

Is the Long Lived Tc-99 from Medical Application Detectable in Environment?

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Abstract- ^{99m}Tc is a long lived radionuclide, a fission product and decay product of its short lived isomer ^{99m}Tc widely used in nuclear medicine. Although past releases to environment are much higher than present input from nuclear medicine, the latest comes at certain input places. Presented are results of ⁹⁹Tc measurements in Vistula River bottom sediments upstream and downstream to Warsaw, similar downstream to Kraków and two samples of solid wastes from Krakow sewage purification station. Results showed large spread of activity concentration. The maximum ⁹⁹Tc activity concentration was detected in sample taken near Kraków (13.4±4.0 Bq/kg). The second highest ⁹⁹Tc value was found in one sample downstream Warsaw, which was 6.8±2.3 Bq/kg. The sewage dry waste has ⁹⁹Tc at about 30 times lower activity concentration, close to 0.4 Bq/kg. However, the latest results prove that ⁹⁹Tc from medical application can be detected at least in some kind of environmental samples.

Keywords- Nuclear Medicine; Environmental Radioactivity; Technetium; Liquid Scintillation Spectrometry; Mass Spectrometry

I. INTRODUCTION

Short lived metastable ^{99m}Tc ($T_{1/2}=6$ h) is widely used for medical application. It decays by isomeric transition (emitting gamma rays) into long lived ⁹⁹Tc ($T_{1/2}=211\,000$ years) which is beta minus emitter. The difference in the half-life time is so huge, that from 1 GBq of ^{99m}Tc originate 3 Bq of ⁹⁹Tc. In medical applications the ^{99m}Tc is milked out of the ⁹⁹Mo ($T_{1/2}=66$ hours) generators. Such generators are now obtained from irradiated ²³⁵U, so the ⁹⁹Mo is carrier (molybdenum) free. In routine application the ^{99m}Tc can be obtained from generator during one week, once a day typically. The ⁹⁹Tc to ^{99m}Tc increases with time when generator is not used (during transport and between the milking out and especially – if it is postponed for longer time). This factor makes, that already during application some ⁹⁹Tc can be present in solution together with the ^{99m}Tc and thus effectively the ⁹⁹Tc from medical application can be a little more active than it might be calculated directly just from the ^{99m}Tc activity and the ratio of half-life time of metastable and ground state of ⁹⁹Tc. The expected activity ratio is on the level of 10^{-8} . This is very low, but if one assumes that worldwide about 20 millions of technetium medical examinations are done yearly [1] and applied activity to each person is ranging from 400 MBq to 1.1 GBq, the total yearly ⁹⁹Tc production is about 0.15 GBq. Still, this seems to be not much. However, due to good solubility of technetium, practically all this activity goes finally to the sewage systems of cities and towns worldwide and finally can go to the water in the rivers. Such level of medical care which uses nuclear medicine in diagnosis is available to roughly speaking 1 billion of man. Thus, one can estimate that city of 1 million of inhabitants in developed part of the world discharges about 0.15 MBq of ⁹⁹Tc yearly.

The ⁹⁹Tc from medical application is not the only source of ⁹⁹Tc in the environment. It is even not the main one. This isotope is a typical fission product with the yield of 6.13% (the total ²³⁵U fission yield for mass 99), and its total produced activity in global fallout was about 160 TBq resulting in cumulated deposition of about 1.5 Bq/m² as worldwide mean [2]. There are other very important sources like Chernobyl where estimation for releases gives 970 GBq [3] and perhaps also Fukushima accident might introduce some ⁹⁹Tc, but no data on this as yet. However, the main environmental source is fuel reprocessing factories mainly Sellafield which released to the sea from 40 TBq up to about 180 TBq of ⁹⁹Tc yearly during 1971-1982 and 1996-2004 [4]. For example, (in Japan) typical environmental level in upper soils for ⁹⁹Tc was reported to be on level below 10 mBq/kg [2].

Therefore it seems interesting if one can observe input from the nuclear medicine application of ⁹⁹Tc from a big city in the river, where purified waters from city sewage system are discharged to the river. Two techniques can be used for detection of long-lived Tc-99: liquid scintillation spectrometry and mass spectrometry. Both required a lot of radiochemical work prior to measurement.

II. MATERIAL AND METHOD

A. Sampling

Warsaw and Kraków, two biggest cities of Poland and Vistula River were chosen for our experiments. Although technetium is well soluble, it also has affinity to the organic matter. The river sediments were collected as samples for present study. Ten sampling locations were chosen in Vistula upstream Warsaw (samples coded TPW) and other eight downstream Warsaw, below the output of the sewage system of the city (coded TZW). Samples were collected in September 2011, when very low water level in river was observed. For comparison some samples of bottom sediments of Vistula river were also collected near Krakow (coded KR) and two samples of dry residue from Krakow sewage purification station (coded OSA) were also collected and analyzed. The location of sampling site is presented in Fig. 1.

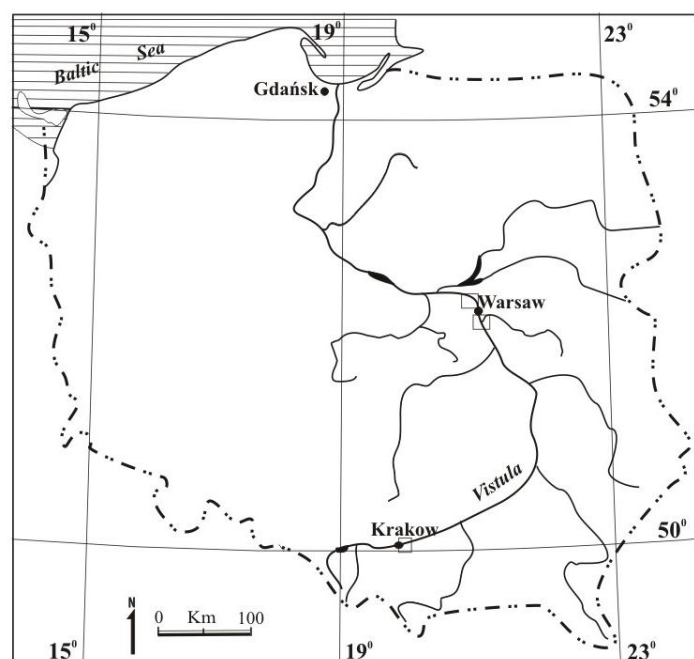


Fig. 1 The map of Poland with marked (as squares) sampling areas along Vistula River
In general the majority of results for ^{99}Tc are below the detection limit which range from 0.10 Bq/kg to 0.32

Prior to any further analytical work samples were dried at 105 °C and homogenized. The dry masses of samples taken for analyses were on the level of 100 g.

B. Radiochemical Analyses

Prior to any radiochemical work, dried at 105 °C and homogenized samples were characterized by means of gamma spectrometry using low background HPGe detector. The laboratory has Polish ISO 17025 accreditation for gamma spectrometric measurements.

Next, samples soaked with ammonia [5, 6] are ashed in 400 °C and leached using 4M HNO_3 . The $^{95\text{m}}\text{Tc}$ was added as tracer. It was home produced at AIC-144 Krakow's cyclotron (60 MeV protons) from natural ruthenium in $^{\text{nat}}\text{Ru}(\text{p}, \text{xn})^{95\text{m}}\text{Tc}$ reaction. After removing of a large part of matrix by precipitation at pH~6 (in this conditions Tc as pertechnetate stays in solution) [6] the Tc was separated using TEVA resin form diluted nitric acid media. The ruthenium was then removed from TEVA using 2 M HNO_3 and finally Tc was removed from the column using 8M HNO_3 . Similar Tc/Ru separation was also applied in case of tracer, prior to using it as spike. However, this purification from Ru appeared not sufficient to successfully apply mass spectrometry techniques (even repeated) due to massive amount of remains of Ru target. The chemical recovery of technetium ($^{95\text{m}}\text{Tc}$) was determined using low background gamma spectrometer with HPGe detector. The chemical recovery was at the range of about 60%.

C. Measurements

Each sample was divided by two similar parts (by mass, controlled at analytical balance). One share was measured using liquid scintillation spectrometer Wallac-Guardian 1414-003, and the other one was used for mass spectrometry measurements using Perkin-Elmer Quadrupol ICP MS. During the LSC measurements the efficiency for ^{99}Tc was determined using ^{87}Rb standard, since both isotopes have very similar maximum beta particles energy close to 300 keV. The quenching corrections were applied to each sample on basis of SQPE parameter given by instrument. The window used for ^{99}Tc calculations was taken between channel 300 and 600, for unquenched samples, because below channel 300 the signal from $^{95\text{m}}\text{Tc}$ was present.

In order to reduce signal from the tracer prior to adding liquid scintillator samples were kept in the refrigerator a couple of months prior to measurements.

The lack of certified reference materials for ^{99}Tc on the market, made unable proper quality assurance.

III. RESULTS AND DISCUSSION

Table 1 presents results from liquid scintillation spectrometry measurements of ^{99}Tc along with results of gamma spectrometric measurements for ^{137}Cs and organic matter (OM) content. Unfortunately, as was already mentioned the results from mass spectrometry, which were intended to be cross check and confirmation of the results were not suitable since the traces of ruthenium added to the samples with tracer were apparently not sufficiently removable using described above TEVA separation (even repeated twice) and resulting uncertainties of corrections for isobaric interference at mass 99 (due to stable $^{99}\text{Ru}^+$ ion) turned all mass spectrometry results into below appropriate detection limits. In Fig. 2 example of LSC spectrum of technetium fraction from dry wastes from Krakow water sewage system (sample code OSA2) is presented.

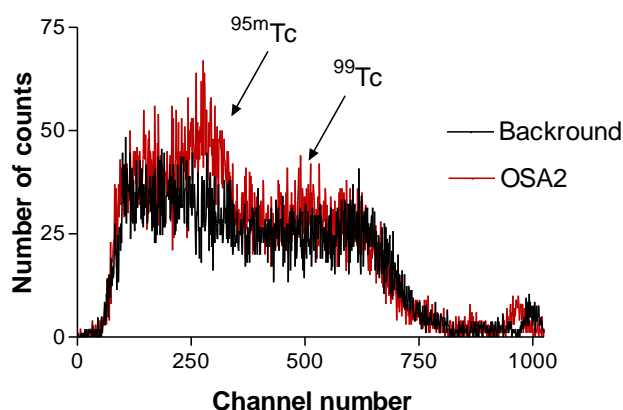


Fig. 2 LSC spectrum of sample of a dry waste from sewage (OSA2 sample)

TABLE 1 RESULTS FOR RADIOMETRIC MEASUREMENTS. GROUP A – VISTULA RIVER BOTTOM SEDIMENTS FROM KRAKOW, B – DRY RESIDUE FROM KRAKOW CITY SEWAGE PURIFICATION, C – VISTULA RIVER BOTTOM SEDIMENTS UPSTREAM THE CITY, D – VISTULA RIVER BOTTOM SEDIMENTS DOWNSTREAM THE CITY, OM – ORGANIC MATTER CONTENT

| Sample code | $^{137}\text{Cs}[\text{Bq/kg}]$ | $^{99}\text{Tc}[\text{Bq/kg}]$ | OM [%] | Group |
|-------------|---------------------------------|--------------------------------|--------|-------|
| KR1 | 6.1 ± 1.1 | 3.8 ± 0.8 | 2.8 | A |
| KR2 | 7.9 ± 1.1 | 13.4 ± 4.0 | 6.4 | |
| KR3 | 10 ± 2 | <0.10 | 7.8 | |
| OSA1 | 7.8 ± 1.0 | 0.35 ± 0.08 | 43.5 | B |
| OSA2 | 10.5 ± 2.2 | 0.44 ± 0.13 | 49.6 | |
| TPW1 | 3.3 ± 0.3 | 0.98 ± 0.38 | 8.8 | C |
| TPW2 | 1.7 ± 0.3 | <0.21 | 1.5 | |
| TPW3 | 0.5 ± 0.8 | <0.10 | 0.8 | |
| TPW4 | 3.1 ± 0.8 | <0.10 | 1.6 | |
| TPW5 | 4.9 ± 0.5 | <0.25 | 4.7 | |
| TPW6 | 0.30 ± 0.1 | <0.20 | 1.3 | |
| TPW7 | <3.6 | <0.10 | 1.6 | |
| TPW8 | 1.3 ± 0.8 | <0.10 | 1.9 | |
| TPW9 | <0.4 | 0.13 ± 0.10 | 1.1 | |
| TPW10 | 0.3 ± 0.1 | <0.32 | 1.2 | |
| TZW1 | 2.8 ± 0.4 | 0.35 ± 0.18 | 5.2 | D |
| TZW2 | 0.3 ± 0.2 | <0.10 | 1.0 | |
| TZW3 | 1.3 ± 0.9 | <0.20 | 4.4 | |
| TZW4 | 6.3 ± 1.8 | <0.13 | 9.1 | |
| TZW5 | 5.7 ± 0.6 | <0.14 | 8.4 | |
| TZW6 | 7.9 ± 0.5 | <0.10 | 7.5 | |
| TZW7 | 13.1 ± 1.0 | 6.8 ± 2.3 | 7.8 | |
| TZW8 | 3.4 ± 0.8 | <0.10 | 3.4 | |
| Blank 1 | | <0.12 | | |
| Blank 2 | | <0.13 | - | |

Bq/kg (for dry mass). Both samples of dry residue from sewage system have ^{99}Tc activity on the level of 0.4 Bq/kg. Surprisingly, some results are much higher, like in cases of samples KR1, KR2 and TZW7. There is no simple explanation of this feature for example by amount of OM. The examined Vistula River bottom sediments collected upstream and downstream Warsaw are different in their OM content. The mean OM content is twice smaller upstream when compared to that for downstream (respectively: mean 2.5% and 5.9% with standard deviation 2.4% and 2.8%). This seems to be a result of fertilizing effect of city sewage discharges which apparently resulted in higher OM fraction in sediments.

The results for ^{137}Cs seem to be much less scattered than those for ^{99}Tc . Certainly the ^{137}Cs to ^{99}Tc is not as high as can be estimated for (decay corrected) global fallout (about $3 \cdot 10^3$ [2]) or Chernobyl fallout (from $8 \cdot 10^3$ to $1.6 \cdot 10^4$) [3]. In some cases activity concentration of those two nuclides is comparable (KR1, KR2, TZW7). In case of solid wastes this ratio is close to 20. In many other samples, where results are below the detection limits nothing can be said about the ratio besides just the limit for it. At present we do not have any clear explanation for large variation of ^{99}Tc activity concentration in examined samples, however, at least the latest results for solid wastes prove that ^{99}Tc from medical application seems to be detectable in such kind of materials.

IV. CONCLUSIONS

The existence of ^{99}Tc from medical application in solid wastes from sewage of about 1 million inhabitants city seems to be proved. In few samples of river sediments much higher ^{99}Tc activity concentration was measured than one would expect. Despite this, for many other very similar samples the ^{99}Tc was below detection limits. This further suggests that more detailed studies could be undertaken to find out the true pathways and mechanism of technetium concentration in river sediments and perhaps also in river water and biota. This is important for future studies, due to wide use of $^{99\text{m}}\text{Tc}$ in nuclear medicine.

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REFERENCES

- [1] UNSCEAR. (2000). Effects of Radiation on the Environment. United Nations Scientific Committee on the Effects of Atomic Radiation. Report to the General assembly, Anex 1, New York: United Nations 2002.
- [2] Tagami. K, Uchida S (1999) Concentration of global fallout ^{99}Tc in rice paddy soils collected in Japan, *Environmental Pollution* 95, 151-154.
- [3] Uchida S., Tagami K., Rühm W., Wirth E. (1999) Determination of ^{99}Tc deposited on the ground within the 30-km zone around the Chernobyl reactor and estimation of ^{99}Tc released into atmosphere by the accident, *Chemosphere* vol. 39 2757-2766.
- [4] Sellafield Annual Report, 2011, http://www.sellafielddesiresites.com/wp-content/uploads/2012/08/Sellafield_Report_2011_800K1.pdf.
- [5] Keller B. J., McKibbin T. T., Erickson A. L., Filby C. W. (1992) "The sequential separation of ^{99}Tc and ^{129}I in waste samples", *Journal of Radio analytical and Nuclear Chemistry*, Articles, 158, no. 1, p. 75-78.
- [6] Kleszcz K. & Mietelski J. W. (2013), "Methodological studies of the determination of ^{99}Tc in matrix-rich environmental samples" *Journal of Radio analytical and Nuclear Chemistry*, vol. 296, iss. 1 (2013), pp. 403-406.