Reports

Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents

Abstract. *Ion exchange, gel filtration chromatography, and gas chromatography–mass spectrometry analyses have demonstrated that ethylenediaminetetraacetic acid (EDTA), an extremely strong complexing agent commonly used in decontamination operations at nuclear facilities, is causing the low-level migration of cobalt-60 from intermediate-level liquid waste disposal pits and trenches in the Oak Ridge National Laboratory burial grounds. Because it forms extremely strong complexes with rare earths and actinides, EDTA or similar chelates may also be contributing to the mobilization of these radionuclides from various terrestrial radioactive waste burial sites around the country.*

From 1951 through 1965, intermediate-level radioactive liquid waste at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee, was disposed of in seven different seepage pits and trenches (*1*). Since 1944, solid waste at ORNL has routinely been buried in shallow trenches in six different burial grounds (*2*). Ground burial of radioactive waste is an effective means of disposal if the radionuclide can be confined to the geologic column through geochemical processes. Although the Conasauga shale, the predominant bedrock of the ORNL burial grounds, has an extremely high adsorption capacity for most fission by-products, trace quantities of certain radionuclides are migrating from both solid and liquid waste disposal sites (*3*).

Several factors have contributed to the radionuclide mobilization. One is that the annual precipitation at ORNL, over 127 cm, is greater than at any other radioactive waste burial site in the country (*2*). As a result, water infiltrates into trenches at a faster rate than it can be dissipated and mixes with the waste. In addition, groundwater levels are comparatively shallow and a high-density surface drainage network is present. There is also an abundance of fractures in the underlying rock, which diminishes the rock's sorptive capacity because the exchange sites adjacent to the fissures are saturated with the exchangeable ions in the waste (*2*). Finally, the presence in the waste of complexing agents such as organic chelates used in decontamination operations and natural organic acids from the soil promotes the formation of strong complexes with certain radionuclides that reduce the adsorption capacity of the shale and soil for the radionuclide.

It is this last factor that is of principal concern in this report. The isotope ^{60}Co has been found in concentrations up to 10^5 dpm/g in the soil and up to 10^3 dpm/ml (450 pCi/ml) in the water in areas adjacent to seepage trench 7 and in lesser concentrations in the vicinity of trench 5 and pit 4 (Fig. 1). Traces of various alpha-emitters such as isotopes of U, Pu, Cm, Th, and Ra have also been detected in water or soil from the area around trench 7 (*2–4*). We show here that ^{60}Co is transported in the groundwater from the trenches and pits as organic complexes. A portion of the migrating ^{60}Co is adsorbed by oxides of Mn in the shale and soil (*4–6*). Additional evidence suggests that some U is migrating by the same mechanism.

The following experimentally measured distribution coefficients (K_d) illustrate the pronounced effects that organic ligands have on the adsorption capacity of sediment for trace metals. We determined that the K_d values for ^{60}Co in weathered Conasauga shale at *p*H 6.7 and 12.0 were approximately 7.0×10^4 and 0.12×10^4, respectively. In the presence of $10^{-5}M$ ethylenediaminetetraacetic acid (EDTA) the K_d values were reduced to 2.9 and 0.8 (*7*).

The actual K_d values calculated from ^{60}Co concentrations in soil and water from various wells in the ORNL burial grounds are similar (*8*). The K_d values for ^{60}Co from wells in the vicinity of trench 7 range from approximately 7 to 70, averaging about 35 (see Table 1). The *p*H of well water ranges from 6.0 to 8.5 (*4*), and the EDTA concentrations are approximately $3.4 \times 10^{-7}M$ (this study). Actual K_d values for ^{60}Co in burial ground waters are therefore significantly lower than the theoretical value for neutral systems containing no EDTA and are somewhat greater than the experimental value for neutral systems containing $10^{-5}M$ EDTA.

The importance of sediment sorption capacity (or K_d) on radionuclide migration rates within geologic substrates has been modeled by Marsily *et al.* (*9*). Using variables such as K_d, rock permeability, and hydraulic gradient, they calculated the migration rates of ^{239}Pu buried at the bottom of geologic formations 500 m thick. The results show that ^{239}Pu with a K_d of 2×10^3, typical of a chemical setting devoid of complexing agents, rock fractures, and similar factors tending to reduce sediment adsorption, will not migrate to ground level until more than 10^6 years after burial, the migration rates being slowest in those geologic formations with lowest permeability. With a half-life of 24,400 years, Pu would essentially be completely decayed by the time of contact with the surface environment. At the other extreme, in a chemical setting characterized by no sorption ($K_d = 0$), Pu would reach the environment in 6 to 14,500 years, depending on the permeability of the geologic formation (*9*). That is, in the most confining formation Pu would have decayed about only one-half of one half-life before it reached the surface. In formations of low to moderate permeability, migration of Pu over 500 m would have occurred in only tens to several hundreds of years, the movement being four to five orders of magnitude more rapid than in the situation $K_d = 2 \times 10^3$.

In the Oak Ridge setting, the adsorption capacity of the Conasauga shale for inorganic forms of Co is very high. Hence, mobilization of this radionuclide in the absence of strong complexing agents, rock fractures, and other factors tending to reduce sorption would be negligible. However, in the presence of strong chelates, rock fractures, and other factors tending to decrease sorption, the K_d is drastically reduced and mobilization rates may be accelerated by several orders of magnitude.

A compilation of selected radionuclide analyses for filtered water, weathered Conasauga shale, and soil samples collected between June 1974 and June 1975 from wells in seeps adjacent to pit 4, trench 5, and trench 7 is given in Table 1 (*10*). Locations of pits, trenches, and sampling sites are shown in Fig. 1.

A surprising initial observation, first

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made by E. A. Bondietti, was that ^{60}Co in groundwater did not readily exchange with cation-exchange resins (Rexyn 101, Na^+-form). Data from several samples show that only about 5 to 10 percent of the ^{60}Co could be adsorbed by the resin, the other 90 to 95 percent being retained in solution as a tightly bonded complex. It seemed apparent that whatever agent was responsible for this effect was also preventing complete adsorption of certain radionuclides by the Conasauga shale and soil.

Subsequent ion-exchange analyses that we carried out demonstrated that the strength of ^{60}Co complexes with possible inorganic groundwater components such as sulfate, nitrate, bicarbonate, carbonate, chloride, orthophosphate, and even stronger ligands such as pyrophosphate and metaphosphate was insufficient to produce the ion-exchange elution behavior of ^{60}Co observed in the samples (*11*). However, in the presence of very low concentrations ($10^{-6}M$ and less) of multidentate chelating agents such as diethylenetriaminepentaacetic acid (DTPA), cyclohexanediaminetetraacetic acid (CDTA), EDTA, and also natural organics such as humic and fulvic acids, ^{60}Co resisted adsorption by the resin.

Table 1. Selected radionuclide analyses of weathered Conasauga shale and soil and filtered water samples (0.22 μm) and corresponding K_d values from wells in the vicinity of pit 4, trench 5, and trench 7.

Well code	Date	Aqueous ^3H (dpm/ml)	Aqueous ^{60}Co (dpm/ml)	Adsorbed ^{60}Co (dpm/ml)	K_d (^{60}Co)*
RS3	24 June 1975	1280	90.0	NA†	
RS5	25 June 1975	1290	39.0	NA†	
RS7	26 June 1974	3050	669.0‡	43,700	65.3
T7-11§	31 July 1974	3930	518.0	16,900	32.6
T7-12	31 July 1974	3450	547.0	28,600	52.3
T7-13	8 August 1974	3740	816.0	24,500	30.0
T7-14	31 July 1974	1900	227.0	6,600	29.1
T7-15	31 July 1974	2090	153.0	1,060	6.9
RS9	24 June 1975	3130	80.9	NA†	

*See (*8*). †Not analyzed. ‡Water from RS7 also contains 7.5 parts per billion of U (99.3 percent ^{238}U and 0.7 percent ^{235}U). §Wells T7-11 through T7-15 are not depicted in Fig. 1. These wells are located within approximately 30 feet (9 m) of well RS7 (*4, 5*).

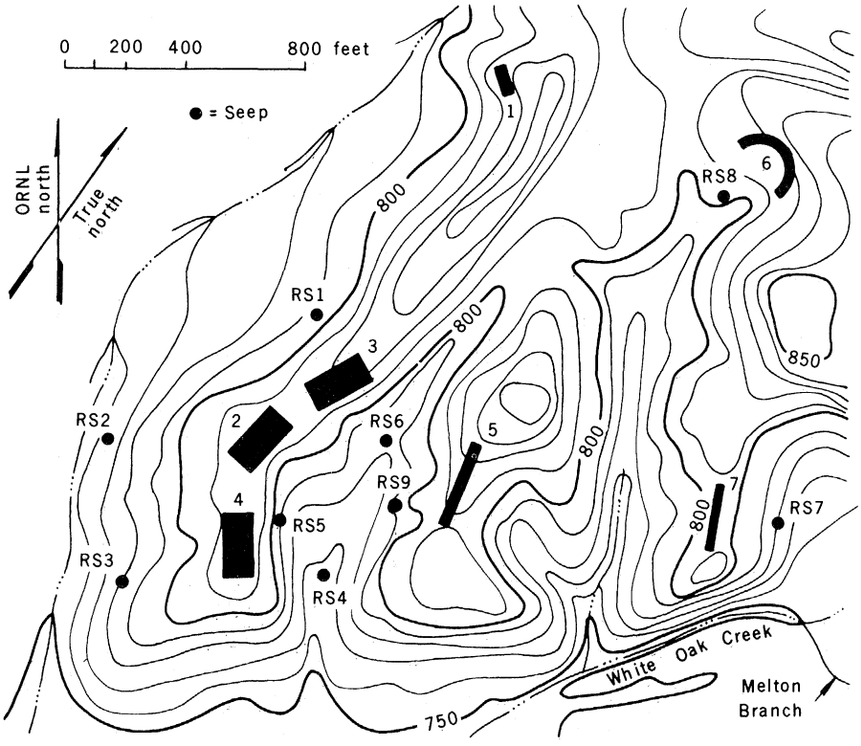

Fig. 1. Location of small seeps associated with pits 1, 2, 3, and 4 and trenches 5, 6, and 7. Contours are in feet [from (*4*)]. [Courtesy of Oak Ridge National Laboratory, Oak Ridge, Tennessee]

In order to differentiate between the radionuclide-mobilizing effects of synthetic chelates of low molecular weight and those of humic substances of higher molecular weight, we fractionated groundwater samples, using gel filtration chromatography (GFC), a process which separates solutes according to size (*12*). Since most weak inorganic, metallic complexes are sorbed during the GFC process, the presence of trace metals in a given fraction of an elution profile demonstrates an association between the trace metal and a ligand in that fraction (*13, 14*).

Elution profiles of a concentrated groundwater sample from location RS7 near trench 7 for Sephadex gels G-10, G-15, and G-25 are illustrated in Fig. 2. Each of these elution profiles contains three fractions decreasing in molecular weight to the right. The blue dextran peak coincides with the fraction of the sample having molecular weights above 700. Between 90 and 95 percent of the ^{60}Co and 70 percent of the U present in the sample are correlated with the middle fraction, which represents a group of organics with molecular weights less than 700 plus the Na^+-salts of several polyvalent anions. Between 5 and 10 percent of the ^{60}Co and 30 percent of the U are associated with the fraction having molecular weights above 700, and no ^{60}Co or U are observed with the smallest molecular weight peak, which through infrared spectrophotometry was determined to be comprised principally of $NaNO_3$ and NaCl. Reliable Pu analyses of the GFC fractions could not be obtained.

Infrared spectrophotometric data indicate that the large molecular weight fractions associated with minor ^{60}Co and U transport are humic substances. Because groundwater in and very close to the trenches is typically low in humic content, we believe that humics are not major contributors to radionuclide transport from the trenches. On the contrary, we believe that humics become associated with radionuclides some distance from the trenches, particularly in the seeps, where groundwater humic concentrations are the greatest.

After we had completed the GFC fractionations, the identities of complexing agents in the major radionuclide-bearing fractions were still unknown. We suspected that these materials were synthetic chelates, but humic substances of lower molecular weight could not be completely ruled out, particularly in view of their greater acidity and metal-complexing capacity relative to the spe-

cies of higher molecular weight (*15*).

We extracted the middle GFC fraction, which contained the largest radionuclide concentrations, with chloroform to remove compounds that would interfere in the subsequent analysis. All the radionuclide remained in the aqueous phase after the chloroform extraction. The aqueous layers were then evaporated to dryness and methylated to facilitate gas chromatography–mass spectrometry (GC-MS) analysis (*16*).

The GC profile for the methylated fraction is illustrated in Fig. 3. We used MS to demonstrate that the dominant peak represents the tetramethyl ester of EDTA, an extremely strong chelate commonly used in decontamination operations at nuclear facilities (*17*). Through use of an internal CDTA standard, the EDTA concentration of this sample has been calculated to be approximately $3.4 \times 10^{-7} M$; EDTA has also been detected in samples RS3 obtained near pit 4 and RS9 near trench 5 (*18*).

Other constituents detected in trench leachates include palmitic acid, phthalic acid (*19*), and other mono- and dicarboxylic acids, which are much weaker complexing agents than EDTA. The concentrations of strong chelates similar to EDTA, such as nitrilotriacetic acid (NTA) and DTPA, are below the detection limit of this analysis, which is approximately $5.0 \times 10^{-9} M$. Because NTA is biodegradable, it would not be expected in significant concentrations in the groundwater even if it had been originally present in the waste (*20*). Both DTPA and other multidentate chelates were used only sparingly in decontamination at ORNL during the 1950's and 1960's and consequently do not appear to be significant in the radionuclide mobilization at this site.

We thus reasoned that EDTA is the dominant mobilizing agent in samples RS7, RS3, and RS9. A minor portion of the migrating ^{60}Co and U is associated with natural organics. Ligands such as phthalic, palmitic, and other carboxylic acids may also be contributing to ^{60}Co and U mobilization to a small extent.

The identification of EDTA as a radionuclide mobilizer in the ORNL disposal area raises a question about the suitability of this chelate in decontamination operations. Although EDTA is used in decontamination because of its powerful metal-binding properties, this same characteristic also leads to radionuclide mobilization. The radionuclide mobilization caused by EDTA in the ORNL burial grounds probably does not at present impose a health hazard. However, its con-

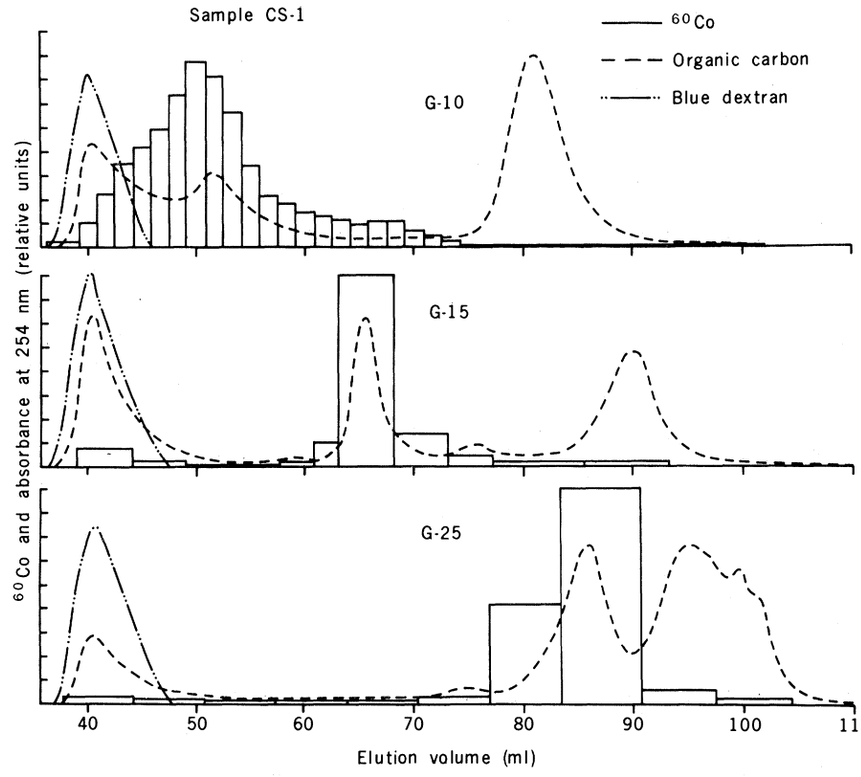

Fig. 2. The GFC elution profiles of groundwater from RS7, a small seep east of trench 7 [from (*13*)]. [Courtesy of *Limnology and Oceanography*, Seattle]

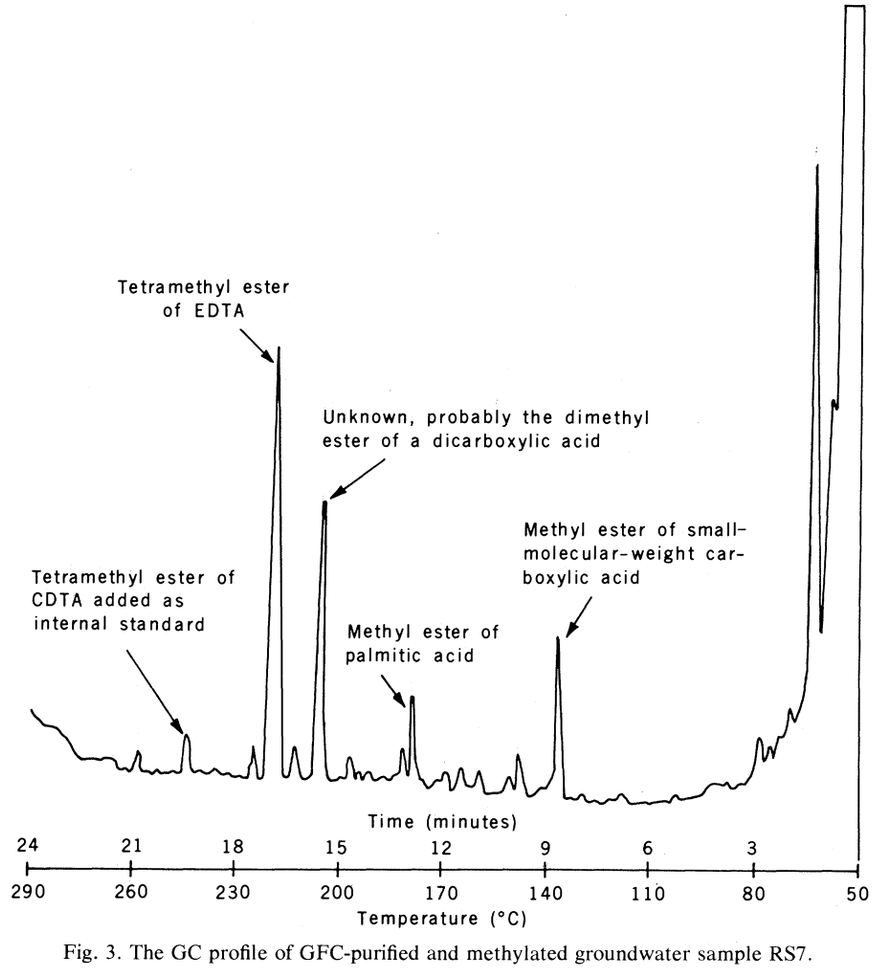

Fig. 3. The GC profile of GFC-purified and methylated groundwater sample RS7.

tinued use in decontamination operations around the country, and therefore its presence in low- and intermediate-level waste, constitutes a potential for the release of undesirable amounts of radionuclides. Because EDTA is resistant to decomposition by radiation (*21*), thermally very stable (*22*), and only slowly biodegradable (*23*), it is extremely persistent in the natural environment. Indeed, the presence of significant concentrations of EDTA in waste 12 to 15 years old attests to its persistence. Therefore, wherever EDTA and similar compounds have been introduced into terrestrial disposal sites, the aqueous transport of transition metals, rare earths, and transuranics, which characteristically form the most stable complexes with chelates, may be augmented.

There can be no question about the strong complexing capacity of EDTA and similar chelates for certain radionuclides including the rare earths and actinides. For example, all of the trivalent rare earths along with Am^{3+}, Cm^{3+}, Pu^{3+}, Pu^{4+}, Pu^{6+}, and Th^{4+} possess at least as high or higher complexity constants, K_1, for EDTA as Co^{2+} (*24*). Both EDTA and DTPA are used in the therapeutic removal of transuranics ingested by humans because of the strong complexes formed with these elements (*25*). Our evidence suggests but does not prove that EDTA is also contributing to the migration of trace levels of Pu, Am, Cm, Th, and Ra, which have been detected in the soil from seep RS7 approximately 100 yards (90 m) east of trench 7. For example, actinides were found in concentrations of 43 ± 8 dpm/g of ^{238}Pu, 110 ± 7 dpm/g of ^{241}Am, and 495 ± 20 dpm/g of ^{244}Cm in a weathered shale sample collected at a depth of 71 cm in well T7-12, which is adjacent to well RS7 (*4, 5*). In addition, chelates increase the uptake of numerous trace elements by plants. Consequently, the ecological recycling rates of certain radionuclides such as ^{239}Pu and ^{241}Am, and therefore the possibility of their entering human food chains, increases in the presence of complexing agents (*26*).

In the United States, there are six commercial and five Energy Research and Development Administration terrestrial radioactive waste burial sites which have in the past received or are currently receiving low- and intermediate-level radioactive wastes (*27*). Varying levels of radionuclide migration from original disposal sites have been observed at four of these waste burial sites other than ORNL, including the Savannah River Laboratory, South Carolina (*28*); the Hanford, Washington, facilities (*29*); West Valley, New York (*30, 31*); and Maxey Flats, Kentucky (*31*). The Chalk River facility in Canada has experienced similar migration problems (*32*). Actual migration of Pu, the presence of Pu in the dissolved fraction of leachates, and the existence of mobile Pu-contaminated leachates in waste pits have been reported at the Hanford, West Valley, and Maxey Flats facilities, respectively (*29–31*). Complexing agents are either present or suspected to be present in waste at Chalk River, West Valley, and Maxey Flats (*31, 32*).

The use of EDTA and similar compounds in decontamination operations, and therefore their presence in low- and intermediate-level waste in the United States and the rest of the world, is widespread (*21*). Throughout the world, low- and intermediate-level radioactive waste is being buried along with chemicals that are likely to cause the migration of hazardous isotopes such as Pu over the long term. Indeed, trace levels of radionuclides are being released by groundwater transport at many radioactive waste disposal sites in this country, and migration of radioactive transition metals, rare earths, and transuranics is probably being aided by chelates such as EDTA. Consequently, if the use of EDTA and similar compounds is to continue, waste solutions should be treated for the removal or destruction of the chelates prior to final disposal in the ground. Another alternative would be to use suitable substitutes, compounds that are effective in decontamination but do not facilitate radionuclide mobilization.

One such useful substitute may be NTA, which is a potential replacement for phosphates in detergents. This compound is rapidly biodegradable (*20*) and is a strong ligand, although slightly weaker in complexing capacity than EDTA.

The biodegradability of other chelates such as triethylenetetraaminehexaacetic acid (TTHA), hydroxyethylenediaminetriacetic acid (HEDTA), *N*-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEEDTA), ethylenediamine di-(*O*-hydroxyphenylacetate) (EDDHA), and DTPA is apparently not well known. Some of these compounds are stronger ligands than EDTA and therefore would be more effective in decontamination. However, the use of such compounds, if nonbiodegradable, could lead to even more migration from disposal sites than that caused by EDTA.

Numerous other alternatives to the use of EDTA and related compounds are available. Hot cells, nuclear equipment, and reactors have been decontaminated by means of a wide variety of reagents including strong acids, bases, or oxidizing agents, which can be neutralized before final burial, or relatively mild complexing agents such as citrate, tartrate, oxalate, gluconate, phosphate, bisulfate, and fluoride, which will contribute to radionuclide mobility in the environment to a much lesser extent than EDTA.

Excellent reviews of different decontamination solutions and techniques are available (*21*). Many of these reagents used either alone, in combination, or in successive treatments have been shown to be extremely effective alternatives to EDTA.

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itored the eluted fractions for radionuclide content and absorbance at 254 nm, using an in-line ultraviolet spectrophotometer. We analyzed ^{60}Co using a multichannel analyzer, and U was determined by MS, with isotope dilution.
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Breeding Patterns of Galápagos Penguins as an Indicator of Oceanographic Conditions

Abstract. *Surface water changes associated with El Niño have been known to affect deleteriously top carnivores along coastal South America. Data on the breeding strategies of Galápagos penguins and other seabirds indicate that the biological effects of El Niño extend much farther west. The breeding biology of these seabirds is adapted to frequent changes in productivity which are associated with El Niño.*

Plants and animals living along the western coast of South America are dramatically affected by an influx of warm water called El Niño (*1*). The frequency, causes, and dimensions of El Niño are not well understood. Oceanographic conditions have been monitored during El Niño, but, despite our knowledge of the extent of physical changes, little is known about the short- and long-term impact on top carnivores. El Niño is accompanied by a large-scale decrease in the intensity of the southeast trade winds, an apparent weakening of coastal upwelling, and a rise in surface water temperatures (*2*). Offshore waters of higher temperature and salinity approach the coast as the upwelling subsides (*3*); warmwater animals appear off the Peruvian coast, and fish stocks become less available to seabirds which cease breeding and die in large numbers (*4*). It has been believed that the effects of periodic warming on seabirds and other animals were limited to the immediate coastal waters (*5*). However, the life-history patterns of the Galápagos penguin (*Spheniscus mendiculus*) show that El Niño affects seabirds far removed from coastal South America and are consistent with two hypotheses about the occurrence of warm water and its associated effects. They are (i) that El Niño occurs more frequently than every 7 years (*2, 6*) and (ii) that the circulation of the South Pacific subtropical gyre prior to El Niño is intensified as a result of strong southeast trade winds (*7*). The reproductive biology of the Galápagos penguin and other seabirds can be utilized to test these hypotheses.

A major El Niño event occurred in the Galápagos Islands in 1972. Because I was studying penguins during this same time period, I will use the 1972 El Niño event to document the normal changes in oceanographic conditions. During most of 1971, equatorial waters in the eastern tropical Pacific were colder than usual, an indication that equatorial upwelling was unusually intense. By January 1972, warm surface waters were present west of Peru but were warmest from June 1972 until January 1973. During the next 3 months, surface water temperatures decreased and normal upwelling conditions were restored (*3*).

The oceanic disturbance of El Niño extends over much of the eastern tropical Pacific, including the water surrounding the Galápagos Islands (*3, 5*). Maxwell measured fluctuations in salinity, primary productivity, and nutrient concentrations in the Galápagos Islands from September 1971 to July 1972 (*8*). These changes were synchronous with changes in the Peruvian water. Therefore, if this relationship between these two bodies of water is "normal," the effects of El Niño should be similar in the Galápagos Islands and along coastal South America.

The Peruvian Current is primarily responsible for the cool surface waters along coastal South America. However, Pak and Zaneveld (*9*) documented that the Cromwell Current flows eastward through part of the Galápagos Islands, and Maxwell (*8*) concluded that the Cromwell Current is responsible for the cool surface waters around Fernandina Island and Isabela Island. As is the case in other coastal environments, primary productivity is greatest when the surface temperature is coolest (*8*). Surface waters around Fernandina Island and western Isabela Island, which have the coolest waters of the island group, are normally between 15° and 22°C (*10, 11*). In keeping with earlier hypotheses for coastal South America, El Niño in the Galápagos Islands should occur more frequently than every 7 years. Moreover, if oceanic circulation is intensified by the trade winds preceding El Niño, the upwelling of the Cromwell Current should be magnified.

Seabirds such as the Galápagos penguin, flightless cormorant (*Nannopterum harrisi*), and brown pelican (*Pelecanus occidentalis*) should be particularly vulnerable to changes in upwelling since their diet consists primarily of small fish associated with the Cromwell Current. The distributions of Galápagos penguins and flightless cormorants are constrained by these cool surface waters (*11, 12*). Feeding frenzies, in which these seabirds repeatedly dive for fish, do not occur when surface waters are warm and schooling fish are presumably absent. Only three out of 25 feeding frenzies at Punta Espinosa, Fernandina Island, oc-

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