Variation of Cesium in the Ocean

Abstract. *Samples of sea water from several oceans and several depths were analyzed for natural cesium by flame photometry with precision of about 3.5 percent. The average of 16 assays of surface water from four oceans was 0.37 microgram per liter, somewhat less than the average previously reported. The average cesium concentration in samples taken between 500 and 1500 meters was about 14 percent higher than the surface average, suggesting that cesium may be transported downward by particulate material. Natural cesium is now somewhat easier to study in the ocean than radiocesium from fallout is, and information on one complements the other.*

Very few analyses have been made of natural cesium in the sea. Its oceanwide distribution has not been reported. Recent reports are in disagreement with earlier ones. Measurements by Smales and Salmon (*1*) in 1955 yielded an average concentration, for one area in the North Atlantic, of 0.5 μg/liter whereas the mean value of 2.0 μg/liter has stood in the literature for many years (*2*). Reported with these newer measurements were concentrations for several depths at one station; however, variation with depth was less than the experimental error. Until recently it was almost as difficult to measure natural cesium as radioactive cesium in the ocean, at least in surface waters. Fortunately, a rapid and economical procedure for concentrating cesium has been developed at Oak Ridge National Laboratory (*3*) as well as a flame photometer specialized for use in the infrared; hence analyses of sea water can now be carried out with replication precision of about ± 3.5 percent, even with relatively small samples.

Two liters of sea water were placed in contact with solid microcrystalline phosphomolybdate (*3*). The solid phase was dissolved with NaOH, and the cesium was then extracted with a hexone-hexane solution of sodium tetraphenyl boron. The extract was burned in an oxyhydrogen flame before a grating spectrometer provided with a photomultiplier having high sensitivity to the 8521.1 Å line of cesium. Chemical yield was monitored initially by adding cesium-137.

Twenty samples of water from four oceans were analyzed. They were originally collected in 50-liter polyethylene carboys for studying the distribution of radioactive cesium; no carrier or acid was added at sea. The 2-liter portions were filtered through Whatman No. 1 paper. Table 1 presents the concentrations of cesium measured, and also the values reduced to a standard salinity of 35.000 per mil. Also shown are the results of replicate analyses made on one sample of coastal water to test experimental precision.

In these studies, salinities vary from 34.033 to 37.515 per mil. Nevertheless, Table 1 indicates a variation in cesium concentration that is surprisingly small for a trace element appearing in the sea in less than one part per billion. This is remarkable because cesium is reported to be concentrated by tissues of some marine organisms (*4*) and still more strongly by clays and zeolites (*5*) that appear in marine sediments.

Smales and Salmon (*1*) likewise found no significant variation in cesium concentrations in surface and deep waters collected in a region near 48° to 49°N, 6° to 15°W. They analyzed eight surface samples, obtaining an average of 0.47 μg/liter with dispersion of ± 0.06. Samples taken by a vertical cast at depths of 20, 1200, 2000, 3000, and 4000 meters yielded an average concentration of 0.51 μg/liter with standard deviation of 0.47. Accuracy "generally better than 10 percent" was claimed for these analyses in which neutron activation was utilized.

It is unfortunate that these workers did not also analyze specimens from depths between 20 and 1200 meters because our data (Table 1) indicate a

Table 1. Variation of natural cesium in the oceans.

Date	Latitude	Longitude	Depth (m)	Cesium (μg/lit.)	Salinity (per mil)	Corrected cesium	(μg/lit.)*	(at 35 sal.)
				Western Pacific				
26 May 1962	34°45.6′N	170°13.5′W	0	0.34†	34.703	0.34		
27 May 1962	35°05′N	180°00′W	0	0.35‡	34.863	0.35		
27 May 1962	35°05′N	180°00′W	500	0.41	34.033		0.42	
27 May 1962	35°05′N	180°00′W	1000	0.32	34.286		0.33	
27 May 1962	35°05′N	180°00′W	1500	0.40	34.429		0.41	
					Surface mean	**0.35**		
					500-, 1000-, 1500-meter mean		**0.39**	
					Mean of all			**0.37**
				Eastern Pacific				
16 April 1962	27°16.5′N	125°34′W	0	0.35§	34.492	**0.36**		
16 April 1962	27°16.5′N	125°34′W	500	0.41	34.143		0.42	
16 April 1962	27°16.5′N	125°34′W	750	0.38	34.360		0.39	
16 April 1962	27°16.5′N	125°34′W	1000	0.42	34.496		0.43	
					500-, 750-, 1000-meter mean		0.41	
				South Pacific				
24 May 1962	10°15.2′S	160°55.6′E	0	0.36	34.546	0.37		
28 May 1962	11°57.2′S	166°13.1′E	0	0.34‖	34.551	0.34		
19 June 1962	9°56.4′S	173°46′E	0	0.33	34.568	0.33		
					Surface mean	0.35		
				North Atlantic				
20 July 1962	24°36′N	37°29′W	0	0.46	37.515	0.43		
24 July 1962	26°41.6′N	22°56.1′W	0	0.38¶	37.051	0.36		
29 July 1962	33°35.4′N	9°43.2′W	0	0.39	36.504	0.37		
29 July 1962	33°35.4′N	9°43.2′W	4000	0.38	34.898		0.38	
					Surface mean	0.39		
					Mean of all			**0.39**
				Southern Indian				
22 May 1963	18°01′S	40°51′E	0	0.33	34.639	0.33		
22 May 1963	18°01′S	40°51′E	2500	0.35	34.932		0.35	
				South Atlantic				
23 June 1963	19°44′S	12°54.2′W	0	0.36	36.504	0.35		
23 June 1963	19°44′S	12°54.2′W	3000	0.34	34.903		0.34	

Mean of all concentrations:	0.37±0.035
Mean of all surface values:	0.35±0.024
Mean of six samples, 500 to 1500 meters:	0.40±0.037
Mean of three samples, 2500 to 4000 meters:	0.36±0.021

Replication tests with coastal eastern Pacific water, sample from Scripps Pier, La Jolla, Calif.
Average of seven replicates, 2 liters each: 0.335±0.012 or ±3.5 percent

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* Corrected for a salt concentration of 35 per mil. † Average of two assays 1 month apart, 0.31 and 0.36. ‡ Average of two assays 1 month apart, 0.31 and 0.34. § Average of two assays on same day, 0.35 and 0.35. ‖ Average of two assays on same day, 0.32 and 0.35. ¶ Average of two assays 1 month apart, 0.38 and 0.38.

significant increase in concentration at this depth interval at two stations. Five of the six measurements between 500 and 1500 meters showed cesium concentration substantially higher than the local surface concentrations; and the mean for this depth band is more than 14 percent higher than the mean for all surface concentrations.

Slight maxima have been reported at depths of 500 to 1500 meters for other trace elements; for example, bulges in the profile of the concentrations of radium and uranium have been reported (*6*), amounting to about 10 percent of the surface value. Concentrations of such nutrients as nitrates and phosphates that are consumed by marine microorganisms often exhibit maxima at these depths. One common explanation is that degeneration of particulate size takes place at these depths, so that the rate of descent decreases. A maximum in cesium concentration at these depths, therefore, suggests that downward transport of cesium by organisms should not be overlooked. There is also the possibility that the penetration of fallout cesium may be influenced by attachment to organisms or to inorganic particles carried by them. Certainly, more sampling of natural cesium and fallout cesium at the intermediate depths should be made to resolve this question.

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References and Notes

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Nicotinic Acid Analogs: Effects on Response of Chick Embryos and Hens to Organophosphate Toxicants

Abstract. *Embryonic abnormalities are known to be induced in chick embryos when they are injected with certain organophosphate insecticides prior to incubation. The marked teratogenic effects of* Bidrin *[3-(dimethoxyphosphinyloxy)* N,N*-dimethyl-cis-crotonamide] can be alleviated by many analogs of nicotinamide and nicotinamide adenine dinucleotide. Successive hydroxylation and* N*-dealkylation of Bidrin in the egg are not greatly altered by injection of nicotinamide. The delayed neurotoxicity in adult hens after administering tri-*o*-cresyl phosphate is also partially relieved by administering certain nicotinamide analogs.*

Certain biological effects of toxic organophosphates appear to be unrelated to the inhibition of acetylcholinesterase activity in the nervous system. These include, among others, a teratogenic effect in the developing chick embryo (*1, 2*) and a neurotoxicity with associated axonal degeneration and demyelination in certain tracts of the central and peripheral nervous system as found in hens in which the syndrome has been studied most extensively (*3*). The teratogenic effect of malathion (*S*-[1,2-bis-(ethoxycarbonyl)ethyl] *O,O*-dimethyl phosphorodithioate) with chick embryos was potentiated by EPN (*O*-ethyl *O-p*-nitrophenyl phenylphosphonothioate), TOCP (tri-*o*-cresyl phosphate), and 2-ethylhexyldiphenyl phosphate (*2*). Paralysis was observed in some chicks hatched from eggs that had been injected with 10 mg of TOCP (*1*). Teratogenic effects in chick embryos are also produced by certain carbamates (*2, 4*), and nicotinamide offers near complete protection against such action of eserine (*5*). No studies have been reported on attempts to alleviate the teratogenic effects of organophosphates with selected biochemicals, but extensive trials in which prophylactic agents for the neurotoxic effect were sought have not been successful (*6*).

A series of vinyl phosphates was injected at the rate of 1 mg per egg into the yolk sac of fertile eggs prior to incubation according to a described procedure (*1*). The hatching ability and the condition of the chicks on hatching, or the appearance of the embryos at 21 days if hatching was unsuccessful, were then observed. Some of the vinyl phosphates always caused marked teratogenic effects. The condition of the embryo in the most extreme cases included complete lack of feathers, parrot beak, shortening and deformation of the legs and spine, edema, growth retardation, and, rarely, syndactylia; all these symptoms have been reported with certain other organophosphates (*2*). Thirteen vinyl phosphates of the type $(R_1O)_2P(O)OC(R_2) = C(R_3)(R_4)$ were examined (*7*). The four most active materials were (R_1, R_2, R_3, R_4): Me, Me, H, C(O)NMe$_2$ or Bidrin; Me, Me, H, C(O)NEt$_2$; Et, Me, H, C(CO)NMe$_2$; and Me, Me, H, C(O)NHMe. The teratogenic effect was less marked with Et, H, H, Cl and Me, Me, Cl, C(O)NMe$_2$, and even higher doses were required for activity with Et, Me, H, C(O)OEt and Me, Me, Cl, C(O)NEt$_2$, or phosphamidon. The following insecticides were inactive, even when injected at the rate of 10 mg per egg: Me, Me, H, C(O)OMe or mevinphos; Me, Me, H, CH(Me)Ph or Ciodrin; Me, H, Cl, Cl, or dichlorvos; Me, OMe, Cl, Cl; and Et, 2,4-Cl$_2$Ph, H, Cl. Also inactive were a variety of possible phosphorus-containing and nonphosphorus-containing hydrolysis products of Bidrin. Teratogenic effects were occasionally observed when 100 μg per egg of the *cis*-crotonamide isomer of Bidrin was injected, and always when 300 μg or more of Bidrin was injected per egg. The severity of effect increased progressively with higher doses. The effect was evident when Bidrin was injected during the first 6 days of incubation, but not after 9 days of incubation.

A number of vitamins and other biochemicals were assayed by simultaneously injecting 1 mg of Bidrin and 1 mg of each substance per egg prior to incubation to ascertain their possible effects in relieving the teratogenic symptoms. Only nicotinic acid analogs or potential precursors thereof were active, many of them yielding embryos normal in appearance at 21 days although hatching was usually unsuccessful. As little as 30 μg of nicotinic acid or nicotinamide per egg was active. Nicotinamide adenine dinucleotide (NAD) and its 3′-phosphate in both their oxidized and reduced forms were very active, as were certain analogs of NAD and nicotinic acid esters and amides.