Chlorine-36 Measurement in the Near-field Environment of a Spent Nuclear Fuel Reprocessing Plant

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1. INTRODUCTION

An evaluation of the dosimetric impact of discharge of low level radioactive effluents authorized to be released from the La Hague Cogema spent nuclear fuel reprocessing plant located in North Cotentin (France) led to an assessment of chlorine-36 (36Cl) dose contribution to local populations [1]. Though not usually systematically included in such assessments, ^{36}Cl is produced in nuclear reactors by activation of ^{35}Cl contained in nuclear fuel. It was measured in lichens sampled in the areas surrounding the Chernobyl NPP, at activity levels from 1 to 100 $mBq.kg^{-1}$ dry [2.]. It may therefore be liberated when processing nuclear fuel and released with the radioactive effluents. It was measured in radioactive effluent injected into the ground of a US reprocessing site in Idaho [3].

^{36}Cl found at natural levels in the environment is continuously produced by a series of natural nuclear reactions occurring in the atmosphere and the earth crust. It was likewise released and scattered at the global level during the explosion of nuclear devices in the atmosphere and particularly those done underwater in the ocean.

Once scattered throughout the environment, this element quickly acquires the anionic form Cl⁻. It is under this pervasive and stable state, that chlorine isotopes ($^{35,36,\ 37}$Cl) are measured. Natural redox processes virtually never involve this form. During geologic eras, it is leached off in the form of soluble salts from the lithosphere to the oceans. Its geological behaviour was relatively simple since, in the presence of common cations, the exception being those of the first group, the chlorine ion Cl⁻ will be maintained in the aqueous phase, the precipitation threshold only being reached after very substantial concentration.

Interactions with geologic and pedologic surroundings are restricted. Chlorine will remain highly mobile in soil where it retains its anionic form and will transfer into the soil solution with minor interaction with absorbant complexes. From soil, its transfers to plants via the root system and its bioavailability will be conditioned by NaCl, KCl concentrations as well as soil pH (humic acid) and also the plant metabolism (ex. halophytes). Via osmotic exchanges, it is concentrated in plants where it likewise plays a part in enzyme reactions linked to photosynthesis.

A study was thus conducted, the main purpose of which was to either substantiate or disprove the presence of ^{36}Cl at levels significantly higher in the La Hague environment than those expected for the environment of a site not subject to spent nuclear fuel reprocessing plant routine releases.

2. MATERIAL AND METHODS

2.1. Sampling

The samples were collected from the inhabited area of the hamlet of Pont Durand which is the area most likely to be contaminated by atmospheric transfer of ^{36}Cl released by the spent nuclear fuel reprocessing plant of la Hague. This area is located at 1250 m, North-West, under the prevailing winds of the plant exhaust stacks (Figure 2.1.). A reference site not subject to releases from this plant, though with similar climate conditions, located at Saint Brieuc in Brittany, was jointly sampled [4, 5].

The samples are components of the food chains either leading to man: pork, milk, eggs, vegetables, wheat, barley, oats or to livestock: grass, oats.

Figure 2.1. : Location of the sampling stations.
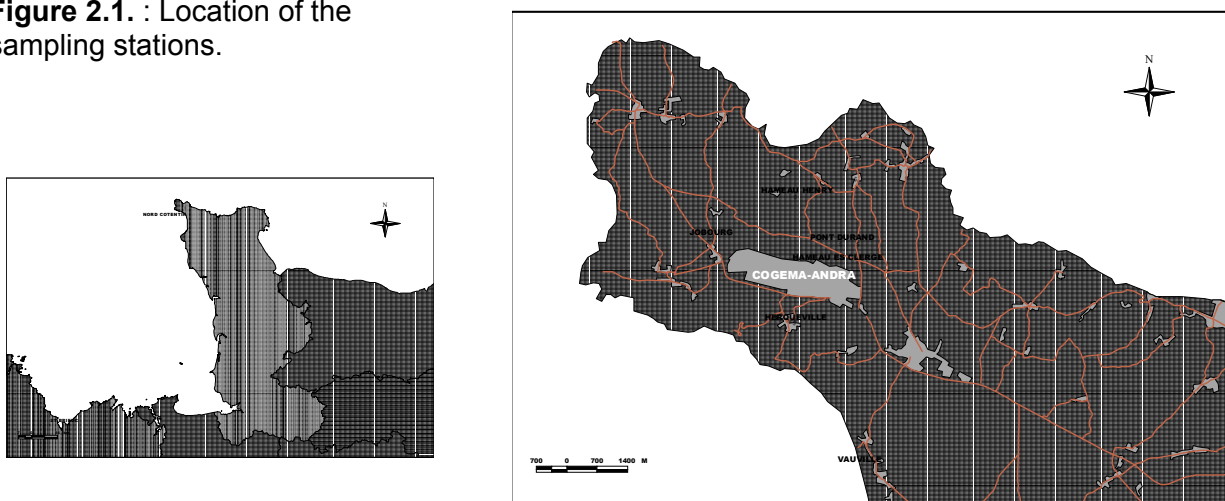
Sample collection and preparation were done in keeping with standards in force [6]. Solid samples were dried at 55 °C [7] and milk samples were freeze-dried.

2.2. Chlorine-36 Measurement

The chlorine isotope 36, $^{36}_{17}$Cl, decays into 98 % of $^{36}_{18}$Ar by β^{-} emission and 1,9 % of $^{36}_{16}$S by electronic capture. Its half-life is estimated at $3,01 \pm 0,02 \ 10^{5}$ years.

The bibliography shows that measurements of urine [8], underground waters [9], Fe, Ca, Ti targets subject to nuclear reactions are done by liquid scintillation or proportional counter after radiochemical processing yielding an AgCl or NaCl salt, 1,2-dichlorohexane [10] or otherwise SiCl$_4$ [9]. The latter method (SiCl$_4$), though certainly more efficient in terms of detection limits was nevertheless excluded in view of the considerable risk when handling and complexity of equipment.

Accelerator mass spectrometry (AMS) of a Tandem type provides the isotopic ratio: R= ^{36}Cl/(^{35}Cl+^{37}Cl). The result is independent of the sample mass yield. On the other hand, the sensitivity is constrained because of purification processes applied to natural

samples intended to eliminate the ^{36}S isobar representing 0,02 % of sulphur isotopes. The detection limit by AMS (for a 4 MV Tandem) is of the order of 10^{-15} ^{36}Cl atom per $^{35+37}$Cl atom. A reference protocol is available in literature for rock analysis [11] though not for other matrices such as biological matrices. The Purdue University PRIME laboratory (USA) has performed analysis of sources prepared in the form of AgCl in our laboratory.

In both cases, preparatory radiochemistry is required prior to measurement in order to isolate ^{36}Cl. Analysis protocols suitable for different sample matrices were developed. A more generic chlorine extraction protocol was developed using standard solutions in order to ensure the quality of separation processes as well as to determine the chemical yield at each stage. The final protocol was tested using the laboratory reference material, the seaweed *Fucus serratus* listed as *FC98*. Its various components were already familiar, particularly beta-gamma emitting radionuclides, such as ^{129}I, the ^{129}I/^{127}I ratio and stable elements such as I, Br and Cl. [12].

An alkaline fusion was selected over combustion; its implementation is being far less complex. An aqueous solution was prepared, after which all halogenides found in the matrix are isolated by silver salt precipitation. They are subsequently separated in a column. The last stage, which is the most sensitive, is intended to prepare the source for counting. In order to reduce the detection limit a sodium salt was sought. This is because the amount of chlorine in sodium salt is greater than in silver chloride the saline charge being equal.

The yield tests were done at various stages: (1) alkaline fusion, (2) precipitation of interfering ions: elimination of sulphates by precipitation of Ba sulphate, (3) precipitation of silver salts, (4) elimination of iodine by extraction in an ammoniacal solution and silver salts precipitation and (5) source preparation for counting. Gamma spectrometry intermediary measurements of silver salt precipitates from stages 3 and 4 ascertain the effectiveness of iodine-chlorine separation. These radiochemical stages produce a pure precipitate (AgCl, NaCl) containing a known proportion of chlorine. For each matrix the mass of retrieved precipitate and the initial quantity of chlorine will allow calculation of each preparation yield.

2.3. Total Chlorine

Measurement by ionic chromatography of total chlorine is prerequisite to determine the chemical yield of the various radiochemical processes. Furthermore, the AMS results are presented as a ^{36}Cl/^{total}Cl ratio, ^{36}Cl activity will be subsequently derived from the known concentration of total chlorine.

3. MEASUREMENT RESULTS

3.1. Total Chlorine

Concentrations observed were highest in eggs (3300 et 4405 ppm), and milk (1888 - 2525 ppm). Plant samples had concentrations of the order of 1500 ppm similar to those of meat at 1000 ppm.

3.2. Chlorine-36

Proportional counter results for ^{36}Cl are all below detection limit from 0,04 to 0,31 Bq.kg^{-1}, i.e. lower than 10^{-7} to 10^{-8} ppm.

Ratio measurements done at Purdue Laboratory combined with total chlorine results give activity values above detection limit for ^{36}Cl (Table 3.2.). The discrepancies between mass activity values vary along the same lines as the isotope ratios, when samples from the two sites, that are equal in nature, are compared. Activities however remained at a very low level including environmental samples from the proximity of la Hague, which vary between 0,026 and 1,201 mBq.kg^{-1} wet weight.

Sample Number	Date	Nature	Sampling site	Cl ppm or mg.l^{-1}		^{36}Cl/^{total}Cl 10^{-15}			^{36}Cl mBq.kg^{-1} wet or mBq.l^{-1}	mBq.kg^{-1} dry
9219-1	23/02/99	Pork	Pont Durand	340	$\pm$ 34	86	$\pm$	4	0,016	0,04
9228-1	24/02/99	Pork	Saint Brieuc (reference)	665	$\pm$ 67	15	$\pm$	3	0,005	0,01
9220-1	23/02/99	Eggs	Pont Durand	3300	$\pm$ 330	464	$\pm$	10	0,533	1,87
9229-1	24/02/99	Eggs	Saint Brieuc (reference)	4405	$\pm$ 441	67	$\pm$	4	0,089	0,36
9221-1	23/02/99	Vegetables	Pont Durand	1550	$\pm$ 155	95	$\pm$	6	0,016	0,18
9230-1	24/02/99	Vegetables	Saint Brieuc (reference)	1645	$\pm$ 165	29	$\pm$	3	0,007	0,06
9225-1	22/02/99	Grass	Pont Durand	1800	$\pm$ 180	2515	$\pm$	48	1,201	5,53
9231-1	24/02/99	Grass	Saint Brieuc (reference)	1690	$\pm$ 169	26	$\pm$	3	0,009	0,05
9222-1	23/02/99	Oats	Pont Durand	605	$\pm$ 61	1044	$\pm$	37	0,676	0,77
9223-1	23/02/99	Barley	Pont Durand	1340	$\pm$ 134	346	$\pm$	12	0,492	0,57
9224-1	23/02/99	Wheat	Pont Durand	556	$\pm$ 56	911	$\pm$	26	0,538	0,62
9215	23/02/99	Milk	Pont Durand	346	$\pm$ 35	737	$\pm$	49	0,311	-
9217	24/02/99	Milk	Saint Brieuc (reference)	238	$\pm$ 24	456	$\pm$	16	0,132	-

Table 3.2. Results of ^{36}Cl/^{37,35}Cl obtained by AMS and ^{36}Cl for the biological samples collected in the reference site located in Brittany and in the near-field environment of the nuclear spent fuel reprocessing plant at la Hague.

The ^{36}Cl/^{35,37}Cl ratio, for similar biological samples, have significantly higher values when taken from sites in the near-field environment at la Hague as compared with the reference site located in Brittany. In terms of the ratio, a minimum discrepancy of a factor 2 was observed between the milk samples, while a maximum discrepancy factor of 100 applied to grass samples.

4. DISCUSSION – CONCLUSION

This study gave rise to a radiochemical extraction-purification process for chlorine using environmental samples. The ^{36}Cl measurement results from a low background noise argon-methane proportional counter show that detection limits below the Bq.kg^{-1} wet weight are reached for biological, plant and animal samples. The very same protocols, when combined with accelerator mass spectrometry measurement provide detection

limits that are much more effective, of the order of $\mu Bq.kg^{-1}$ wet weight for the same samples.

Discrepancies found for total chlorine concentrations between the same matrices for samples taken from both sites reach a factor of 2 at the most while ^{36}Cl discrepancies reach a factor of 100 at the most. The predominance of the site-bound effect was confirmed.

The ^{36}Cl/^{35,37}Cl ratio in biological samples of similar nature is systematically higher for those stations located in the Cotentin when compared with those of the Brittany reference site. These levels, though they are very low, confirm the contamination of the terrestrial environment by ^{36}Cl input stemming without any doubt from the authorized low level radioactive effluents released by the la Hague plant. The restricted number of results does not enable a mapping of those areas most contaminated by effluents discharged by the plant. Supplementary ^{36}Cl measurements would be required for a more realistic assessment of the impact of such releases.

Acknowledgements

5.   REFERENCES

[1] Estimation of Exposure levels to Ionizing Radiation and Associated Risks of Leukemia for Population in the North Cotentin, North Cotentin Radioecology Group, 2000 July, 357p

[2] Chant, Andrews, Cornett, Koslowski, Milton, Van den Berg, Verburg, Wolterbeek, 1996. ^{129}I and ^{36}Cl concentrations in lichens collected in 1990 from three regions around Chernobyl. Appl. Radiat. Isot., **47**(9/10): p. 933-937,

[3] Beasley, Cecil, Sharma, Kubic, Fehn, Mann, Gove, 1993. Chlorine-36 in the snake river plain aquifer at the Idaho national engineering laboratory : origin and implications. Ground Water. **31**(2): p. 302-310.

[4] Fraizier, Baron, 1982. Radioactivité d'un secteur littoral de la Manche : Données nouvelles sur les sources et transferts au continent par aérosols et embruns marins. Rapport CEA-R-5193.

[5] Germain, Guegueniat, 1993. Impact of industrial nuclear releases into the English Channel. Environmental impact of nuclear installations. Radioprotection, Special issue.

[6] AFNOR M60-780, 1997. Nuclear Energy.Measurement of Radioactivity in the Environment. Bioindicators. Part 3 : general guide for the storage and handling of samples and Part 4 : general guide for the preparation of samples.

[7] Sheppard, Evenden, Macdonald, 1999. Variation among chlorine concentration ratios for native and agronomic plants. Journal of environmental radioactivity, **43**, 65-76.

[8] Kramer G. H., Sidney J., 1984. The simultaneous analysis of chlorine-36, sulphur-35 and phosphorus-32 in urine, Can. J. Chem., 62, 2344-2345.

[9] Roman, Airey, 1981. The application of environmental chlorine-36 to hydrology-I. Liquid scintillation counting, Int. J. of Appl. Rad. and Isot., 287-290.

[10] Washington , Hohorst, 1993. A process for determining radiohalogens, rapport WINCO1169, 19p.

[11] Sharma, Gove , Fehn, 1993. Accelerator mass spectrometry measurements of natural and anthropogenic Cl-36, Bull. of Am. Phys. Soc. **38**, 929.

[12] Frechou C., Calmet D., Bouisset P., Piccot D., Gaudry A., You F., Raisbeck G., 2001. ^{129}I and ^{129}I/^{127}I ratio determination in environmental biological samples by RNAA, AMS, and direct gamma-X measurement. J Radioanalytical and Nuclear Chemistry, **249**, 1, 133-138.