# Reports

### **Environmental Radiation: Measurements of Dose Rates**

Abstract. The exposure dose from environmental sources of radiation was determined by means of an ionization chamber, by gamma-ray spectrometry in the field, and by measurements of radioactivity in soil cores. The exposure dose from cosmic radiation was found to be  $4.4 \pm 0.2 \ \mu r/hr$ , that from natural radioactivity  $8.0 \pm 0.3 \ \mu r/hr$ , and the contribution from fission products varied from 2.0 to 7.5  $\ \mu r/hr$  during the interval in question.

Natural background radiation has been measured for many years; more recently, measurements have indicated changes due to the testing of nuclear weapons. Although many measurements have been made with some degree of precision (1), the results vary widely.

Various measuring devices, including electroscopes, Geiger-Mueller counters, "air equivalent ionization chambers," high pressure nitrogen or argon-filled ion chambers, and organic and inorganic scintillation counters have been used. To measure exposure dose (roentgens) or absorbed dose (rads), all of these devices require certain corrections for wall effects, energy response, electrical leakage, self-scattering, and other factors often difficult to derive or apply. The agreement among values derived by the various methods and devices cited in the past literature (2) is on the whole rather poor and in some cases largely fortuitous, one error canceling another.

Recently, a tissue equivalent ionization chamber designed by Rose and Shonka and built by Shonka at St. Procopius College has been used for an extensive investigation of the components of background radiation and accurate measurement of the absorbed dose (3). The use of the sodium iodide scintillation counter for dose measurements requires the precise knowledge of absorption coefficients and scattering theory, both of which are now well known, and can be applied with some assurance for deriving accurate numbers.

It is our purpose in this report to describe methods by which good agree-

ment can be demonstrated between the dose measured by the sodium iodide crystal  $\gamma$ -ray spectrometer and the tissue equivalent (TE) ionization chamber as used in the field. Furthermore, the dose rates calculated from measurements of the concentration of radio-activity in soil appear to be in accord with the chamber and spectrometer values (4).

The TE ionization chamber was constructed by welding six molded sections of electrically conducting tissue-equivalent plastic (5) to form a nearly spherical container having a volume of 16.5 liters. An insulated conducting-plastic guard ring was welded into the neck assembly, which carried the insulated collecting electrode. The chamber was filled at 760 mm-Hg with a gas mixture which was equivalent to the standard muscle of the International Commission on Radiological Units (6). The energy response of the filling gas was equal to or better than that of the TE plastic. All ionization produced in the system would arise only from TE materialsno metals or cements were used. The Shonka oscillating fiber electrometer (7) was mounted directly on the neck of the chamber in contact with the conducting TE guard ring. The chamber was readily operable in the field with a small portable power supply that supplies the electrometer control voltages, the bucking voltage, and a chamber collecting potential of 90 volts, sufficient for saturation at field rates and for calibration with a radium standard. Tests indicated that the contribution from contamination of the walls with alpha-emitting radioactivity was negligible at this potential. The outfit is rugged, readily portable, independent of gravity (operates well in a rowboat), and is nondirectional to radiation. The chamber system has remained essentially stable for more than a year.

The chamber was calibrated and checked routinely with a 1.11-mg Ra element standard enclosed in Pt, 0.5 mm thick, a specific  $\gamma$ -ray constant of 8.25 r mg<sup>-1</sup> hr<sup>-1</sup> at 1 cm being assumed. The usual corrections were made for air absorption, floor and wall scattering, inverse square law, and chamber wall thickness. This yielded a calibration factor of 0.32  $\pm$  0.005 mv sec<sup>-1</sup>  $\mu$ r<sup>-1</sup> hr<sup>-1</sup>. If the various constants [namely, volume, 16.5 liters; chamber capacitance, 5.5 micromicrofarads; and W', the energy required to produce an ion pair in the gas, 26.2 ev/ion pair (8)] are substituted in the usual equation, the derived factor is within 1 percent of that obtained from the radium calibration. The major error appears to be in the radium standard and the assumed specific  $\gamma$ -ray constant for radium. It is believed the over-all accuracy is better than  $\pm 2$  percent; thus the precision of background readings is set by their natural variation.

A cylindrical NaI(Tl) crystal, 10 cm in diameter by 10 cm thick, was used for obtaining  $\gamma$ -ray spectra in the field and for making activity measurements of soil cores in the laboratory. The crystal was optically coupled to an EMI 9530QA photomultiplier tube which has a 12.7-cm diameter photocathode, and a quartz and glass envelope with low inherent potassium content. Data on the pulse height from the detector were fed via a cathode follower and cable (up to 45 m in length, in the case of the variation-with-height experiment) into a RIDL (9) transistorized 400channel analyzer for pulse-height analysis and storage. Energy calibration of the spectrometer was made by using  $Cs^{{\scriptscriptstyle 137}}$  and  $Co^{{\scriptscriptstyle 60}}$  sources, and the gain was set so that each channel spanned 10 kev. Accumulated spectra were read out of the analyzer onto an IBM electric typewriter. A portable gasoline generator was used to supply power for field operation of the entire spectrometer system. When soil measurements were made in the laboratory, the crystal, photomultiplier, and soil sample were placed inside an iron shield with 15-cm thick walls for low background counting.

In the field, the ion chamber was sup-

ported on a lightweight tripod, placed so that the center of the chamber was 1 m above the surface of the ground, and exposure dose rates were obtained directly.

Gamma-ray spectra obtained in the field, hereafter referred to as the spectra obtained in situ, were obtained with the NaI crystal mounted face downthat is, with the phototube above the crystal. The crystal was supported on a lightweight boom with the face of the crystal 1 m above the ground. The exposure dose in microroentgens per hour was derived by first considering the true energy absorption in the NaI crystal itself. The corresponding energy absorption in air was then determined, taking a volume of air identical in size and shape to the crystal. This method is straightforward and requires knowledge of the mass absorption coefficients in air and NaI, the partition between total absorption and Compton absorption as a function of energy in a crystal of this size and shape, and a measure of the mean chord of the volume involved. The method is similar to techniques used by other investigators (10).

A third method used for dose determination was one in which the concentration of natural and fission product radioactivity serves as a basis for dose calculation. This technique has been in use at this laboratory for several years (4). Soil cores 10 cm in diameter and 15 cm deep were collected in the field, and the initial weights were recorded. Each core was then air dried and pulverized, and a portion was placed in a cylindrical stainless-steel container for  $\gamma$ -ray counting. The container is so designed that a 2.5-cm layer of soil surrounds the crystal and covers one face. The container holds approximately 2 kg of soil, and the usual counting time is 100 minutes. By solving a series of simultaneous equations based upon appropriate reference spectra, the concentrations of thorium, uranium, and potassium are determined, as well as those of the principal  $\gamma$ -emitting fission products. The concentration of natural activity per unit mass of moist soil is then used to find the dose contribution from U, Th, and K by means of Hulqvist's equations (11), which derive the dose from an infinite plane of infinite depth containing a uniform distribution of activity. The activity of various fission products is expressed in terms of activity per unit area, and the dose is calculated by Dunning's method (12) for

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 $\frac{10^{4}}{10^{4}}$ 

Fig. 1. Spectrum obtained *in situ* on Lake Michigan. Solid curve, total spectrum; dashed curve, cosmic-ray continuum.

the infinite plane modified to account for depth distribution (13).

The largest single uncertainty in deriving the dose from the core measurements is that of establishing the degree of radon equilibrium that exists in the field. The dose from a given concentration of uranium will depend upon the amount of radon that stays in the ground. Because of its 3.8-day halflife, an appreciable portion of the radon may leave the upper layers of soil before decaying into nongaseous form. Initially, little attention was paid to this effect; soils were merely placed in the containers, sealed with masking tape, and counted. It was observed that subsequent measurements of a sample sealed in this manner led to higher values of uranium content based upon the concentration of radon daughters in the soil specimen. Attempts have been made to determine the radon equilibrium in situ by sealing up soil cores in the field immediately after collection. These indicate, at least during summer and autumn, that the radon concentration in the top 15 cm of soil is approximately 70 percent of equilibrium. Further determinations with 2.5-cm layers extending from the surface to 15 cm



Fig. 2. Variation of terrestrial dose rate with height above ground.  $\triangle$ , Ion chamber;  $\times$ , total spectrometry *in situ*;  $\bigcirc$ , hard  $\gamma$ -component (0.5 to 3.0 Mev) of spectra *in situ*; +, soft  $\gamma$ -component (< 0.5 Mev) of spectra *in situ*.

depth do not show any significant departure from this figure in any one level. As one would expect, the laboratory measurements indicate that thoron *in situ* is essentially in equilibrium.

Soil moisture content, as it affects the calculated dose, provides another uncertainty that is sometimes greater than that of radon equilibrium. The moisture in local soils may vary from a few percent of the total mass to 25 to 30 percent, and this produces a corresponding change in the apparent concentration of natural activity.

The three methods of exposure-dose determination under consideration are capable of measuring different portions of the total environmental exposure. The total exposure is the sum of terrestrial radiation, from natural and fission product radioactivity, and extraterrestrial, or cosmic radiation. The ion chamber responds to all three and hence measures the total exposure dose rate. Spectrometry in situ measures terrestrial radiation and that portion of the cosmic radiation which loses between 0 and 3.0 Mev in the crystal. Dose rates based upon soil core measurements include natural and fission product sources only, and provide the best opportunity to assess the magnitude of these two components.

To make a meaningful comparison of the dose rates determined by these methods it is necessary to compare only the dose from the same source or sources, namely, that from natural and fission activity in the ground. To do this one must first find the cosmic radiation component in both the ion chamber and the spectrometry measurements in situ. To minimize terrestrial radiation so that the cosmic radiation component would be predominant, spectral and chamber measurements were made 3.2 km out in Lake Michigan from a 12-m Coast Guard vessel. The NaI crystal was placed on the stern, as far as possible from the radium dials on equipment in the wheelhouse. The ion chamber was placed close to the crystal. Spectral measurements taken at various positions between the stern and wheelhouse door failed to indicate increases in radon daughter  $\gamma$ -ray lines until the crystal was placed in the open wheelhouse door. Hence it was assumed that the exposure dose measured was not influenced by radium aboard the vessel, and that it came solely from cosmic radiation and radioactivity in the surrounding air and water.

Table 1. Terrestrial exposure dose in  $\mu r/hr$  determined by ionization chamber measurements and spectrometry *in situ*.

Height above ground (m)	Ionization chamber*	Spectrometry in situ
	July 1963	
1 '	$13.9 \pm 1.0$	$13.8\pm0.3$
2.0	$12.2\pm0.3$	$12.4\pm0.2$
5.2	$10.4\pm0.3$	$11.1\pm0.1$
9.2	$10.2\pm0.3$	$10.9\pm0.1$
13.3	$9.8\pm0.3$	$10.1\pm0.1$
17.3	$9.6 \pm 0.3$	$9.8\pm0.1$
21.4	$9.4\pm0.3$	$9.4\pm0.1$
25.4	$9.2 \pm 0.3$	$9.0\pm0.1$
29.5	$9.0 \pm 0.3$	$8.3\pm0.1$
34.6	$8.7\pm0.3$	$8.1\pm0.3$
	October 1963	
1.0	$10.7\pm0.4$	$10.7\pm0.3$

\* These values were obtained by substracting 4.5  $\mu$ r/hr from the total chamber reading. The value of 4.5  $\mu$ r/hr was obtained by correcting the Lake Michigan cosmic-ray readings for barometric pressure.

The  $\gamma$ -ray spectrum obtained on the lake is shown in Fig. 1. The portion of the spectrum due to cosmic radiation is presumed to be a continuum as indicated. The shape and magnitude of the continuum were determined in the region above 2.6 Mev and the portion below 2.6 Mev was obtained by extrapolation. The total dose computed from the spectrum over the range 0 to 3.0 Mev was 0.96  $\mu$ r/hr; that from cosmic radiation was 0.09  $\mu$ r/hr and the remaining 0.87  $\mu$ r/hr came from activity in air and water. Air samples were taken and analyzed by Lucas (14), and the water was examined by y-ray analysis. The dose rate from radon was calculated (11) to be 0.76  $\mu$ r/hr and that from the activity in water (the lake being assumed to be an infinite plane of uniform concentration with depth) was 0.09  $\mu$ r/hr. The sum of these two measurements, 0.85  $\mu$ r/hr, agrees well with the value of 0.87  $\mu$ r/hr derived from the spectrum. Hence the

Table 2.	Terre	strial	expo	sure	dose	e in	μı	:/hr
determine	d by	ioniza	ation	cha	mber	m	eas	ure-
ments an	d soil	core	calc	ulatio	ons.	Th	e d	lose
due to n	atural	radic	activ	ity v	vas	8.0	+	0.3
$\mu$ r/hr in all instances.								

	Soil	cores	Ionization	
Month	Fission product	Total	chamber	
		1962		
Sept.	$2.0 \pm 0.1$	$10.0 \pm 0.3$	$9.3\pm0.4$	
Oct.	$2.4 \pm 0.1$	$10.4 \pm 0.3$	$10.0\pm0.2$	
Nov.	$2.9 \pm 0.1$	$10.9\pm0.3$	$10.5\pm0.2$	
		1963		
March	$4.7 \pm 1.1$	$12.7 \pm 1.1$	$12.2\pm0.2$	
April	$5.8 \pm 0.6$	$13.8\pm0.7$	$12.8\pm0.4$	
May	$6.1\pm0.7$	$14.1\pm0.8$	$13.1\pm1.0$	
June	$7.5\pm0.3$	$15.5\pm0.4$	$9.7\pm0.1$	
July	$6.5 \pm 0.2$	$14.5\pm0.4$	$13.9 \pm 1.0$	
Sept.	$4.1\pm0.4$	$12.1\pm0.5$	$13.3\pm0.5$	
Oct.	$3.3\pm0.3$	$11.3 \pm 0.4$	$10.7 \pm 0.4$	

cosmic ray contribution in the energy region up to 3 Mev has been assessed correctly, and under normal circumstances on land this amounts to roughly 1 percent of the total dose, as measured by the spectrometer.

The dose rate with the ion chamber was observed to be 5.25  $\pm$  0.2  $\mu$ r/hr. After substraction of the water activity and air radon contribution, the net dose was 4.4  $\mu$ r/hr. It was assumed that the major portion of this dose rate was due to penetrating cosmic rays, that is mu-mesons. Accordingly, an attempt was made to determine this flux by examining the spectral region corresponding to the energy deposited by a relativistic charged particle in 6.35 cm of NaI and also in 12.7 cm of liquid organic scintillator. The number so obtained was 0.015 mu-mesons cm<sup>-2</sup> sec<sup>-1</sup>, which is in excellent agreement with that obtained by Moroney and Parry (15). Assuming an average chord for the chamber of 11/3 times the radius and using the W of the filling gas, we calculated the apparent dose rate due to this flux to be 2.1  $\mu$ r/hr; thus, approximately 50 percent of the cosmic-ray dose rate determined by the chamber is presumably due to the hard component. As this component constitutes approximately 3/3 of the total particle flux, the soft component, as expected, is more effective in energy deposition.

Since September 1962, periodic measurements of the total exposure rate have been made with the ion chamber at two locations on the Argonne site. These locations are those from which soil cores were taken for fission product deposition studies. In July and October 1963, the spectra in situ were obtained at these same locations, and the dose rate was computed. Also during July 1963, a series of ion chamber and spectral measurements were made from different positions on the Argonne meteorology tower (14). The purpose of the latter investigation was to determine the spectral variation of terrestrial dose rate as a function of height above the ground, up to 35 m. The NaI crystal was placed on a 4-m boom so that shielding of the ground by the tower structure was at a minimum; however, this was not possible with the chamber, which had to be operated on wooden landings located on the tower.

The results obtained with the ion chamber and by spectrometry *in situ* are given in Table 1. The agreement between these two methods is within the experimental errors of the measurements.

Additional dose rates obtained with the ion chamber, again with the cosmic radiation dose rate subtracted, are given in Table 2, along with the natural and fission product dose rates calculated from the soil core analyses. With few exceptions, the results agree within the experimental errors; however, the soil core data generally give higher values. This may reflect the influence of radon equilibrium (an overestimate, in this case) or soil moisture content or both.

The average calculated dose rate from natural activity over this period was  $8.0 \pm 0.3 \ \mu r/hr$ , and the largest single deviation was less than 10 percent of this figure. Because of the general agreement for the total dose rate obtained by all the methods, the dose rates computed for fission products appear to be reliable and to indicate the varying magnitude of this dose component with time.

The spectral data obtained at the meteorology tower were examined in an effort to establish with greater clarity the effect of height on dose-rate attenuation. As seen in Fig. 1, the intensity of the spectrum in situ is considerably greater at low energy. This is equally true over land and is not due primarily to decreased total absorption efficiency in the crystal at higher energy. Hence one might conclude that the principal cause of dose-rate reduction with height above ground would be due to absorption of the low-energy radiation. The result would be that at greater height the spectrum would become harderthat is, contain relatively more highenergy photons.

This is not the case over the range of height from the surface to 35 m, as is shown in Fig. 2. Here the total terrestrial dose rate from both chamber and spectral measurements is plotted as a function of height. The exposure dose measured by spectrometry was divided into that arising from photons of energy less than 0.5 Mev and those between 0.5 and 3.0 Mev. The main effect of height comes from attenuation of the hard component, the soft portion remaining essentially constant over this range. This does not imply that there has been no attenuation of the soft component, but merely that it has been replenished by the degradation of more energetic photons and hence appears to have been unaffected.

The environmental dose rates from terrestrial sources obtained by the three methods discussed appear to be in reasonable accord. The dose rate from cosmic radiation on Lake Michigan was found to be 4.4  $\pm$  0.2  $\mu$ r/hr. The dose rate from U, Th, and K on the Argonne site amounted to 8.0  $\pm$  0.3  $\mu$ r/hr. From September 1962 through October 1963 the dose rate from fission products on the site ranged from a low of 2.0  $\mu$ r/hr to a high of 7.5  $\mu$ r/hr. The decrease in terrestrial dose rate with height from the surface to 35 m was attributed to absorption and scattering of photons of energy greater than 0.5 Mev.

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## Infrared Study of Selective Deuteration of Kaolinite and Halloysite at Room Temperature

Abstract. Deuteration of expanded hydrazine-kaolinite complex at room temperature shifts the infrared stretching frequencies of the inner-surface hydroxyls from 3695, 3670, and 3650 cm<sup>-1</sup> to 2725, 2710, and 2698 cm<sup>-1</sup> respectively, and the inner hydroxyls absorbing at 3620 cm<sup>-1</sup> to 2675 cm<sup>-1</sup>. The OH-OD exchange for the inner-surface hydroxyls varies from 60 to 67 percent, whereas it is only 22 percent for the inner hydroxyls.

Assignment of infrared absorption bands to specific groups is facilitated by the use of isotopes. Deuterium exchange is particularly helpful for assignment to OH stretching vibrations -v(OH)—where the hydrogen is exchangeable. At room temperature and at atmospheric pressure the internal hydroxyls of nonexpanded kaolinite are not sufficiently exchangeable for deuteroxyls to yield any  $\nu(OD)$  absorption band (1). However, when koalinite was exposed to D2O vapor at 180°C during a period of 3 months, 36 percent of the internal hydroxyls were exchanged (2). When the kaolinite-D<sub>2</sub>O system is submitted to hydrothermal conditions, that is, at temperatures of 300° to 400°C and at pressures of 700 to 2100 bars (3), the OH-OD exchange reaches about 50

percent. Stubican (4) accomplished complete OH-OD exchange only by resynthesis of kaolinite and halloysite with D<sub>2</sub>O from heated specimens at 1000°C.

Hydrothermal deuteration of kaolinite has indicated that the 3800 to 3000 cm<sup>-1</sup> region is not the only region where OH absorptions occur. A comparison of the infrared spectra of OH and OD kaolinite shows that the absorption doublet at 938 and 910 cm<sup>-1</sup> is shifted to 720 and 687 cm<sup>-1</sup>; the dependence of this doublet on the cations suggests it is an OH-Al vibration (5). However, the hydrothermal deuteration does not provide any evidence for the assignment of the v(OH) absorption frequencies to different OH sites in the lattice of kaolinite. The relative intensities of the absorption bands

to 2200 cm<sup>-1</sup>) as in the original OH region (3800 to 3000 cm<sup>-1</sup>) (3). The only exchange mechanism that would provide evidence for a correlation of the v(OH) to lattice sites should selectively deuterate the hydroxyls according to their accessibility for the exchange reaction. The "outer hydroxyls" (6) are readily accessible for deuteroxyl exchange but they do not yield any  $\nu$ (OD) absorption band. The remaining hydroxyls are located inside the microcrystals and are not easily exchangeable. However, it has been shown by Ledoux and White (6) that the expansion of kaolinite with potassium acetate greatly facilitates the exchange of the internal hydroxyls. Our study is an attempt to show that the expansion of kaolinite and halloysite allows selective deuteration of internal hydroxyls and to provide evidence for the assignments of v(OH) - v(OD) shifts.

are the same in the OD region (2800

Three kaolinite samples (7) were intersalated with potassium acetate; one was washed three times with pure formamide, another with a saturated solution of urea, and the last sample with anhydrous hydrazine. X-ray diffraction (8) of oriented film specimens on a glass slide showed that the largest amount of expansion was obtained with hydrazine. A small portion (2 ml) of the expanded hydrazine-kaolinite complex (10.4 Å) was washed twice with 1 ml of D<sub>2</sub>O; the residue was redispersed in 3 ml of D2O and was allowed to remain in contact 30 minutes. A 1-ml portion of the D<sub>2</sub>O suspension was evaporated at 110°C on an Irtran window (9) and the spectrum of the oriented clay film was determined by x-ray diffraction and infrared spectroscopy. The x-ray pattern of the D<sub>2</sub>Otreated kaolinite shows that the mineral has collapsed to its original spacing, 7.13 Å. Figure 1 shows a comparison of the infrared spectra (10) of natural kaolinite with the D2O-treated sample; the spectra were determined with two orientations of the clay film. In the infrared spectrum of natural kaolinite (Fig. 1a), four v(OH) absorption frequencies are observed at 3695, 3670, 3650, and 3620 cm<sup>-1</sup>. Both absorptions at 3695 and 3620 cm<sup>-1</sup> are more intense than the 3670 and 3650 cm<sup>-1</sup>. The spectrum of deuterated kaolinite (Fig. 1b) shows a reduction in the intensity of the 3695, 3670, and 3650 cm<sup>-1</sup> absorptions, and the occurrence of strong bands at 2725 and 2698 cm<sup>-1</sup> and weak absorptions at 2710 and 2675 cm<sup>-1</sup>; the intensity of the 3620 cm<sup>-1</sup> band is not