terpreted to mean that, in the presence of physiological concentrations of tetracycline, cell wall synthesis is not inhibited, and may even be accelerated. The increase in size and electron density is interpreted to mean that at least some of the internal synthetic processes have continued. The electron-dense material most likely could be nucleic acid. There is no ready explanation for the absence of transverse septa (*6*).

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6. We thank Mary Englert and Marcia Wishnick for technical assistance. Chemical evidence that cell-wall synthesis is unimpaired by physiological concentrations of tetracycline has been obtained.

4 September 1962

Penetration of Fallout Fission Products into an Indiana Soil

Abstract. Although most of the radioactive fallout reaching the earth stays in the leaf layer and the top inch of soil, some is carried further into the soil and can be detected to a depth of several inches. This report describes a gamma-ray spectrometric study of fallout activity as a function of depth of soil. Total gamma activity deposited from recent tests was found to be over 1.5 curies per square mile at a site in eastern Indiana during July, 1962.

Nuclear bomb tests currently being carried on and previous tests, especially during the 1954–58 period, have produced a variety of radioisotopes. A portion of these, the delayed fallout, is carried great distances in the atmosphere and eventually is returned to the earth's surface, primarily by the scavenging effect of rain and snowfall. Because these radioisotopes are associated with small fallout particles ranging in size from a few microns on down, they are initially deposited in a thin surface layer of leaves, grass, and soil. Eventually, penetration into deeper layers of soil takes place.

The gamma spectrum and activities of three fallout radioisotopes in the 0- to 2-inch layer of soil samples in 1960 have recently been described by Mortensen (*1*). In our work we were concerned with learning more about which isotopes enter the soil most easily and the rate at which penetration takes place, particularly for the longer-lived isotopes.

Soil samples were collected in 1-inch layers, dried, and ground to give them uniform mixing. The counting cans were designed with an inner cylinder to fit around a 3- by 3-inch thallium-activated sodium iodide scintillation crystal. The sample can was filled to the same level each time. Thus by reproducing the shape and volume of the sample, counting was carried out under constant geometry conditions. The pulse-height analysis was carried out with a 512-channel multichannel analyzer. Background was minimized by means of a lead shield surrounding the crystal and can.

Gamma-ray spectra of surface samples indicated the presence of several unnatural gamma-emitting isotopes. The peak energies from these isotopes, however, were primarily below 1 Mev, a region which also shows gamma radiation from the naturally radioactive elements in the soil. The latter consist essentially of the uranium decay series, the thorium decay series, and potassium-40. To separate the fallout counts, we made use of the ability of the pulse-height analyzer to subtract one spectrum from another. By this means it was possible to "peel off" the natural radioisotope contribution to the composite spectrum. The method has been described in some detail by Gustafson *et al.* (*2*). First, background was subtracted. Then a thorium mock soil was made by thoroughly mixing monozite sand of known thorium content (*3*) into a blend of $NaSO_4$ and $NaSO_3$, thus reproducing the soil density and counting geometry. This mock soil was used to "peel off" the gamma spectrum of an equilibrated thorium series by subtracting counts from the soil spectrum until the 2.62-Mev peak of the thorium series was reduced to zero. Similarly, a uranium mock soil was made with a 4 percent uranium ore calibration sample (*4*) in order to subtract the 1.76-Mev peak of Bi^{214}, a member of the uranium series (*5*). A potassium mock soil consisting of KCl was used to "peel off" the K^{40} counts occurring at the 1.46-Mev peak. The remaining spectrum then corresponded to gamma counts from the fallout isotopes.

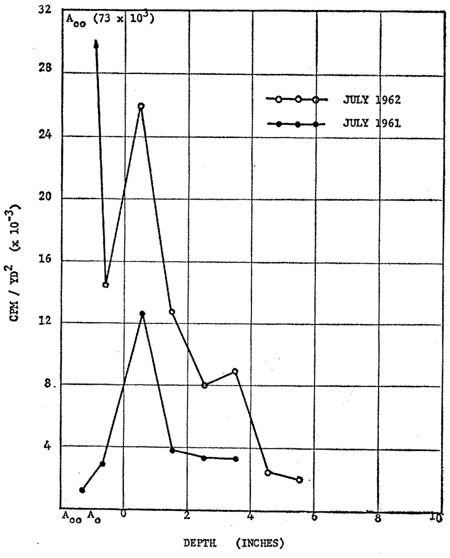

Fig. 1. Total gamma activity of fission products versus soil depth.

Two sets of Miami silt loam samples were run; one set was collected in July 1961, and the other in July 1962; both sets were collected from the same location. Because we wished to study an undisturbed soil profile, sampling was done in a virgin forest. The 1961 samples contained only the fallout products from the earlier testing series, while the 1962 samples included isotopes from the recent testing. The A_{00} layer refers to the undecomposed and the A_0 to the decomposed vegetable matter on the surface.

The gamma counts remaining after compensating for natural radioactivity

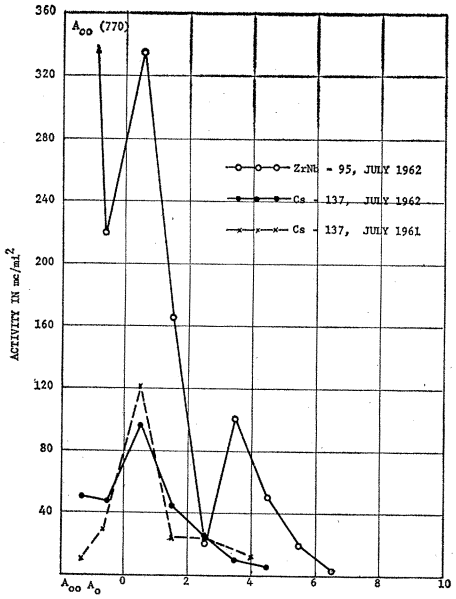

Fig. 2. Cs^{137} and $ZrNb^{95}$ concentrations in soil.

were totaled and converted to counts per minute per square yard. These counts, interpreted as total fallout activity, are shown as a function of depth in Fig. 1.

In order to make quantitative estimates of the activities of Cs^{137} and of $ZrNb^{95}$, mock soils were made in the same manner as before, but with known quantities of these isotopes (*6*). Instead of "peeling off" these spectra, the method of Hurley (*7*) was used. Two gamma energy regions were selected, one corresponding to the 0.662-Mev peak of Cs^{137} and the other to the 0.764-Mev peak of $ZrNb^{95}$. These regions permitted good resolution of the two peaks, but contained relatively few counts from the backscatter of other fallout isotopes. From the known spectra of these isotopes, appropriate corrections were made. In no case did they correspond to more than 2 percent of the total counts in question.

In Fig. 2 the distribution in depth of $ZrNb^{95}$ and Cs^{137} is presented. The amount of Cs^{137} below the second inch of soil is about the same for both 1961 and 1962. This indicates that cesium is leached or transported more slowly than $ZrNb^{95}$ and that very little is carried below the fourth inch. The high value for the 1961 0- to 1-inch sample (greater than the 1962 0- to 1-inch sample) could have been caused by a sampling error. Because the transition from the A_0 layer to the top of the soil is often hard to define, it is possible that part of the A_0 layer (which has a higher specific activity) was included in the first inch of soil.

The rise in the concentration of $ZrNb^{95}$ in the fourth inch was quite unexpected. The action of earthworms or other soil organisms in transporting surface organic matter to lower levels in the soil may have contributed to this rise and to the corresponding rise in total fallout activity. Measurements on duplicate samples would, of course, be necessary before general conclusions could be drawn about such effects. However, one may safely conclude (i) that total activity of Cs^{137}, accumulated up to July 1962, was of the order of magnitude of 270 mc/mi^2 for this particular site, and (ii) as a result of the nuclear weapons testing resumed in September 1961, the July 1962 accumulated activity of $ZrNb^{95}$ (due to both Zr and Nb) was approximately 1650 mc/mi^2 (*8*).

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3. Supplied by the Lindsay Chemical Division, American Potash Chemical Corp.
4. Supplied by the New Brunswick Laboratory, U.S. Atomic Energy Commission.
5. Bi^{214} is the principal gamma emitter of the uranium series. Soil samples were counted after being sealed in gas-tight counting cans for at least 2 weeks, thus assuring equilibrium with Ra^{226}. Members of the series above Ra^{226} are low-energy or weak-gamma emitters and thus contribute a negligible amount to the portion of the spectrum with which we are concerned.
6. Supplied by G. J. Karches of the Taft Sanitary Engineering Center, Cincinnati, Ohio.
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8. This work was supported by the National Science Foundation, undergraduate research program grant No. G16300.

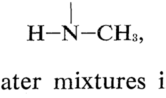
28 September 1962

Catalysis by Imidazole of Deuterium-Hydrogen Exchange in Amide N-H Groups

Abstract. Imidazole, at concentrations of 0.05*M* to 0.2*M*, has been found to increase the rate of deuterium-hydrogen exchange in a model amide by 40-fold or more. Since imidazole side-chains occur in proteins, deuterium exchange in these macromolecules may be strongly affected by the presence of these or similar activating groups.

It has been implicitly assumed in computations based on the rates of deuterium-hydrogen exchange in proteins which contain hydrogen-bonded N-H groups that these groups will exchange deuterium more slowly than will free N-H groups. As one outcome of a recent study of such hydrogen-bonded groups at equilibrium in a model peptide system, it has proved feasible to examine the rates of N-H→N-D exchange in a system with a fixed content of NH···O=C bonded groups. These rates of deuterium-hydrogen exchange have now been found to vary over a range of fortyfold or more with small additions to the solvent, the amounts of which are too small to affect the percentage of N-H groups which are hydrogen-bonded to the carbonyl group.

Exchange rates were followed for N-methylacetamide,



$$\begin{array}{l} CH_3C{=}O \\ \quad\;\; | \\ H{-}N{-}CH_3, \end{array}$$

in dioxane-water mixtures in which, as judged from equilibrium studies, about three-fourths of the amide groups were hydrogen-bonded in molecular aggregates (*1*). All solutions contained 5*M* methylacetamide, and 5*M* D_2O dissolved in dioxane. *p*H was changed by the addition of DCl or NaOD in D_2O. The kinetics were followed from changes in absorbance at 1.42 μ in the near-infrared region of the spectrum.

It was found immediately that the rate of exchange was acid- and base-catalyzed. Such catalysis has already been reported in purely aqueous solutions of N-methylacetamide in which the solute is entirely in the monomeric form (*2*). In our dioxane-water solutions the rates varied only a few percent in the limited *p*H range of about 6.6 to 7.6. To examine the dependence of rate upon ionic strength we also compared the kinetics in 0.01*M* and 0.1*M* tetramethylammonium chloride; the tenfold increase in salt concentration increased the exchange rate by only about 20 percent.

In contrast, additions of imidazole produced striking effects on the velocity of the exchange (Fig. 1). At *p*H 7.4 a tenfold increase in rate was achieved with 0.2*M* imidazole. Even more pronounced catalysis was observed at *p*H 6.7, where the rate constant in the presence of 0.2*M* imidazole was 87 × 10^{-4} liters per mole per minute compared to 2.0 × 10^{-4} in the control (which contained 0.01*M* tetramethylammonium chloride). Exploratory experiments point to even larger effects when the *p*H is lowered further.

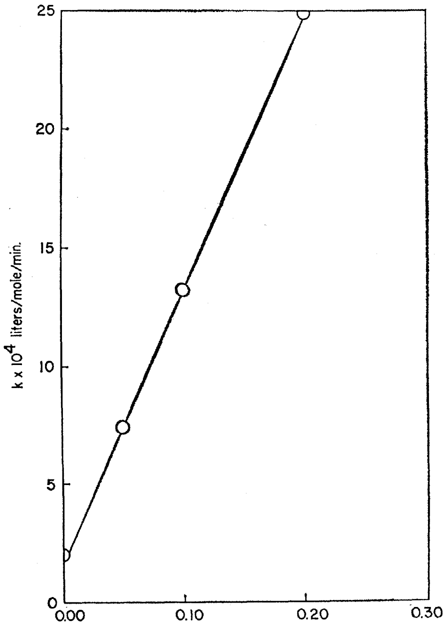


Fig. 1. Rates of deuterium-hydrogen exchange for solutions of D_2O and N-methylacetamide in dioxane, as a function of molarity (*M*) of added imidazole. Temperature, 25°C; *k* is a second order rate constant.