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CHARACTERISTICS OF CHERNOBYL FALLOUT IN THE SOUTHERN BLACK SEA

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ABSTRACT

The input to the Black Sea of fallout radioisotopes from the 26 April 1986 Chernobyl nuclear accident may be used to study both physical and biogeochemical processes in this unusual oceanic setting. We describe measurements of the concentrations, distributions, and particle associations of  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{144}\text{Ce}$ ,  $^{106}\text{Ru}$ , and transuranic elements in surface waters of the southern Black Sea sampled in June and September 1986. Our measurements indicate that the Chernobyl tracer signal in surface waters of the southern Black Sea is both substantial and widespread -  $^{137}\text{Cs}$  concentrations in the range 40-250 Bq/m<sup>3</sup> characterized waters from the Bosphorus to the Caucasus. In addition, several vertical profiles of Cs isotopes down to the upper boundary of the anoxic bottom waters are used to address the question of the extent of physical mixing of the Chernobyl tracer signal after delivery to the sea surface. The vertical profile data permit an evaluation of the total Chernobyl Cs isotope deposition to these Black Sea water masses.

A comparison of the relative nuclide composition of surface waters sampled at different locations over time permits preliminary conclusions be drawn on the extent and relative rates of removal of reactive radionuclides from Black Sea surface waters. Other data relevant to these questions come from measurements of the partition of the Chernobyl radiotracers between the filterable suspended particulate and dissolved phases of surface waters.

## INTRODUCTION

The Black Sea and the Baltic Sea are the two marine bodies of water geographically closest to the site of the Chernobyl nuclear reactor accident in the U.S.S.R. The accident, starting on 26 April 1986, led to the contamination of much of Europe with a wide variety of radionuclides released to the atmosphere (1,2). In addition to direct deposition, the Black Sea may receive additional input via river run-off to its northwestern corner (Fig. 1) from the heavily contaminated watersheds of the Danube and Dnepr Rivers. In this paper we present data which address the question of the amount and composition of Chernobyl fallout initially delivered to the Black Sea. It is our belief that the data discussed represent fallout delivered directly and that subsequent measurements will permit an assessment of riverine inputs. As a first attempt to characterize the geochemical behavior of Chernobyl-derived radionuclides in the Black Sea, we describe our observed measurements of the distributions of various radionuclides between the filterable and filtered phases of Black Sea surface waters and of changes in the relative composition of the various radionuclides during the first year following the accident.

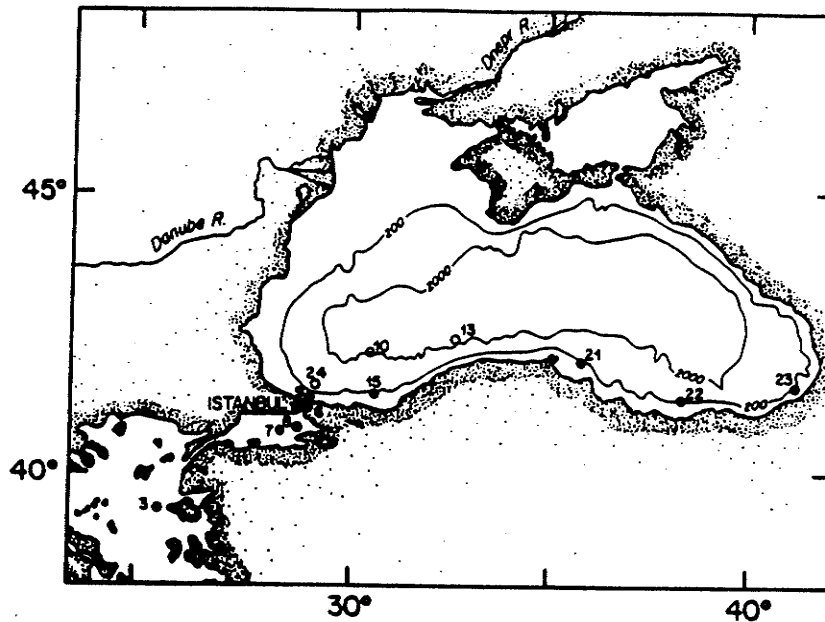


Figure 1. Location map of Black Sea sampling stations. The open circles are off-shelf stations (>200 m), while the filled circles are shelf stations (<200 m). Depth contours are in meters.

The Black Sea has unique properties set by the physical characteristics of its location and water balances. The major features include a shallow brackish surface layer overlying a more saline and anoxic deep water mass. The upper layer derives its freshwater component mostly from the large riverine inputs in the Northwest. The surface circulation is thought to consist of two cyclonic gyres, and the only outflow of surface water occurs through the shallow Bosphorus straits. This outflow overrides a subsurface influx of Mediterranean derived water which provides a major ventilation source for the slow renewal of the deeper waters of the Black Sea basin.

## Magnitude of Chernobyl Fallout in the Black Sea

$^{137}\text{Cs}$  was the major long-lived radionuclide released from the Chernobyl nuclear reactor accident (1). Also, the shorter lived  $^{134}\text{Cs}$  ( $T_{1/2} = 2.06$  years) accompanied  $^{137}\text{Cs}$  ( $T_{1/2} = 30.2$  years) at activity levels slightly greater than 50% of those of  $^{137}\text{Cs}$ . The total deposition of Chernobyl radioactivity to a specific location is to a first approximation assessable through measurement of Cs isotope inventories in soils. In such determinations it is necessary to subtract pre-existing  $^{137}\text{Cs}$  present from atmospheric nuclear weapons testing fallout - making use of the absence of  $^{134}\text{Cs}$  in the latter and the known and constant  $^{134}\text{Cs}/^{137}\text{Cs}$  ratio (= 0.53) in the Chernobyl release. A number of such soil measurements made throughout Europe (but not including Turkey) were reported by Krey et al. (3).

As we were not aware of any comprehensive assessment of the scale of Chernobyl fallout to the Black Sea, we attempted to evaluate this through Cs isotope measurements in the southern Black Sea. Sampling was carried out in June and September of 1986 from the R/V K. PIRI REIS of the University of Izmir, Turkey. Preliminary measurements and sampling details have already been reported from the June 1986 cruise (4) and from the September 1986 cruise (5). In addition, measurements of material collected in time-series sediment traps have been described (6-8).

Samples for measurement of surface radionuclide concentrations were collected only in the June cruise but, in addition, several vertical profiles were collected and measured in September. The latter permit the determination of the total Cs isotope inventory in the water column at a given sampling location. The former provide an approximate scaling of the total Cs isotope delivery when viewed in the context of hydrographic measurements and of other vertical concentration profiles. The Cs isotopes were collected and measured using two different approaches. The first approach was used in surface water sampling and involved absorption of Cs isotopes from large volumes of water pumped through cotton fiber filter cartridges impregnated with cupric ferrocyanide (4). These filters have high affinities for Cs absorption and the total Cs absorbed is calculated from comparison of activities collected on two serial filters (9). The activities on each filter were measured by direct Ge(Li) gamma-spectrometry using a coaxial detector. Calibration was achieved using filters loaded with standardized amounts of  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ . The second approach, used for analyses of 10-liter Niskin bottle samples for vertical profiles, involved radiochemical separation of Cs isotopes and activity measurement by both gamma-spectrometry and low-level beta counting - using standard techniques (10,11).

Data for additional isotopes were obtained by either the direct gamma-spectrometric analysis of ashed  $\text{MnO}_2$  cartridges which were placed in line after the Cs absorbers (for  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$ ) or by their wet acid digestion followed by radiochemical transuranic analysis (11,12).

The concentrations of  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ , and other nuclides (decay corrected to 1 May 1986) measured in surface water samples in the southern Black Sea in June and September are provided in Table 1. The positions of the sampling stations are shown in Figure 1. The levels of  $^{137}\text{Cs}$  found are broadly an order of magnitude higher than the reported pre-Chernobyl range of values (12-16  $\text{Bq}/\text{m}^3$ ) (13). We believe that these surface values are

Table 1. Radionuclides in Black Sea surface water - large volume filtration/absorption data

Table 1a. Total Activities(a)

Sta. No.	(Bq/m <sup>3</sup> )				(mBq/m <sup>3</sup> )			
	<sup>137</sup> Cs	<sup>134</sup> Cs	<sup>106</sup> Ru	<sup>144</sup> Ce	<sup>239,240</sup> Pu	<sup>238</sup> Pu	<sup>241</sup> Am	<sup>242</sup> Cm
<u>14-18 June 1986</u>								
3	45±21	19±8	l.e.	1.6±0.8	22±1	0.3±0.2	0.5±0.1	2.0±0.5
7	41±4	17±2	9.5±1.5	1.6±0.7	8±1	0.3±0.2	0.1±0.3	3.8±1.6
6	64±2	20±1	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
9	78±2	37±1	l.e.	0.5±0.4	7±3	1.1±0.6	2±9	0.2±0.4
10	193±4	93±2	l.e.	23.8±0.6	17±3	3.9±0.9	2.1±0.7	44±3
13	41±4	19±2	30±6	6.3±0.4	10±2	0.9±0.3	1±5	10±3
15	56±1	27±1	19±4	3.9±0.5	7±1	0.7±0.3	1±4	6±4
<u>7-13 September 1986</u>								
21	118±3	56±1	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
22	119±2	60±1	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
23	148±4	70±2	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
<u>19-23 September 1986</u>								
8	60±2	29±1	16±9	1.7±0.6	8±5	0.5±0.5	0.5±0.5	1±1
10	183±2	92±1	28±1	15.3±0.4	9±1	2.2±0.4	2±1	26±2
24	250±2	126±1	47±2	21±1	12±1	2.8±0.5	1.6±0.5	34±3

Table 1b. Percent particulate (filter activity/total activity)

Sta. No.	<sup>137</sup> Cs	<sup>134</sup> Cs	<sup>106</sup> Ru	<sup>144</sup> Ce	<sup>239,240</sup> Pu	<sup>238</sup> Pu	<sup>241</sup> Am	<sup>242</sup> Cm
<u>14-18 June 1986 (b)</u>								
3	0.02±0.01	(c)	l.e.	11±6	9±1	(d)	0±15	0±10
7	0.05±0.01	(c)	6±2	18±18	7±2	(d)	11±22	13±1
6	0.12±0.01	(c)	n.c.	n.c.	n.c.	(d)	n.c.	n.c.
9	0.05±0.01	(c)	l.e.	10±17	3±2	(d)	1±8	0±10
10	0.03±0.01	(c)	l.e.	11±1	3±1	(d)	11±5	19±2
13	0.06±0.01	(c)	2±1	9±1	2±1	(d)	2±5	3±1
15	0.05±0.01	(c)	3±1	9±2	3±1	(d)	0±15	16±10
<u>7-13 September 1986</u>								
21	0.06±0.005	(c)	n.c.	n.c.	n.c.	(d)	n.c.	n.c.
22	0.06±0.005	(c)	n.c.	n.c.	n.c.	(d)	n.c.	n.c.
23	0.07±0.005	(c)	n.c.	n.c.	n.c.	(d)	n.c.	n.c.
<u>19-23 September 1986</u>								
8	0.17±0.03	(c)	0±3	20±16	3±3	(d)	0±15	0±10
10	0.06±0.01	(c)	4±1	11±1	3±1	(d)	17±13	22±4
24	0.07±0.01	(c)	0.9±0.5	9±1	2±1	(d)	3±16	3±1

(a) = Data reported as either Bq/m<sup>3</sup> or mBq/m<sup>3</sup> ( $\times 10^{-3}$  Bq/m<sup>3</sup>), and decay corrected to 1 May 1986. All data reported with a propagated error which includes one sigma counting uncertainties and an uncertainty associated with the large volume cartridge collection efficiencies as described in (12).

(b) = Particulate data corrected to account for differences between June (cotton) and September (polyethylen) wound cartridge filters due to direct adsorption of activity onto the cotton filters (23).

(c) = See <sup>137</sup>Cs.

(d) = See <sup>239,240</sup>Pu.

n.c. = Not collected; i.e., at these stations, only Cs cartridge data are available.

l.e. = Poor quality data due to low absorption of Ru by MnO<sub>2</sub> cartridge.

representative of the values throughout the surface mixed layer. Even the June sampling was sufficiently long after the input to have allowed substantial dilution and mixing in this layer. An indication of the extent of vertical penetration through physical mixing and transport can be seen from the profiles of  $^{137}\text{Cs}$  concentrations, temperature, and salinity at a station north of the Bosphorus (station 24) in September 1986 (Fig. 2). Below the mixed layer, defined by the break in the temperature profile, the levels of  $^{137}\text{Cs}$  are consistent with pre-Chernobyl bomb fallout values - a conclusion supported by the absence of  $^{134}\text{Cs}$  in any of these deeper samples. No Chernobyl Cs isotopes are therefore detectable in the higher salinity deeper layers representing water entering by the Mediterranean inflow.

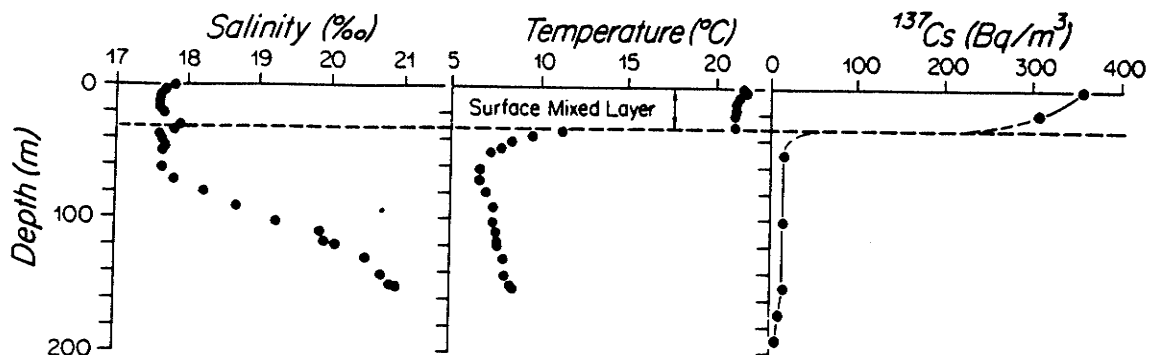


Figure 2. Vertical profiles of salinity (‰), temperature (°C) and  $^{137}\text{Cs}$  (Bq/m<sup>3</sup>) at station 24 in September 1986.  $^{134}\text{Cs}$  (not shown) levels are zero below the surface mixed layer.

The measured Chernobyl  $^{137}\text{Cs}$  inventory at station 24 was 11.2 kBq/m<sup>2</sup> (304 mCi/km<sup>2</sup>) in September 1986. The total Chernobyl  $^{137}\text{Cs}$  inventory in the upper mixed layer may be compared with the total bomb fallout  $^{137}\text{Cs}$  deposition to the latitude of the Black Sea - estimated by conversion of  $^{90}\text{Sr}$  deposition data (14) (by multiplication by 1.5) to be 2.69 kBq/m<sup>2</sup> (72.5 mCi/km<sup>2</sup>) as of 1 May 1986. Our preliminary assessment, based on the assumption that the surface measurements at all stations can be scaled to mixed layer values (as in Fig. 2), would suggest that  $^{137}\text{Cs}$  deposition from Chernobyl in the southern Black Sea was in range of 1-4 times that delivered from fallout from nuclear weapons testing. This estimate also assumes that all the measurements made on the June/September 1986 samples represent direct deposition of Chernobyl fallout to the Black Sea, as opposed to any subsequent additions via riverine input.

The trend with time in surface Cs isotope concentration at some of the sampling locations is also relevant to physical mixing. At most of the southwestern Black Sea stations sampled in both June and September,

the concentrations of Cs isotopes were found to have risen sharply and significantly between the two sampling intervals. Our inclination at present is to interpret this change in the context of variability in deposition to the Black Sea. Due to the rapidity of the surface circulation, the water sampled in September is likely to have been at a more northerly location in the Black Sea in June and would have been transported to the sampling positions in the cyclonic gyral circulation. This scenario would imply that deposition in the northern Black Sea may have been higher than in the south. This situation is supported by meteorological models which show higher deposition of Chernobyl fallout to the northern vs. the southern Black Sea (15).

### Composition of Chernobyl Fallout in the Black Sea

It has been widely recognized that not only was the depositional pattern of Chernobyl radioactivity highly variable throughout Europe but so also was the isotopic composition of the release over the time course of the accident (1,3,16). Krey et al. (3) addressed this question using data for the isotopic composition of Chernobyl fallout in soil, vegetation and other materials from various sampling locations throughout Europe. These authors divided the isotopic compositional types observed on the basis of whether the nuclide mixture was enriched in refractory nuclides (represented by  $^{103}\text{Ru}$ ) or volatile nuclides (represented by  $^{131}\text{I}$ ).

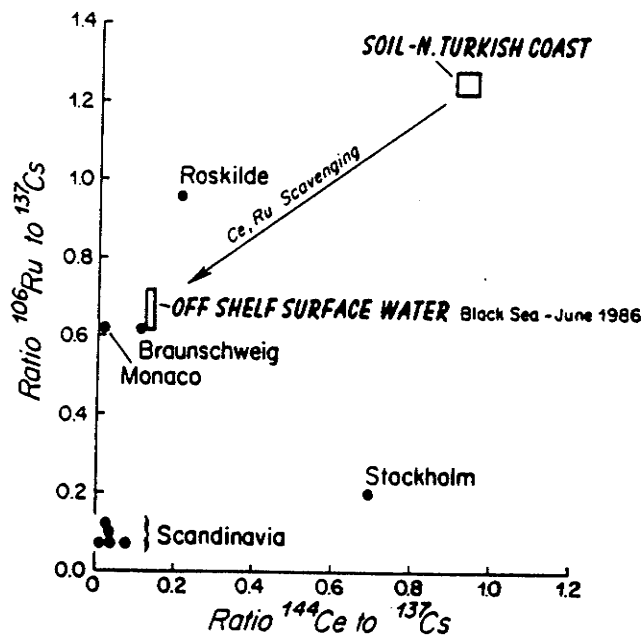


Figure 3. Composition of Chernobyl fallout in the Black Sea region - comparisons with other European locations. See text for discussion.

We attempted to describe the nature of the isotopic composition of Chernobyl radioactivity deposition in the Black Sea using a similar approach. In our approach we plotted in Figure 3  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$  data at various points in Europe from Krey et al. (3) normalized as their activity ratio to  $^{137}\text{Cs}$ . This approach revealed that differing degrees of enrichment of  $^{106}\text{Ru}$  or  $^{144}\text{Ce}$  were found at different points, e.g. Stockholm (relatively  $^{144}\text{Ce}$  rich), Roskilde, Denmark (relatively  $^{106}\text{Ru}$  rich).

We only have Chernobyl radioactivity deposition data from one location in the vicinity of the Black Sea - from Kefken Island on the northwestern Turkish coast (17). These data are plotted in Figure 3 and represent fallout rich in both  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$ . If this sample is representative of Chernobyl fallout delivered to the Black Sea, it would imply a refractory isotope-rich deposition.

It is not possible to compare this soil sample radionuclide composition directly to fallout detected in the surface waters of the Black Sea. The difficulty lies in the fact that the particle reactive nuclides  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$  have been exposed to preferential removal processes through particle scavenging. The effect of this is to lower the ratios of  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$  to  $^{137}\text{Cs}$  relative to their deposition ratios. Our  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$  data are from large volume surface samples pumped through particle filters and manganese dioxide impregnated filter absorbers (4,11). As will be mentioned later, the least affected surface waters sampled with respect to their scavenging history are the offshelf (i.e., from stations at water depths >200 m) samples collected in June. The data for total  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$  relative to  $^{137}\text{Cs}$  in the surface waters at offshelf stations 10 and 13 are plotted in Figure 3 and are found to be depleted in both  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$ , relative to the soil sample. If the composition of the soil sample was representative of that delivered to the Black Sea, one could conclude that substantial removal of both  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$  had occurred by the June cruise. The alternate explanation is that these water masses had received less  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$ -rich fallout than that delivered to the soil of the Northwest Turkish coast. Recently reported data (18) would tend to favor the former hypothesis. Also, data to be presented subsequently on nuclide particle association and removal rates would be more consistent with this scavenging explanation rather than that of input variability.

Since transuranics were not determined in the Kefken Island soil sample, it is not possible to make a similar comparison. However, the high  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios and readily measurable  $^{242}\text{Cm}$  in several surface water samples in Table 1 are clear indications that transuranics originating from the Chernobyl source had reached the Black Sea.

#### Reactive Nuclide Particle Association and Removal Rates

The particle reactivity of any element in seawater is reflected by the extent to which it associates with particulate suspended material which in turn is thought to be correlated with the residence time or removal rate of the element from surface waters (19). Our large volume surface samples were first filtered through a 0.5 micrometer wound fiber filter cartridge. This filter cartridge has been used in fallout studies in the Atlantic to measure actinide partition between particulate and dissolved phases (20). The fractions of each nuclide in each phase are measured and calculated using the same approach described by Livingston and Cochran (20). The particulate data obtained for  $^{137}\text{Cs}$ ,  $^{106}\text{Ru}$ ,  $^{144}\text{Ce}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ , and  $^{242}\text{Cm}$  are shown in Table 1(b) as the particulate nuclide percentages of the surface water activity found on particles relative to the total activity. In both cruises, and including stations located both on and off the shelf, the median fraction of the total surface radionuclide found on filtered particles increased in order:  $^{137}\text{Cs}$  - 0.1%;  $^{106}\text{Ru}$  - 3%;  $^{239,240}\text{Pu}$  - 3%;  $^{144}\text{Ce}$  - 9%;  $^{242}\text{Cm}$  - 22% (or 3% for  $^{242}\text{Cm}$ ; see later discussion). This partition pattern indicates that the fallout from

Chernobyl in the Black Sea which we observed had entered into the system and become highly solubilized in a manner consistent with the chemistries of each radioelement.  $^{137}\text{Cs}$ , for example, was almost entirely in the soluble phase and, as with the case of bomb fallout  $^{137}\text{Cs}$ , will act as a tracer of pure physical mixing and transport processes. At the other extreme,  $^{144}\text{Ce}$  and  $^{242}\text{Cm}$  exhibited relatively strong particle associations and their geochemistries will therefore be strongly controlled by particle cycling and sinking processes. For comparison, particulate  $^{230}\text{Th}$  in much of the Northwest Atlantic Ocean water columns, represents about 15% of the total  $^{230}\text{Th}$  concentration (20). Certainly Ce, with redox chemistry involving both  $^{\text{III}}\text{Ce}$  and  $^{\text{IV}}\text{Ce}$ , appears to resemble Th in its particle affinity.

### $^{144}\text{Ce}$ removal from surface waters

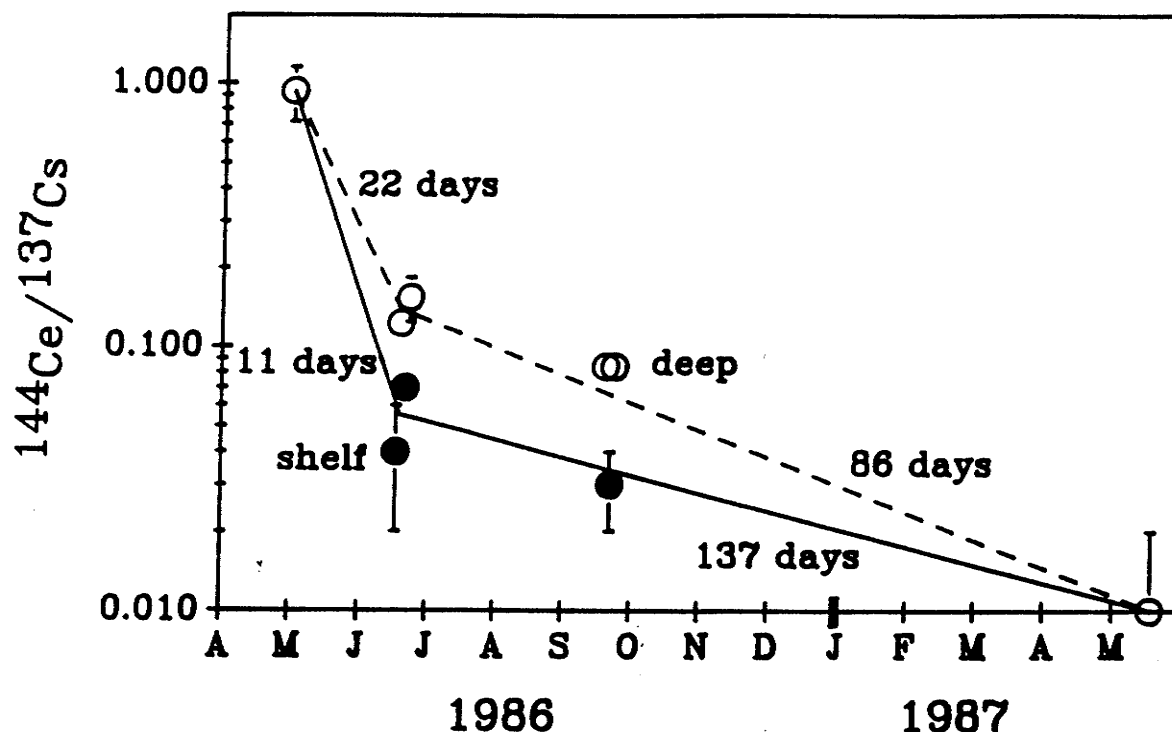


Figure 4. Plot of  $^{144}\text{Ce}/^{137}\text{Cs}$  activity ratios in surface water with time. Open circles represent off-shelf and filled circles shelf samples, respectively. The value for 1 May represents a soil  $^{144}\text{Ce}/^{137}\text{Cs}$  ratio. Half-removal time for  $^{144}\text{Ce}$  is calculated and shown for the different time periods and sample types.

A final clue to the differing reactivities of the various Chernobyl radionuclides follows from their associations with sinking particle fluxes (6,7) and the temporal pattern of their removal from the surface of the Black Sea. The latter question is first addressed through data on  $^{144}\text{Ce}/^{137}\text{Cs}$  ratios in surface water - plotted in Figure 4. Shown in this figure are the ratios of these nuclides to  $^{137}\text{Cs}$  measured in the soil sample from the Northwest Turkish coast (17) and in surface waters in the southwestern



Black Sea sampled in June and September 1986, and preliminary data from May 1987. The soil  $^{137}\text{Cs}$  data were adjusted to subtract pre-Chernobyl fallout  $^{137}\text{Cs}$  - using a  $^{134}\text{Cs}/^{137}\text{Cs}$  ratio of 0.53, and all data are decay corrected to 1 May 1986. The ratios in the soil are taken to represent the input ratios to the Black Sea from Chernobyl fallout. The use of the nuclide ratio of  $^{144}\text{Ce}$  normalized to  $^{137}\text{Cs}$ , removes the effects of physical mixing with respect to isotope concentration changes. The resultant ratio changes thus represent either removal through scavenging or input compositional variability. For the purposes of this discussion, we assume that the input isotopic composition to the Black Sea is constant. Using a vertical scavenging model with first-order removal kinetics, the removal rates can be calculated from the slope of the  $^{144}\text{Ce}/^{137}\text{Cs}$  ratio change with time ( $\partial N/\partial t = -kt$ , where  $k$  = removal rate and  $\ln 2/k$  = half-removal time).

The first point to note is the pattern of lower ratios on samples collected at stations on the shelf of the southern Black Sea. This trend is in keeping with the open ocean/coastal ocean trend reported for many other reactive species such as  $^{210}\text{Pb}$ ,  $^{234}\text{Th}$ ,  $^{238}\text{Th}$ ,  $\text{Pu}$ , etc. (e.g., for  $^{228}\text{Th}$  see Li et al. (21)). The trend is caused by the combination of higher productivity and suspended particle concentrations on the continental shelves which results in the enhanced scavenging of particle reactive elements in coastal regions.

Secondly, during the five months following input to the Black Sea of fallout from Chernobyl, substantial removal of the reactive  $^{144}\text{Ce}$  is implied by the observed reduction in its ratio to  $^{137}\text{Cs}$  in these surface waters. The ratios for  $^{144}\text{Ce}/^{137}\text{Cs}$  over the 150-day interval between May and September 1986 vary by a factor of roughly 10 and 30 for the deep and shelf locations, respectively. If the assumptions above are correct,  $^{144}\text{Ce}$  removal would appear to be a two component process - an initially rapid step with half-removal times of 11 and 22 days for shelf and deep stations respectively, followed by slower removal rates with about three to four month half-removal times. There are too little data to permit elucidation of the nature of this apparent two stage removal process. Obvious candidates to consider are the effects of spring coccolith blooms (8) or differences in the rate of  $^{144}\text{Ce}$  removal related to redox chemistry, i.e. faster initial removal of  $\text{IVCe}$ , for example.

The continued scavenging of Ce with time is supported by our most recent  $^{144}\text{Ce}$  surface water data from May of 1987, approximately one year after the Chernobyl fallout inputs. Using the  $\text{MnO}_2$  cartridge technique and gamma spectrometry, essentially no  $^{144}\text{Ce}$  could be detected ( $^{144}\text{Ce}/^{137}\text{Cs} = 0.1 \pm 0.1$ ). This fits the 1986 summer trends and results in a calculated half-removal time of 87-137 days at all sites.

The corresponding change for  $^{106}\text{Ru}/^{137}\text{Cs}$  is a little less than a factor of 2 between May and September 1986. The behavior of the  $^{106}\text{Ru}$  in the Black Sea will obviously be closely dependent on its oxidation state and chemical speciation. Our data do not speak directly to this question, but clearly the chemical form cannot be such as would cause particle association and removal as rapidly as would be found for trivalent or tetravalent actinides or lanthanides. Preliminary data for May 1987 suggest that the ratio change  $^{106}\text{Ru}/^{137}\text{Cs}$  since September 1986 is not more than a further factor of 2.

The few transuranic data in Table 1 may be viewed in like manner for their removal patterns from surface water. Only the Pu and Cm data had analytical uncertainties which were of satisfactory quality. As no transuranic analyses were made on the Kefken Island soil sample (17), changes in observed ratios relative to soil values could not be made.  $^{242}\text{Cm}/^{137}\text{Cs}$  ratios declined from  $0.23 \times 10^{-3}$  in June (stations 10,13) to  $0.14 \times 10^{-3}$  in September (stations 10,24). The direction and magnitude of this change is not unlike that noted above for  $^{144}\text{Ce}$  and would result in a calculated half-removal time of 124 days. Curiously,  $^{242}\text{Cm}$  partitioning between dissolved and particulate phases of surface water varied more than was found for  $^{144}\text{Ce}$ . Although total  $^{242}\text{Cm}/^{137}\text{Cs}$  ratios in surface water at stations 13 and 24 were similar to those found at station 10, much smaller fractions of  $^{242}\text{Cm}$  were associated with filterable particulates at stations 13 and 24 - ~3% at stations 13 and 24 as opposed to 19% and 22% at the two occupations of station 10. Particulate data for  $^{242}\text{Cm}$  at the other stations were mostly accompanied by rather large analytical uncertainties. These low values appear anomalous and we presently do not have an explanation to offer. It is worth noting that a low value for  $^{106}\text{Ru}$  partition was also observed at station 24.

The fraction of surface  $^{239,240}\text{Pu}$  associated with a filterable phase was observed to range from 2-3% for the samples in the Black Sea. The higher values at stations 3 and 7 lie in the Aegean and Sea of Marmara. These values are very similar to the oceanic partition observed for Pu derived from atmospheric weapons testing fallout in the western North Atlantic Ocean (20). The higher particle association observed for  $^{242}\text{Cm}$  over Pu in Black Sea water parallels the higher values for  $^{241}\text{Am}$  relative to Pu in the western North Atlantic (20). This trend is in accord with the strong chemical similarity between Am and Cm and their stronger particle associations relative to Pu.

A significant fraction of the observed surface Pu concentrations in the Black Sea can be calculated to derive from Chernobyl fallout on the basis of the observed  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios of 0.09-0.24. This can be estimated assuming a two source model of Pu input, with a  $^{238}\text{Pu}/^{239,240}\text{Pu}$  end member ratio of 0.036 and 0.55 (22) for global weapons testing and Chernobyl fallout, respectively. At station 10 for example, in September 1986 one calculates that approximately 40% of the Pu in the surface waters originated from the Chernobyl source. All of the observed  $^{242}\text{Cm}$  has to derive to from Chernobyl as it is not present in atmospheric weapons testing fallout (due to its short half-life of 0.4 years).

On the basis of the observed distributions of these transuranic elements between particle and solution phases of Black Sea surface water it may be concluded that the transuranics deposited there from the Chernobyl accident have entered the biogeochemical cycle in a similar fashion to transuranics from global fallout. This rapid entry of Chernobyl nuclides into biogeochemical cycles is in fact noted for all the nuclides we have observed and hence allows them to be used as tracers of their stable elemental analogues in those cycles.

#### SUMMARY

Measurements of  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ ,  $^{144}\text{Ce}$ ,  $^{106}\text{Ru}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ , and  $^{242}\text{Cm}$  introduced to waters of the southern Black Sea are described. Surface  $^{137}\text{Cs}$  concentrations in June and September 1986 are in the range 40

to 250 Bq/m<sup>3</sup> - between one or two orders of magnitude greater than the pre-existing bomb fallout <sup>137</sup>Cs signal. At that time, Chernobyl Cs isotopes were confined to the surface mixed layer. Inventory estimates suggest that the Chernobyl <sup>137</sup>Cs input may range from one to four times that from nuclear weapons testing fallout to the region. The composition of the Chernobyl fallout delivered to the Black Sea appears relatively enriched in the refractory radionuclides, such as <sup>144</sup>Ce and <sup>106</sup>Ru. The behavior of the various radionuclides appears predictable on the basis of their known elemental geochemical behavior. The reactivities with respect to surface water particle association increase in order <sup>137</sup>Cs (0.1%), <sup>106</sup>Ru (3%), <sup>239,240</sup>Pu (3%), <sup>144</sup>Ce (9%), and <sup>242</sup>Cm (20%). Rates of removal from surface water would be in the reverse order to this sequence, with higher removal rates being found in shelf as opposed to deep water locations.

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