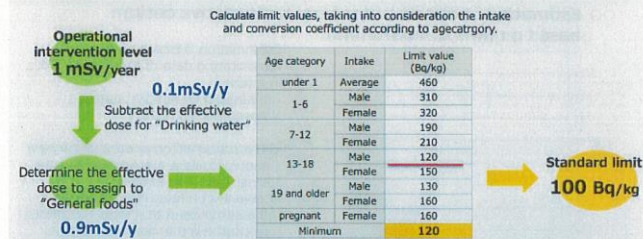
Regulated Radionuclides	Physical Half-life
Cs-134	2.1 years
Cs-137	30 years
Sr-90	29 years
Pu	14 years or more
Ru-106	367 days



Ministry of Health, Labour and Welfare

5

■ The Concept of standard limit for "General Foods"



<Effective dose for "Drinking water" = Standard limit for "Drinking water" (Bq/kg) × Intake of drinking water according to age category × Dose Coefficient according to age category>

● In line with WHO's guidance level for radioactive cesium in drinking water, the standard limit for "Drinking water" is established as 10 Bq/kg, and the effective dose is about 0.1 mSv/year.

● The effective dose to assign to "General foods" is determined as about 0.9 mSv/year by subtracting the effective dose for "Drinking water" (about 0.1 mSv/year) from the operational intervention level (1 mSv/year)

● Limit values are calculated by dividing this effective dose by the intake and conversion coefficient according to age category. (On the assumption that 50% of the marketed foods are contaminated.)



Ministry of Health, Labour and Welfare

7

The range of "Infant Foods"

New Standard limits for Radionuclides in Foods (MHLW, 2012)

Category

- Foods approved to be labeled as "fit for infants" based on Article 25 Paragraph 1 of the Health Promotion Law
- Foods and drinks sold as intended for infants → foods which can be recognized by consumers as products intended for infants from the appearance and labeling of outer package, etc.

The range of foods

- Infant formula
- Formulated milk powder for young children (including follow up milk etc.)
- Drinks for young children The limit for "drinking water" applies to tea drinks
- Foods for young children (snack etc.)
- Others (jelly-type sugarcoat, dietary supplement for infants etc.)
- Baby foods (Weaning foods etc.)

New standard limits in milk and infant food

50Bq/kg

<Foods included in "Milk" category> New Standard limits for Radionuclides in Foods (MHLW, 2012)

The "Milk" category covers milk and milk drinks.

Milk drinks are drink products which are made mainly of milk as the main ingredient, and they include those which are recognized by consumers as similar kinds of drinks to milk and processed milk.

Foods included in "Milk" category

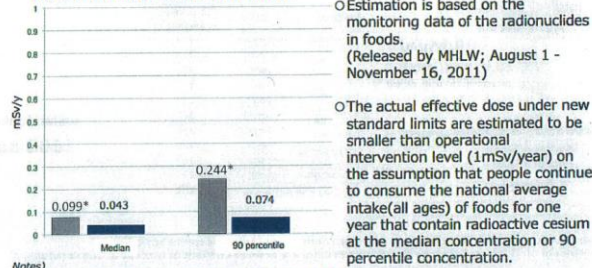
Milk, Low-fat milk, Processed milk-based drinks

Foods not included in "Milk" category

Lactic acid bacteria drinks, Yogurt, Cheese

Estimation of effective dose from radionuclides in foods

○ Estimation of effective dose from radioactive cesium based on new standard limit.



○ Estimation is based on the monitoring data of the radionuclides in foods. (Released by MHLW; August 1 - November 16, 2011)

○ The actual effective dose under new standard limits are estimated to be smaller than operational intervention level (1mSv/year) on the assumption that people continue to consume the national average intake (all ages) of foods for one year that contain radioactive cesium at the median concentration or 90 percentile concentration.

○ For non-detection data, detection limits (up to 20 Bq/kg) for Cs-134 and Cs-137 were used.

○ When the detection limit was not shown, 50Bq/kg was applied to food groups for which the ratio of ND was not less than 80%, 10 Bq/kg was applied to food groups for which the ratio of ND was 60% to 80%, and 20 Bq/kg to others. This was taken into consideration the view of GEMS/food of WHO.

○ Effective dose from radionuclides other than radioactive cesium are added to these estimates in reality, because these values are estimated only from radioactive cesium.

* Estimation of effective dose from I-131, Cs-134 and Cs-137 based on the provisional regulation values

Ratios of excesses over the standard limit for radioactive cesium in monitoring tests

New Standard limits for Radionuclides in Foods (MHLW, 2012)

Commodity	Ratio	Fukushima Prefecture				Other prefectures			
		March-June	July-September	October-November	March-June	July-September	October-November		
Rice	The number of excesses/tests (%)	-/1 (0.0%)	0/669 (0.15%)	1/619 (0.16%)	-/1 (0.0%)	0/2061 (0.05%)	0/503 (0.05%)		
Vegetables	The number of excesses/tests (%)	159/1517 (10.5%)	310/1517 (20.4%)	5/1366 (0.4%)	13/1124 (1.2%)	29/2190 (1.3%)	1/1264 (0.08%)		
Fruits	The number of excesses/tests (%)	11/188 (5.9%)	71/188 (37.8%)	6/779 (0.8%)	48/779 (6.2%)	6/489 (1.2%)	0/152 (0%)	3/478 (0.6%)	
Tea leaves	The number of excesses/tests (%)	1/1 (100%)	0/2 (0%)	-/1 (0%)	42/301 (14%)	29/187 (15.5%)	121/1755 (6.9%)		
Mushrooms	The number of excesses/tests (%)	38/212 (17.9%)	88/212 (41.5%)	15/342 (4.4%)	25/324 (7.7%)	67/324 (20.7%)	4/87 (4.6%)	2/175 (1.1%)	
Milk	The number of excesses/tests (%)	0/285 (0%)	4/285 (1.4%)	0/137 (0%)	0/91 (0%)	0/283 (0%)	4/283 (1.4%)	0/338 (0%)	
Beef	The number of excesses/tests (%)	1/47 (2.1%)	13/47 (27.7%)	56/1165 (4.8%)	122/1165 (10.5%)	2/1644 (0.1%)	0/12 (0%)	77/8519 (0.9%)	
Fish and shellfishes	The number of excesses/tests (%)	15/322 (4.7%)	167/322 (51.6%)	55/872 (6.3%)	336/872 (38.5%)	301/919 (32.8%)	4/487 (0.8%)	34/487 (7%)	
Others	The number of excesses/tests (%)	9/148 (6.1%)	18/148 (12.2%)	2/450 (0.4%)	53/450 (11.8%)	43/926 (4.6%)	108/926 (11.6%)	8/136 (5.9%)	
Total	The number of excesses/tests (%)	270/2725 (9.9%)	671/2724 (24.6%)	139/5782 (2.4%)	610/5780 (10.6%)	1136/6136 (1.8%)	75/3648 (2.1%)	218/3347 (6.5%)	

※1 The notation "/-" shows that tests number is zero.
 ※2 As for "Tea leaves", new standard limit for "Drinking water" (100Bq/kg) applies to a liquid extract obtained after brewing process.
 ※3 As for "Milk", the number of excesses shows the number of cases for which 50 Bq/kg, the new standard limit for "Milk", is exceeded.

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Conclusion

- ✓ The provisional regulatory level was set for radioactive materials in foods with reference to the index levels designated by the Nuclear Safety Commission on March 17, 2011.
- ✓ Relevant prefectures were notified of the MHLW's report on the status of formulation and implementation of survey plans on radioactive materials within foods and tap water, compiled based on the relevant prefectures' reports on April 28, 2011.
- ✓ Estimation of effective dose from radioactive cesium based on new standard limit is shown as 0.044 mSv/y, and then that from I-131, Cs-134 and Cs-137 based on the monitoring data of the radionuclides in foods and water (March-August, 2011) in the provisional regulation values were 0.099 mSv/y.
- ✓ New standard limits for radionuclides in food shall come into effect as from April 1, 2012 (the day of enforcement).

2. 自組電解装置所需設備一覽表（高田兵衛副教授提供）

別表 トリチウム電解濃縮装置用資機材一覽

品名及び規格	数量	会社名	品番
トリチウム電解濃縮装置(マツコウケン製) 1.電解濃縮装置 2.減圧蒸留装置 3.常圧蒸留装置 4.冷却水循環装置 (内訳)	1式 1式 1式 1式		
1.電解濃縮装置 コントローラー 10本用×1台 直流安定化電源 60V-20A 電源取出盤 充電クリップ 渡り線 赤10 ; 電解ガラスセル 電解電極盤スペーサー含む 冷却水槽(3面/バランス扉)200L 局所排気装置 排気ファン 制御盤 ON/OFF 水素ガス感知器	1台 1台 1台 1式 12本 12組 1台 1式 1台 1台	マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン マツコウケン	
2.減圧蒸留装置 エバポレーター ポータブルアスピレーター 三角フラスコ	2台 2台 2	東京理化学器械㈱ アルバック機工㈱ 柴田科学	ロータリーエバポレーター—式N-1110SF-W ポータブルアスピレーター—MDA-015 共通すり合わせ共栓三角フラスコ(栓付)
3.常圧蒸留装置 リービッヒ型冷却管 ガラストラップ球 共通すり合わせ連結管 曲管 SPC連結管 採取アダプター マントルヒータ スライダック 両開クランプ ジョイントクランプ 蒸留用冷却水用シリコンチューブ	12 12 12 12 10 5 10 4 10	柴田科学 マツコウケン 柴田科学 東京硝子器械㈱ アズワン (有)春日無線変圧器) アズワン 柴田科学 アズワン	共通すり合わせ冷却器19/3819/38300mm 19/38+29/42 両端オス形 上部19/38 下部19/38 TGK SPC連結管上部SPC-15 HF-100S V-130-3スペック 自在ムップCMF-50 テーパ—用15/25用(10個入) 6×8 1巻(1m)
4.冷却水循環装置 冷却水循環装置	1	東京理化学器械㈱	CA-2600

3. 福島周圍海水氚調查結果 (高田兵衛副教授提供)

7 Nov 2024
Tritium in coastal water before and after the release of ALPS treated water
Hyoe Takata (高田兵衛)

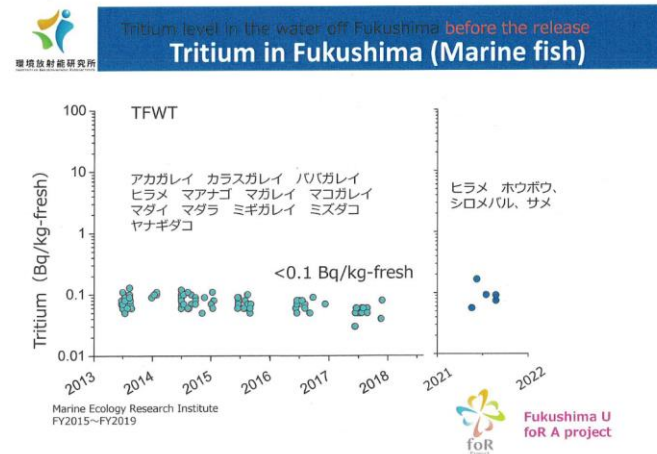
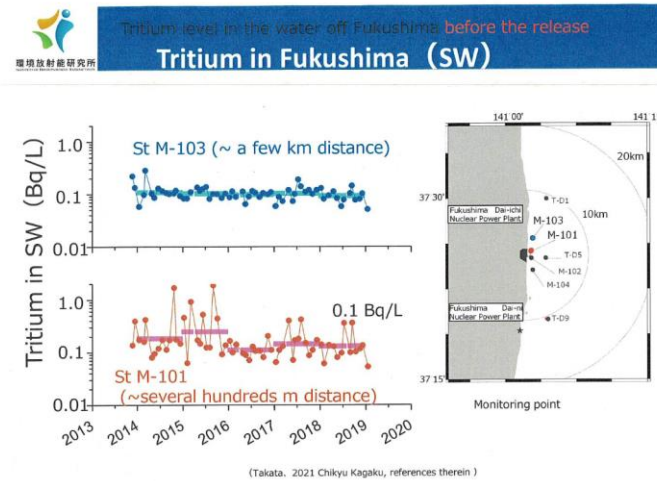
国立大学法人 福島大学
Fukushima University
IER

Release of ALPS-treated water

The Advanced Liquid Processing System ALPS
Storage tanks
-Amount of tritium : ~700TBq (FY2022)
Dilute with SW to <1500 Bq/L
Monitor to less than 1500 Bq/L (< 700 Bq/L in operation)
Marine

GW
Contaminated water
debris

First release : 24 Aug~ 11 Sep (~1.1TBq)
Second release : 5 Oct~23 Oct (~1.1TBq)
Third release : 2 Nov~20 Nov(~1.0TBq)
Fourth release: 28 Feb ~ 17 Mar (~1.7 TBq)



Monitoring system for ALPS treated water

Sampling seawater and fishes by fishery boat

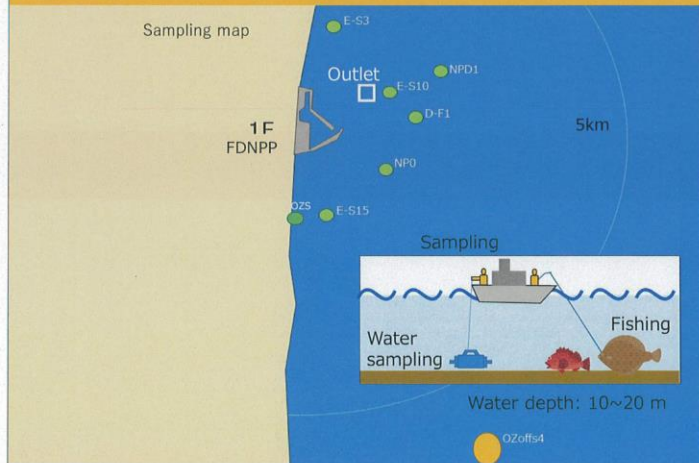


四倉港 第三弘明丸



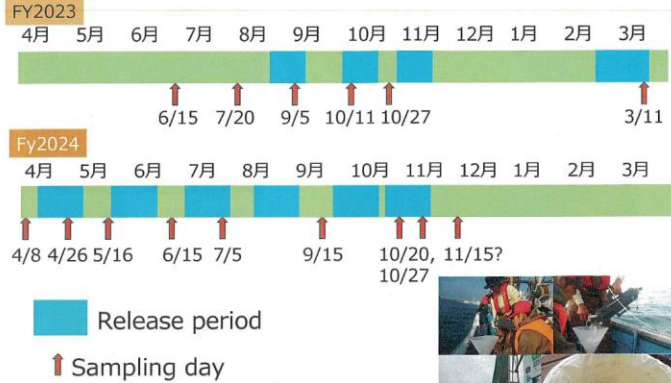
第三弘明丸

Sampling area

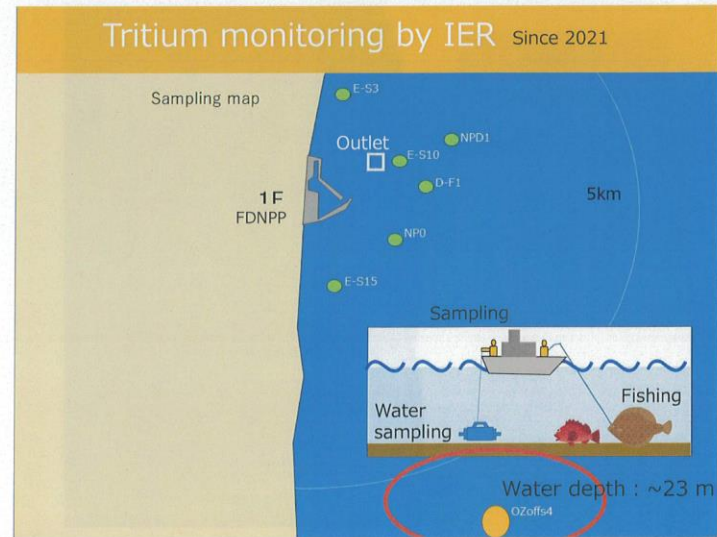
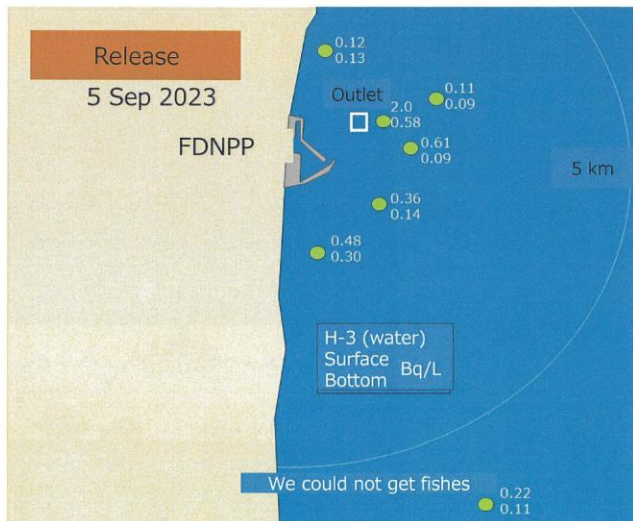
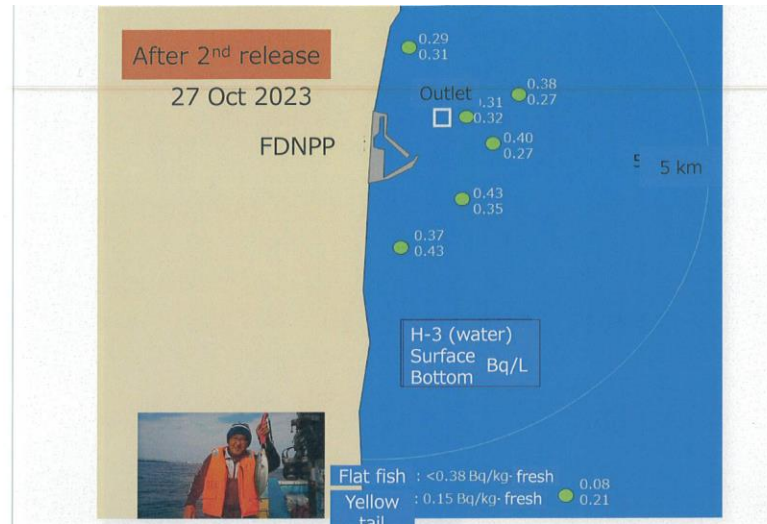
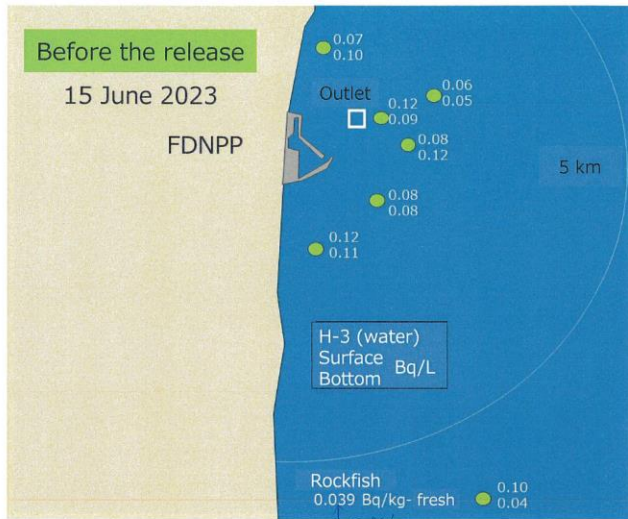


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Sampling schedule

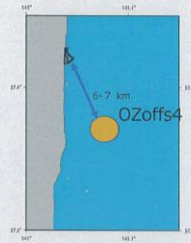


Results

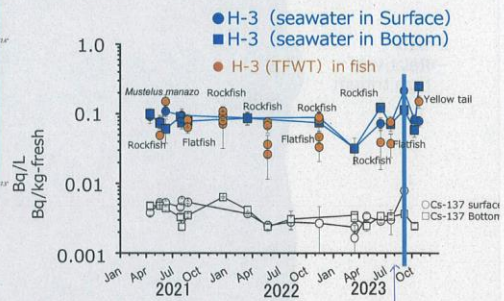


Tritium monitoring by IER Since 2021

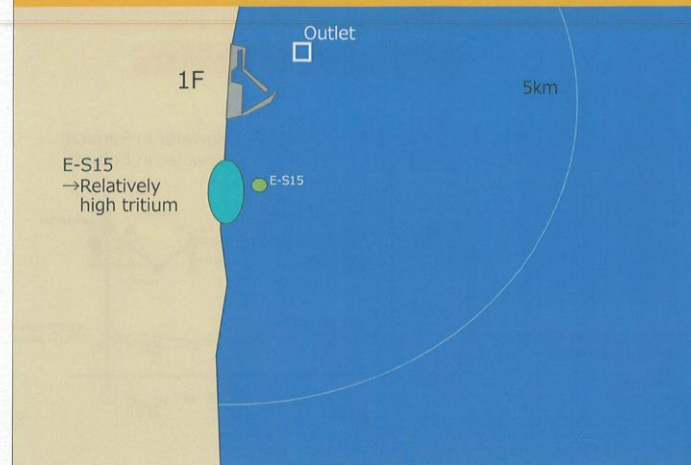
OZoffs4 Water depth : ~23 m



Monitoring tritium level in seawater and marine fishes from 2021



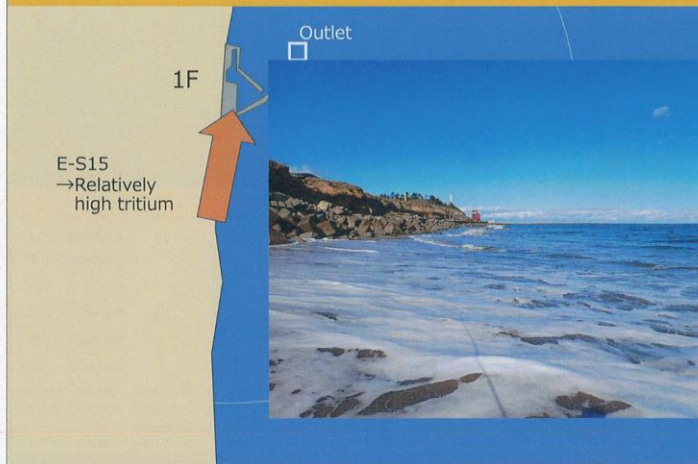
Sampling 原発近傍 河口



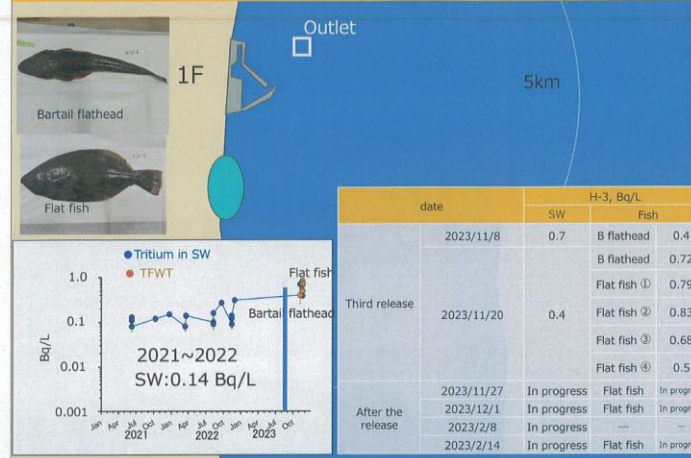
Sampling at beach nearby 1F



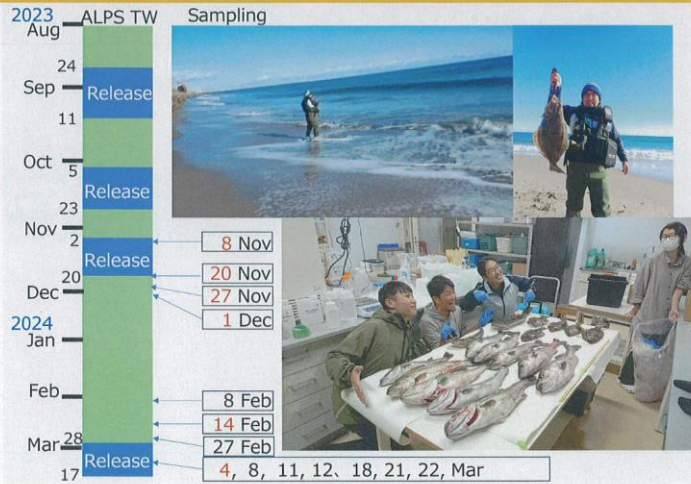
Sampling at beach nearby 1F



Results Sampling ② from 2023



Sampling from 2023

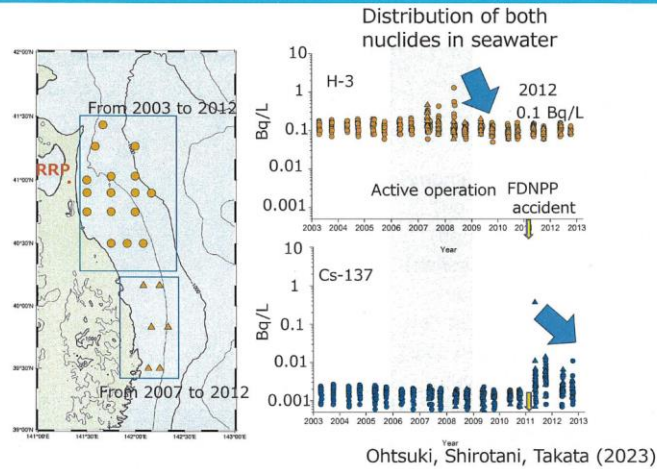


Topics

① トリチウムとセシウムの海洋での動態比較

② ALPS 処理水海洋放出前後のトリチウム動態

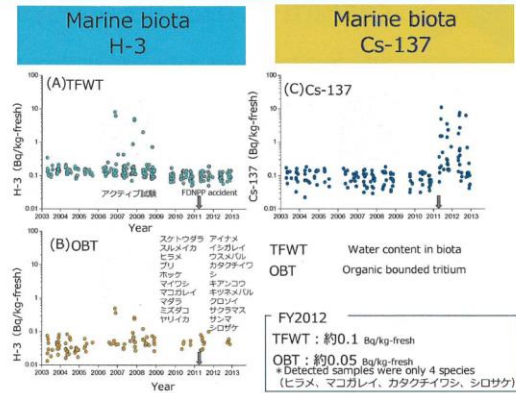
Comparison of distribution of tritium with cesium



Concentration ratio for two nuclides

Species	CR (Concentration ratio)			
	H-3 (TFWT)		Cs-137	
	Ave.	error	Ave	error
カタクチイワシ (Anchovy)	1.3	0.4	—	—
スケトウダラ (Cod)	0.8	0.2	74	10
マダラ (Pacific Cod)	0.9	0.2	73	8
キアンコウ (Y Goosefish)	0.9	0.3	33	7
シロサケ (Salmon)	1.1	0.2	49	6
ヒラメ (Japanese flat fish)	0.9	0.2	74	6
マコガレイ (Marbled sole)	1.1	0.3	46	12
ミスダコ (Octopus)	1.1	0.4	—	—
スルメイカ (Squid)	0.9	0.2	—	—
Range of average	0.8~1.3		33~74	

Comparison of distribution of tritium with cesium



Distribution of tritium and cesium in marine ecosystem

	Tritium (OBT TFWT)	Cesium
Depuration from biota	Quick	Slow
Accumulation (CR)	No (~ 1)	Yes (ten to hundreds)

➡ Different accumulation system