

Progress report: Studies on the behaviour of technetium (Tc-95m) in marine biota and sediments.\*\*

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### Abstract

The radionuclide Tc-95m has proved to be very useful as a tracer for experimental studies on the behaviour of technetium in the marine environment at realistic mass concentrations. It has been shown that, in agreement with thermodynamic considerations, the anion pertechnetate is the most stable chemical form of technetium in seawater and aerobic sediments. When hydrazine-reduced technetium is added to seawater, its oxidation to pertechnetate occurs rapidly and does not follow simple first-order kinetics. In the presence of anaerobic sediments, pertechnetate present in seawater may be immobilized as highly insoluble compounds. Although redox conditions should be responsible for reduction and fixation of technetium, diffusion through the sediment could be a rate-limiting factor. Marine biota do not accumulate technetium to a remarkable extent, but in a few species relatively high concentration factors have been observed. Since accumulation kinetics are generally slow, it is difficult to achieve steady-state conditions in laboratory experiments; thus, the application of mathematical models has proved useful in reducing the duration of the experiments aimed at obtaining concentration factors.

### Résumé.

*On a observé l'utilité du radionucléide Tc-95m comme indicateur dans les études expérimentales du comportement du technétium dans le milieu marin à concentration réaliste de la masse. On a démontré qu'en accord avec les considérations thermodynamiques, l'anion pertechnétiat est la forme la plus stable dans l'eau de mer et dans les sédiments oxydés.*

*Quand on ajoute du Tc obtenu à partir de la réduction par l'hydrazine du  $TcO_4$  en eau de mer, son oxydation a lieu rapidement et ne suit pas une cinétique de premier ordre.*

*En présence de sédiments réducteurs, le pertechnétiat présent dans le milieu marin peut être immobilisé comme composant hautement insoluble.*

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*En outre, les conditions redox pourraient être responsables de la réduction et de la fixation du Tc, la diffusion dans les sédiments pouvant être un facteur limité par la fixation.*

*Les organismes marins n'accumulent pas beaucoup de technétium, mais on a observé des espèces ayant des facteurs de concentration très élevés.*

*La cinétique d'accumulation est lente et il est difficile d'atteindre les conditions d'équilibre dans les expériences en laboratoire, mais on peut obtenir avec l'application de modèles mathématiques une réduction de la durée de ces expériences pour définir les facteurs de concentration à l'équilibre.*

The presence and increasing concentrations of the long-lived radioisotope Tc-99 in the environment are mainly a consequence of nuclear explosions in the past and discharges of effluents from nuclear fuel reprocessing plants (1). A further potential source of increments in present-day inventories of technetium represent the rising quantities of Tc-99 deposited in considerable amounts in radioactive wastes destined to final disposal. Principle objectives of our radioecological studies were aimed at gathering further information on the environmental behaviour of technetium and the transfer through food chains.

Thermodynamic considerations clearly indicate pertechnetate ( $\text{TcO}_4^-$ ) as the most stable chemical form of technetium considering ranges of pH and Eh values normally occurring in the marine environment (2). The stability of pertechnetate in seawater has been confirmed experimentally. When hydrazine-reduced technetium is added to well oxygenated seawater, it is rapidly oxidized to  $\text{TcO}_4^-$ . The reaction does not follow simple first-order kinetics: 90% of Tc(IV) is transformed at a fast rate ( $t/2$  10min), the remaining 10% being oxidized slowly. The rapid reoxidation of reduced technetium has also been confirmed electrochemically using a rotating disk electrode.

A considerable amount of work has been performed on the disappearance of pertechnetate from seawater in the presence of reducing sediments. Slow fixation of technetium by sediments rich in organic carbon has been reported and related to the bacterial activity (3). Since geological migration potentials suggest an important role of redox conditions (4), we made investigations using anaerobic sediments rich in organic carbon (3.8%). We found rapid disappearance of pertechnetate from seawater in the presence of such sediments. Factorial experiments provided useful information on the influence of several factors and on their interactions, which finally may determine fixation of technetium in anaerobic sediments. It was found that the fixation rate is dependent on several factors such as physico-chemical characteristics of the sediment, mass ratio between sediment and water, area of the sediment-water interface etc. In laborato-

ry experiments fixation of technetium, present in picomolar concentrations, was faster at higher sediment/water ratios. On the other hand, the amount of technetium fixed by the sediment was approximately proportional to the concentrations of pertechnetate in seawater (5).

Bacterial activity and organic matter should have an indirect role, in that they contribute in determining chemical and physical characteristic of the sediment. The fixation rate in our experiments was not influenced by the presence of antibiotics and humic acids neither adsorb nor bind pertechnetate. On the basis of the information collected, we could indicate redox conditions as responsible for the immobilization of technetium. Diffusion of the anion pertechnetate through the sediment into deeper layers, where it can be transformed and immobilized by a reducing environment, is most probably the rate-limiting factor in the fixation process of technetium. Once fixed to the sediment, technetium cannot be leached by seawater and alkaline or acid solutions. Concentrated nitric acid is required, suggesting formation of highly insoluble compounds (i.e. such as metal sulfides).

The recent, rapidly developing body of literature (6) indicate that technetium initially supplied as pertechnetate anion is accumulated to limited extents by marine organisms. Only in a few species of macrophytic brown algae, polychaetes and crustaceans the concentration factors are higher than 1000. We have performed several studies on the behaviour of technetium in marine organisms in order to acquire information on its transfer to man through food chains. As a consequence of the instability of Tc(IV) in well oxygenated seawater, the experiments on the bioavailability of technetium to marine organisms have been carried out using pertechnetate. Accumulation from seawater apparently followed first-order kinetics: both rate constant and concentration factor at equilibrium are highly species dependent. The macrophytic brown alga Fucus virsoides accumulates to remarkable extent (CF=1100). In polychaete worms concentration factors ranged between 300 (Nereis sp.) and 800 (Marphysa bellii). Much lower values were obtained for the octopus Eledone moschata (CF=8), the shrimp Palaemon elegans (CF=8)(7). Water temperature had only some influence on the rate of uptake but did not alter the final concentration factor (8). Bioaccumulation in two crabs (Pachygrapsus marmoratus and Carcinus mediterraneus) did not show substantial differences in technetium concentrations: concentration factors in both species were slightly higher than 10. In the fish Dicentrarchus labrax fed on a diet of polychaetes, which previously had accumulated Tc from seawater, most of the whole-body radioactivity was distributed among liver(25%), stomach(20%), kidney(20%), and gut(5%). The biological half-lives ( $T_{b/2}$ ) of technetium were determined in marine organisms which had accumulated the radioisotope either from water or from contaminated diets. Elimination of tech-

netium by the shrimp Palaemon elegans is rapid ( $T_{b/2} = 5d$ ) and independent from the source of contamination. In Dicentrarchus labrax the loss of technetium accumulated from contaminated food is biphasic: 50% of the radioactivity is released in a short time ( $T_{b/2} = 1d$ ), the remaining being slowly excreted ( $T_{b/2} = 15d$ ). After accumulation from seawater, Tc is strongly retained by the octopus Eledone moschata ( $T_{b/2} = 120d$ ). In the two crab species the kinetic of release occurred in three distinct phases, which are represented by the hepato-pancreas, the G.I. tract, and the muscle tissue and the gills. The biological half-lives of technetium present in these compartments were 18, 28, and 50 days, respectively.

A series of kinetic experiments have been made on the accumulation of Tc by the shrimp Palaemon elegans. The results obtained for accumulation of technetium from seawater and subsequent release in an uncontaminated environment were applied to a three-compartment model (8). The organism was divided into two sub-compartments; a compartment for the hepato-pancreas with a rapid turnover rate, and another for the remaining organs and body tissues, in which the turnover of technetium was relatively slow. Since the components had nearly constant values of biomass during the experiment, a linear donor-controlled mathematical model was used to calculate body burdens and steady-state concentrations of technetium in the shrimp (9). The calculated body burdens and the concentration factors showed that after approximately one month exposure of the shrimp to a constant concentration of pertechnetate, the hepato-pancreas reached steady-state conditions and acted as an intermediate reservoir for the slow transfer of technetium to other body organs and tissues. Although accumulation of technetium in the hepato-pancreas occurred at a fast rate, it took several months to approach the equilibrium value of the concentration factor for the whole animal.

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### Discussion

A. MANGINI: You have shown very different factors of Tc enrichment for different species. Wouldn't it be more useful to perform multi-isotope studies and compare enrichments of Tc to some specific element?

E. SCHULTE: Studies on competition of other radioisotopes with accumulation of Tc should be done especially for molybdenum. However, experiments should focus first on one radioisotope only in order to better understand its biokinetics.

H. UYSAL: How did you prepare your tissue samples? Did you digest them?

E. SCHULTE: Tissues were obtained by dissection and measured directly by gamma spectrometry, i.e. Tc-95m is a gamma emitter, therefore, there is no need to digest samples.

P. MIRAMAND: Avez-vous mesuré le distribution du Tc dans les tissus du cephalopode Eledone?

E. SCHULTE: Oui, mais je n'ai pas les résultats ici, aucune concentration particulière n'a été observée dans le branchiaux.

L. MUSANI-MARAZOVIC: You said the predominant form of Tc in sea water is  $TcO_4^-$ , e.g. VII valency state. In my opinion the reduced form of Tc can be fixed on the sediments since it is negatively charged in sea

water. Reduction of  $TcO_4^-$  might be caused by the presence of organic matter adsorbed on sediments. You have not found any interaction of Tc and humic and fulvic acids. There is a completely different behaviour if you have dissolved or undissolved humic acid as concerns complexation or adsorption mechanisms.