



## Evidence of $^{99}\text{Tc}$ in Ural River Sediments

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### ABSTRACT

Sediments collected from the Techa River at Nadirov Bridge were analysed for  $^{99}\text{Tc}$ . The maximum concentration was found at a depth of 14–18 cm. This layer was sedimented around 1950, i.e. at a time when the maximum releases of waterborne radionuclides occurred to the river from the MAYAK plutonium production plant in the Urals. The vertical distribution of  $^{99}\text{Tc}$  in sediments followed that of  $^{137}\text{Cs}$ , and the mean ratio between  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  in the sediments at the time of discharge was  $0.41 \times 10^{-3}$ . Laboratory experiments showed that  $^{99}\text{Tc}$  under anoxic conditions, e.g. when organic material is decomposing, will be retained by sediments. © 1997 Elsevier Science Ltd

### INTRODUCTION

The implementation of the nuclear programme by the Former Soviet Union in the Cheliabinsk region in the Urals involved contamination of the environment with long-lived fission products resulting from both accidental conditions and routine operation of the utility (MAYAK), particularly in the initial period, i.e. the late 1940s and early 1950s.

During 1949–1952, 100 PBq of liquid, medium and low-level radioactive waste was thus discharged directly into the Techa river system (Akleyev and Lyubchansky, 1994). The Techa river is part of the Iset–Tobol–Irtys–Ob river system (Figs 1 and 2). In the upper reaches, it passes the MAYAK nuclear facility. The detailed composition of the liquid discharges to Techa river is not known, but the amounts of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  were

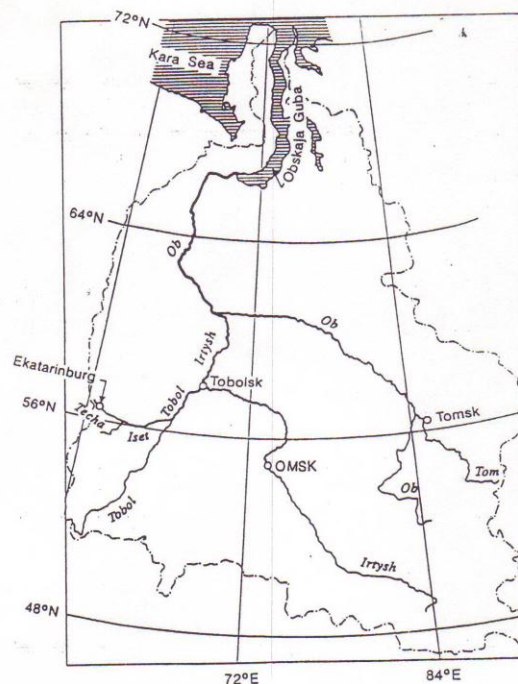


Fig. 1. Drainage area of the Ob river system.

11.6 and 12.2 PBq, respectively (Akleyev and Lyubchansky, 1994). Now, more than 40 years since the primary contamination to the river occurred, water, sediments and biota still contain enhanced levels of longer lived radionuclides, viz.  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$  and transuranic elements (Trapeznikov *et al.*, 1993), in particular in the upper reaches of the river. The present study deals with a highly contaminated sediment column collected by the Institute of Plant and Animal Ecology (IPAE) in September 1992, at Nadirov Bridge 49 km from the point of discharge.

#### MATERIALS AND METHODS

The basic parameters for the Techa river are shown in Table 1.

The chemical composition and pH of the Techa river water were measured at Pershinskoje: pH = 7.4, 40.3 mg  $\text{Ca}^{2+} \text{ l}^{-1}$ , 13.2 mg  $\text{Mg}^{2+} \text{ l}^{-1}$ ,

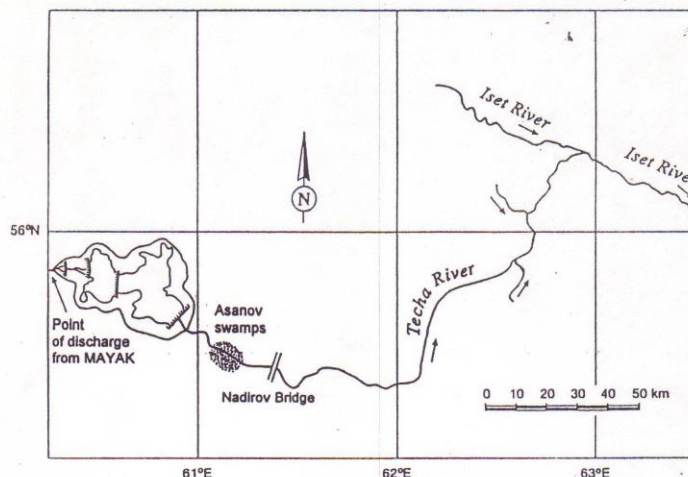


Fig. 2. Techa river.

4.3 mg  $\text{Na}^+\text{K}^+ \text{ l}^{-1}$ , 134.2 mg  $\text{HCO}_3^- \text{ l}^{-1}$ , 30.4 mg  $\text{SO}_4^{2-} \text{ l}^{-1}$ , 16.4 mg  $\text{Cl}^- \text{ l}^{-1}$ , 3 mg  $\text{Fe l}^{-1}$ , 8.8 mg  $\text{O}_2 \text{ l}^{-1}$  and 7.3 mg  $\text{Si l}^{-1}$ . The sediments at Nadirov Bridge are sandy silt, sometimes containing peat.

The sediments were collected with a coring device with a sample area of  $33.2 \text{ cm}^2$  (diameter: 6.5 cm). The samples were collected to a depth of 40 cm and cut into 2-cm-thick slices. The dry weight of the 0–4-cm layer was  $220 \text{ mg cm}^{-3}$ , and the mean weight below 4 cm was  $400 \pm 50 \text{ mg cm}^{-3}$ . The ash weight of the sediments was 98% of the dry weight, indicating an organic dry matter content of not more than 2%. During the sampling, the lower layers had been contaminated by surface material, and so material collected below a depth of 34 cm was not included. Risø analysed the samples for  $\gamma$ -emitters ( $^{137}\text{Cs}$ ) by Ge-spectroscopy. Based upon methods previously developed for radiochemical determination of  $^{99}\text{Tc}$  (Holm *et al.*, 1984; Chen *et al.*, 1990), a special method was developed for the determination of  $^{99}\text{Tc}$  in the highly contaminated sediments (see Appendix A). The method was designed to remove large amounts of interfering  $\beta$ -emitters, because  $^{99}\text{Tc}$  was determined by a  $\beta$ -counting. In order to demonstrate that the activity measured in fact was  $^{99}\text{Tc}$ , a  $\beta$ -absorption analysis was made with Al-absorbers of varying thickness (see Appendix B). Furthermore,  $\gamma$  and  $\alpha$  spectroscopy was carried out on the  $^{99}\text{Tc}$  counting discs in order to ensure that no interfering radionuclides were present.



TABLE 1  
Main Hydrological Characteristics of the Techa River (Trapeznikov et al., 1993)

Location	Distance from discharge (km)	Mean width (m)	Mean depth (m)	Water flow <sup>a</sup> (km <sup>3</sup> year <sup>-1</sup> )	Sediment transport (kg year <sup>-1</sup> )
Nadirov Bridge	49	37	2.1	~0.02	~1.66 × 10 <sup>6</sup>
Muslimovo	78	20.5	1.1	0.06	~5 × 10 <sup>6</sup>
Verknaja Techa	177	25.5	0.5	~0.14	~12 × 10 <sup>6</sup>
Pershinskoje	214	78.5	0.7	0.18	~15 × 10 <sup>6</sup>
Zatechenskoje	237	25.5	1.0	0.35	~30 × 10 <sup>6</sup>

<sup>a</sup>In the spring, the water flow is due to snow-melting, increased five to 10 times compared with the winter flow.

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The unsupported  $^{210}\text{Po}$  ( $\text{Bq kg}^{-1}$ ) may be described by an exponential model  $y = e^{(a+bx)}$ , where  $x$  is the weight of the sediment layer in  $\text{kg m}^{-2}$ ,  $a = 4.3 \pm 0.14$  and  $b = 0.0254 \pm 0.0067$ . The half-life of  $^{210}\text{Pb}$  (which is in equilibrium with  $^{210}\text{Po}$ ) is 22.3 years, and the annual sediment rate at Nadirov Bridge thus becomes

## DISCUSSION

Figure 3 shows that the  $^{99}\text{Tc}$  activity in the sediments follow the distribution of  $^{137}\text{Cs}$ . The mean  $^{99}\text{Tc}/^{137}\text{Cs}$  in 1992 was  $(1.09 \pm 0.28) \times 10^{-3}$  ( $\pm 1\text{SD}$ ;  $N = 16$ ) corresponding to a ratio of  $0.41 \times 10^{-3}$  between the two radionuclides in 1950.

In nuclear reactors the  $^{99}\text{Tc}/^{137}\text{Cs}$  is  $1.3 \times 10^{-4}$  (Till, 1986), and in the accumulated liquid discharges from reprocessing at Sellafield a ratio of  $2.1 \times 10^{-2}$  (BNFL, 1978–1994) has been measured. Although it is not strictly appropriate to compare these ratios with those observed in sediments, because differences in  $K_d$  for  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  will influence the ratio found in sediment, it appears that the measured ratios in Techa sediments lay between the above ratios. It is, however, a surprise that  $^{99}\text{Tc}$  was found in sediments. Usually, Tc will be present in the aquatic environment as  $\text{TeO}_4^-$  which will behave as a conservative element, i.e. follow the water

TABLE 2  
Radionuclides in Tcha River Sediments from Nadirov Bridge Collected During September 1992

Layer (cm)	Cumulative weight ( $\text{kg m}^{-2}$ )	$^{99}\text{Tc}$			$^{137}\text{Cs}$			$^{99}\text{Tc}$ $^{137}\text{Cs}$		
		$\text{Bq kg}^{-1}$	$\pm \text{ISE}$	N	$\text{Bq kg}^{-1}$	$\pm \text{ISE}$	N	Ratio	$\pm \text{ISE}$	N
0-4	8.9	540	21	2	290	1 <sup>a</sup>	2	1.86		
4-6	17.8	230	11	2	196	20	2	1.17	0.13	2
6-8	26	260	3	2	206	16	2	1.26	0.10	2
8-10	36	540	28	4	430	2 <sup>a</sup>		1.26		
10-12	43	500	18	4	460	2 <sup>a</sup>		1.09		
12-14	51	550	12	2	630	1 <sup>a</sup>		0.87		
14-16	58	780	13	2	860	3 <sup>a</sup>		0.91		
16-18	66	770	11	4	780	2 <sup>a</sup>		0.99		
18-20	75	660	11	4	580	2 <sup>a</sup>		1.14		
20-22	84	520	15	2	450	21		1.16	0.06	2
22-24	94	310	8	2	490	11	2	0.63	0.02	2
24-26	102	177	5	2	260	1 <sup>a</sup>	2	0.68		
26-28	109	88	2	2	91	1 <sup>a</sup>		0.97		
28-30	116	74	2	2	65	1 <sup>a</sup>		1.14		
30-32	123	68	1	2	61	1 <sup>a</sup>		1.11		
32-34	131	14.6	0.02	2	11.7	0.1 <sup>a</sup>		1.25		
								$\bar{x}$		
								ISD		
								0.28		

<sup>a</sup>1SD due to counting statistics.



TABLE 3  
Lead-210 Measured as in Sediments Collected at Nadirov Bridge During September 1992

Layer (cm)	Reference depth ( $\text{kg m}^{-2}$ )	Total $^{210}\text{Po}$ ( $\text{Bq kg}^{-1}$ )	$\pm 1\text{SD}$	Supported $^{210}\text{Po}$ ( $\text{Bq kg}^{-1}$ )	$\pm 1\text{SD}$	Unsupported $^{210}\text{Po}$ ( $\text{Bq kg}^{-1}$ )	$\pm 1\text{SD}$
0-4	4.4	158	11			106	9
4-6	13.4	108	16			56	13
6-8	22	80	11			28	10
8-10	31	79	1			27	6
10-12	39	84	1	52	8	32	6
12-14	47	66	8			14	8
14-16	55	78	6			26	7
16-18	62	76	3			24	6
18-20	70	65	1			13	6

The reference depth of the 0-4-cm layer is the weight ( $\text{kg m}^{-2}$ ) of the 0-2-cm layer, the reference depth of the 4-6-cm layer is the weight of the 0-5-cm layer, etc.

The standard deviation of the  $^{210}\text{Po}$  was determined from double analysis.

The unsupported  $^{210}\text{Po}$  is the difference between the total  $^{210}\text{Po}$  and the supported  $^{210}\text{Po}$ .

**Techa river sediment samples collected at  
Nadirov Bridge. September 1992.**

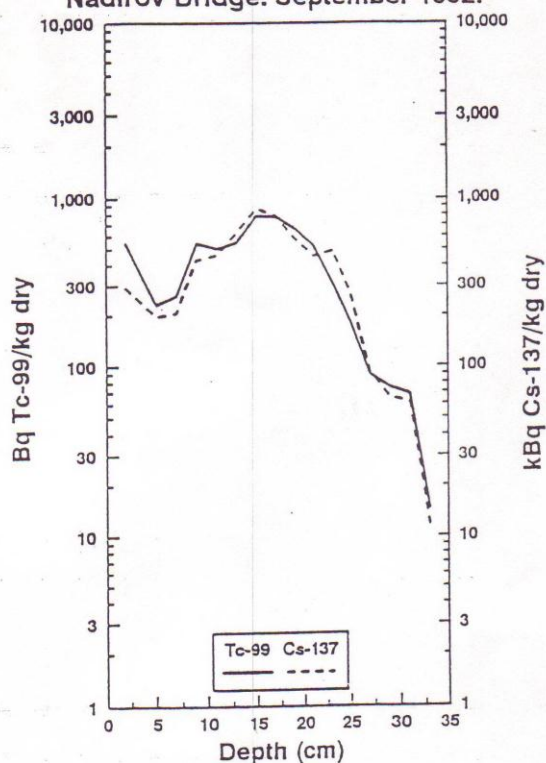


Fig. 3. Depth distributions of  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  concentrations.

masses instead of being precipitated. That is why  $^{99}\text{Tc}$  has been used so successfully as a marine tracer (Aarkrog *et al.*, 1987; Dahlgaard, 1995) for the last decades. Blaylock *et al.* (1986) have found that  $\text{TcO}_4^-$  released into an experimental freshwater pond had a very low affinity for particulate matter and sediments. If  $^{99}\text{Tc}$  should be retained by sediments, it must be on a reduced form as  $\text{Tc}^{4+}$ . In order to investigate this possibility, a number of experiments were carried out. The experiments were made with Danish lake water and lake sediments.

In the first test,  $^{99\text{m}}\text{Tc}$  and 1 ml 30%  $\text{H}_2\text{O}_2$  were added to 2 g lake sedi-



ments and 100 ml lake water at pH 7. No absorption by the sediments was observed over a period of 60 h. In the oxidized form, no absorption on the sediments occurred either in basic ( $\text{pH} \geq 8$ ) or in acid ( $\text{pH} \leq 6$ ) solutions.

In the second experiment,  $^{99\text{m}}\text{Tc}$  and 1 g FeS was added to 2 g lake sediments and 100 ml of water ( $\text{pH} = 7$ ). In 30 min, all Tc was retained by sediments.

The third experiment was carried out with 1 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  instead of FeS. At pH 7, no Tc was left in the water phase after 80 min of treatment. This experiment was also carried out at other pH values. In acid solutions ( $\text{pH} \leq 6$ ), no absorption by the sediments was observed, even after 150 min of treatment, but in basic ( $\text{pH} \geq 8$ ) solutions, the technetium went rapidly (within 6 min) to the sediments.

The fourth experiment was made with 100 ml lake water, which, for 4 days had been treated with 4 g grass, whereby the grass had decomposed. When 2 g sediments and  $^{99\text{m}}\text{Tc}$  were added to the treated lake water, only 40% of the  $^{99\text{m}}\text{Tc}$  remained in the water after 50 min of treatment. A similar observation was made if the lake water had been treated with 5 g fish instead of grass. The decomposing of the organic matter thus reduced Tc from oxidation step +7 to +4.

Finally, if 2 g of lake sediments and 100 ml lake water were treated for 20 h with  $\text{H}_2\text{S}$  gas, only 20% of the  $^{99\text{m}}\text{Tc}$  remained in the water phase.

From these experiments, it is concluded that Tc will go to the sediments in a reducing, neutral or basic environment but will remain in the water phase in the oxidized form at any pH. Reducing conditions may occur in a river system if organic materials decompose. Fulvic or humic acids act as reducing agents, regardless of the redox conditions in the bulk water. That is, in many well oxygenated waters, 'normal' redox potential diagrams for trace elements fail to predict the oxidation state of the metal in question because of the presence of humics. Stalmans *et al.* (1986) have furthermore shown that the organic matter fraction in soils and sediments constitute an important geochemical sink for technetium. Tc-humic acid complexes thus appeared to be quite stable. We have no information on the chemicals that may have been discharged to the Tcha river along with radionuclides in the late 1940s and early 1950s, but of course this may have also influenced the redox conditions in the river; toxic agents thus may have killed animal life.

The presence of relative high levels of  $^{99}\text{Tc}$ , even in the upper sediment layers, may indicate annual run-off from the Asanov swamps, which, during each spring, are flooded by the Tcha river in connection with the snow-melting. Other recent contributions of  $^{99}\text{Tc}$  to the Nadirov Bridge sediments may come from contaminated groundwater or from leakage from the reservoirs at MAYAK, constructed in the early 1950s to retain the activity in the liquid discharges to Tcha (see Fig. 2).

If the  $^{99}\text{Tc}$  to  $^{137}\text{Cs}$  ratio found in the sediments is representative of the ratio in the liquid discharges from MAYAK, i.e. if  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  under the given circumstances had the same  $K_d$ , the discharge of  $^{99}\text{Tc}$  is calculated to  $0.41 \times 10^{-3} \times 12.2 \text{ PBq} = 5 \text{ TBq } ^{99}\text{Tc}$ . However, this figure is probably a minimum estimate of the  $^{99}\text{Tc}$  discharge as it seems unlikely that all  $^{99}\text{Tc}$  should have been retained just as readily by the sediments as  $^{137}\text{Cs}$ . If the ratio in the discharge had been the same as in the discharges from Sellafield, i.e.  $2.1 \times 10^{-2} \times 12.2 \text{ PBq} \approx 0.3 \text{ PBq } ^{99}\text{Tc}$  had been discharged, most of this would then have reached the Arctic Ocean through the Ob river system. If such an input of  $^{99}\text{Tc}$  had occurred in the Arctic Ocean around 1950, it should be possible to see a signal in brown algae (e.g. Fucoids), which concentrate Tc from seawater by a factor of  $10^5$  (Aarkrog *et al.*, 1987) if any seaweed, e.g. in herbarium, has been preserved from that time.

### CONCLUSION

Discharges of  $^{99}\text{Tc}$  from the plutonium production site MAYAK peaked during 1949–1952. The total amount of  $^{99}\text{Tc}$  discharged from MAYAK to the Techa river may have been in the range of  $10\text{--}10^3 \text{ TBq}$ . Some of this  $^{99}\text{Tc}$  can still be found in the Techa river sediments.

This occurrence of  $^{99}\text{Tc}$  suggests the presence of reducing agents in the river system, probably as a result of decomposition of organic matter. Technetium thus may not behave totally conservatively in freshwater systems, and thus under appropriate redox conditions sediments may be used as an indicator for previous liquid discharges to such systems.

### ACKNOWLEDGEMENTS

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### APPENDIX A

Determination of  $^{99}\text{Tc}$  in highly contaminated sediments.

1. Five grams of sediments are digested in a 500-ml flask for 2 h on a  $200^\circ\text{C}$  hot plate with 40 ml (aqua regia,  $^{99\text{m}}\text{Tc}$  spike (for yield



- determination) and hold back carriers of Sr, Y, Ba, Cs, Ce, Eu and Ru).
2. Five grams of  $\text{K}_2\text{S}_2\text{O}_8$  are added to the filtrate and heat to boiling. The solution is adjusted to 0.5 M NaOH with 6 M NaOH and filtered through of GF/F filter. The precipitate is washed with 0.1 M NaOH. The precipitate, which contains U, Th, Po, Pu, Am, Cm, rare earth elements, Ba and Fe, is discarded.
  3. The solution is passed through an anion-exchanger column ( $13 \times 1.5$  cm, AG1-X<sub>4</sub> 100–200 mesh) at a flow rate of  $2\text{--}3\text{ ml min}^{-1}$ . The column is washed with 100 ml 0.5 M NaOH and afterwards with 200 ml 1 M  $\text{HNO}_3$  ( $3\text{--}6\text{ ml min}^{-1}$ ). The Tc on the column is stripped with 60 ml 14 M  $\text{HNO}_3$  ( $1\text{ ml min}^{-1}$ ) into a beaker.
  4. Add 0.5 ml 3 M  $\text{NaNO}_3$  to the solution and evaporate the sample to 0.5 ml. Dilute to 40 ml with water. Add carriers of Sr, Y, Ba, Ce, Cs and Eu and 4 mg  $\text{Fe}^{3+}$  together with 15% NaClO. Adjust to pH 9 with NaOH. Filter on a GF/F filter and wash the precipitate with 10 ml 0.5 M NaOH. Discard the precipitate. Add 1 ml 15% NaClO and heat for 10 min on a  $250^\circ\text{C}$  hot plate. Add 15% NaClO again and adjust pH=3–4 with 5 M  $\text{H}_2\text{SO}_4$  and heat for 15 min on a  $250^\circ\text{C}$  hot plate to volatilize  $\text{RuO}_4$ .
  5. Adjust the solution with 5 M  $\text{H}_2\text{SO}_4$  to 1 M  $\text{H}_2\text{SO}_4$ . Extract with 40 ml 5% Triisooctylamine in xylene. Shake for 2 min and wash the organic phase twice with 40 ml  $\text{H}_2\text{O}$ . Back extract with 20 ml 2 M NaOH. Shake for 2 min. Make a second back extraction with 5 ml 0.5 M NaOH.
  6. Evaporate the solution to about 15 ml before electro-deposition on a stainless steel disc at 300 mA ( $150\text{ mA cm}^{-2}$ ) for 5 h or overnight. Clean the disc for NaOH by dipping it twice for 2 s in 100 ml  $\text{H}_2\text{O}$ .
  7. Cover the disc with thin mylar foil and measure the chemical yield by  $\gamma$ -counting of  $^{99}\text{Tc}$  in a NaI well crystal. Let the  $^{99\text{m}}\text{Tc}$  decay for at least 1 week. Then, count the  $^{99}\text{Tc}$  on a low level betacounter, which has been calibrated with a  $^{99}\text{Tc}$  standard source.

#### APPENDIX B

Table B1 shows that there was no significant difference between the Al-absorption curves for the Techa Tc-samples and the  $^{99}\text{Tc}$  source. On this basis, it can thus not be rejected that the  $\beta$ -activity in the two samples consisted of pure  $^{99}\text{Tc}$ .



**TABLE BI**  
Comparison Between Beta Aluminium Absorption for Two Tcha Sediment Tc-samples and a  $^{99}\text{Tc}$  Source

Sample	Al thickness ( $\text{mg cm}^{-2}$ )	1.8	3.6	6.2	7.2	9.2	12.3	15.4	21.5	26.3	52.7	79.0
20-22 cm	Absorption %	20.9	36.4	51.8	58.7	66.9	75.5	79.3	89.9	94.4	99.6	99.8
22-24 cm	Absorption %	25.1	36.7	55.3	57.9	65.8	72.7	81.8	90.1	93.7	99.6	99.6
$^{99}\text{Tc}$ source	Absorption %	22.1	37.6	54.1	58.4	66.6	75.5	82.0	90.3	94.7	99.7	99.97

## REFERENCES

- Aarkrog, A., Boelskifte, S., Dahlgaard, H., Duniec, S., Hallstadius, L., Holm, E. and Smith, J.N. (1987) Technetium-99 and caesium-134 as long distance tracers in Arctic waters. *Estuarine Coastal Shelf Science* **24**, 637–647.
- Akleyev, A. V. and Lyubchansky, E. E. (1994) Environmental and medical effects of nuclear weapon production in southern Urals. *Science of the Total Environment* **142**, 1–8.
- Blaylock, B. G., Frank, M. L., Hoffman, F. O. and DeAngelis, D. L. (1986) Behaviour of technetium in freshwater environments. In *Technetium in the Environment*, ed. G. Desmet and C. Mytteneare. Elsevier Applied Science Publishers, London, pp. 79–90.
- BNFL (1978–1987) *Annual Report on Radioactive Discharges and Monitoring of the Environment*. British Nuclear Fuels Ltd, Risley, UK.
- Chen, Qingjiang, Dahlgaard, H., Hansen, H. J. M. and Aarkrog, A. (1990) Determination of  $^{99}\text{Tc}$  in environmental samples by anion exchange and liquid-liquid extraction at controlled valency. *Analytica Chimica Acta* **228**, 163–167.
- Dahlgaard, H. (1995) Radioactive tracers as a tool in coastal oceanography: An overview of the MAST-52 project. *Journal of Marine Systems* **6**, 381–389.
- Holm, E., Risoseco, J. and Garcia-Leo, M. (1984) Determination of  $^{99}\text{Tc}$  in environmental samples. *Nuclear Instrumentation and Methods in Physics Research* **223**, 204–207.
- Stalmans, M., Maes, A. and Cremers, A. (1986) Role of organic matter as a geochemical sink for technetium in soils and sediments. In *Technetium in the Environment*, ed. G. Desmet and C. Mytteneare. Elsevier Applied Science Publishers, London, pp. 91–113.
- Till, J. E. (1986) Source terms for technetium-99 from nuclear fuel cycle facilities. In *Technetium in the environment*, ed. G. Desmet and C. Mytteneare. Elsevier Applied Science Publishers, London, pp. 1–20.
- Trapeznikov, A. V., Pozolotina, V. N., Chebotina, M. Ya., Chukanov, V. N., Trapeznikova, V. N., Kulikov, N. V., Nielsen, S. P. and Aarkrog, A. (1993) Radioactive contamination of the Techa River, The Urals. *Health Physics* **65**, 481–488.