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# RUTHENIUM: ITS BEHAVIOR IN PLANT AND SOIL SYSTEMS

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RUTHENIUM: ITS BEHAVIOR IN PLANT AND SOIL SYSTEMS

by

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CONTENTS

# LIST OF TABLES

# INTRODUCTION

Numerous investigators have studied the biological behavior of ruthenium in both plant and soil systems. These studies were prompted by the release of ruthenium isotopes into the biosphere by the military weapons and Plowshare nuclear testing programs conducted by the U.S. Energy Research and Development Administration (ERDA), formerly the U.S. Atomic Energy Commission.

Following the signing of the nuclear test ban treaty in 1963, the scientific interest in radioruthenium decreased apparently because of the discontinuance of atmospheric nuclear testing and later, due to a reduction in the Plowshare Program's nuclear excavation experiments.

However, a number of investigators have indicated that due to the high concentrations of radioactive materials being discarded in waste disposal sites, and also, because of the expanding nuclear power industry, ruthenium may ultimately become an important environmental pollutant (Booth, 1975).

It was once thought that ruthenium, which is the rarest of the six elements in the platinum series (Amy, 1971), contributing only 0.004 parts per million of the earth's crust, would not become incorporated into living organisms. However, one of the first indications that ruthenium could become biologically available, via soil, was shown by Selders (1950), and by Cowser and Parker (1958) when they reported that ruthenium which had been discarded as radioactive waste was quite mobile in soils near the Oak Ridge National Laboratory. The incorporation of ruthenium by plants was shown by Selders (1950), Neel et al. (1953), Auerbach (1957a), (1957b), Klechkovsky (1956), Goss and Romney (1959), and later summarized by Auerbach and Olsen (1963) when they reported that ruthenium was found in a variety of plants grown in both soils and hydroponic nutrient solutions containing ruthenium. These studies, plus others similar to that conducted by Crossley (1967), which showed that ruthenium-106 was being taken up by plants, and eventually becoming incorporated into the food chain of herbivorous animals, accounted, to a large extent, for the continuance of studies concerning the environmental behavior of this pollutant.

One of the chemical characteristics of ruthenium which complicates the identification of this element in its biological and environmental behavior is that it can be found in a variety of valence states, ranging from 0 through +8. Numerous chemical complexes of ruthenium have already been identified in environmental samples; some of the more common include: oxides, amines, halogens, and the nitrosyls. The two common oxides include: dioxide, $RuO_2$, and tetroxide, $RuO_4$. The halogen elements, frequently chlorine, form compounds and various chemical complexes with ruthenium, commonly in the di-, tri-and tetravalent states.

1

Perhaps, the most biologically important compounds are ruthenium in the form of amines and nitrosyl ruthenium complexes. These complexes are formed primarily in radioactive waste systems, and during treatments of irradiated nuclear fuels by nitric acid. There are two recognized classes of nitrosyl ruthenium complexes: (1) the unstable nitrato complexes having the general formula $[RuNO(NO_3)_x(OH)_y(H_2O)_z]^Q$ where the sum of x, y, and z is equal to 5, and the charge Q is equal to $3-(x+y)$; and (2) the more stable complex, nitro, with a general formula including at least one $NO_2$ group, such as $[RuNO(NO_2)_x(NO_3)_y(OH)_{3-x-y}(H_2O)_z]$, where x=1. The nitro complexes can have a neutral, cationic, or anionic character, depending on the values of x and y (Amy, 1971). Because of their importance, a number of investigators, Fletcher et al. (1955), Rudstam (1959), and Amy (1971), have identified and isolated many of the ruthenium-nitrosyl compounds.

Of the 16 ruthenium isotopes, 4 are considered to be of biological importance (Radiation Protection Handbook 69, NCRP, 1959). These four nuclides include ruthenium-97, -103, -105, and -106, having radioactive half-lives ($T_{eff}$) of 2.8 days, 39.5 days, 4.4 hours, and 368 days, respectively. The two longer-lived isotopes, $^{103}Ru$ and $^{106}Ru$, have received more consideration in the scientific community primarily due to their longer half-life and also because, as reported by Tikhomirov and Petrukhin (1967), their yield, up to 20% during the fissioning of nuclear fuels, contributes a significant amount to the growing quantities of radioactive wastes.

This review was undertaken to assemble and summarize the available data concerning the distribution and behavior of ruthenium in both the soil and plant systems. The evaluation and integration of this data will also be used to identify areas in need of investigation.

## SUMMARY

Environmental levels of ruthenium in selected areas have increased in recent years above the amounts contributed by atmospheric fallout. These trends in ruthenium accumulation will continue to rise as the uses of nuclear power and the reprocessing of nuclear fuels increase. These increasing concentrations have, however, provided opportunity for biological investigation.

Experimentation dealing with various inorganic and organic compounds of ruthenium found in waste effluents have shown that these compounds may become incorporated and/or taken up by plants in greater or less quantities, or behave differently when exposed to a variety of environmental media. This sometimes erratic and unpredictable behavior has been attributed to ruthenium's various and sometimes changing chemical forms.

As the available data concerning the biological behavior of ruthenium are reviewed, it becomes apparent that many questions concerning the qualitative identity and behavior of this element still exist. For example, previous investigations have made it clear that ruthenium will become fixed by varying degrees on most environmental

2

media. However, the identity of the fixation, incorporation, or bonding, whether by mechanical or chemical means, is not well understood. Ionic exchange of ruthenium in soil systems, which appears to be nonexistent based on available data, requires additional study. Also, the biological availability of ruthenium, which may be influenced by exchangeable cations, may also be, in all probability, affected by microbial assimilation and metabolism. Data concerning these parameters are lacking.

Because of the chemical complexity of this element, interpretation of its behavior in both plant and soil systems at present requires a considerable degree of caution. This is primarily due to studies that have not reported in sufficient detail the mechanical or chemical makeup of the environmental media that are being treated.

Perhaps the single most important parameter that is in need of investigation is the identity of ruthenium species. Evidence indicates that ruthenium chemistry is very complex and identification in many cases is extremely time consuming. However, identification of the ruthenium species must be taken into account before valid interpretations can be made.

It is generally agreed that ruthenium may become a greater environmental liability than had been originally anticipated. As a result, a complete documentation of its distribution, fate, and behavior in our environment is essential, especially in view of our expanding nuclear industry.

## RUTHENIUM IN SOIL SYSTEMS

Investigations concerning the behavior of selected pollutants in terrestrial environments have been initiated, primarily to determine and identify a pollutant's transfer rate and pathway between various biotic compartments within an ecosystem and, also, to determine the magnitude of dispersion within the biota and to locate and define abiotic and biotic sinks. Additionally, studies designed to utilize local soils, flora, and fauna as biological sensors to measure a pollutant's impact on the biota through cellular accumulation and biological effects are now in progress (Crockett, 1975). Many studies have been initiated following accidental and/or continual releases of radioactive pollutants into our environment, while other studies have been conducted under controlled conditions using radioisotopes as tracers. Both types of investigations have added to our understanding and knowledge of the complexity of ruthenium in the environment.

Other important contributions concerning the behavior of ruthenium in soil systems have been provided by the numerous surveys conducted in many geographical areas throughout the world. These studies, such as conducted by Ritchie et al. (1970), Mishra and Sadasivan (1972), Plummer and Helseth (1965), Tikhomirov and Petrukhin (1967) and Matsunami et al. (1974), tend to show the distributions and patterns of radioruthenium in soils and their associated ground waters following atmospheric fallout. Ritchie et al. (1970) also point out that, due to the discontinuance of

3

atmospheric testing, these sampling results may be of historical interest as long-range benchmark comparisons of nuclide distributions over extensive undisturbed landscapes.

Studies involving ruthenium in soils have been conducted near nuclear reactor sites, and on the ERDA's Nevada Test Site following nuclear testing. Extensive experimentation has also been conducted in areas used for the disposal of both liquid and solid radioactive wastes. These studies were initiated due to practices of using soils to sorb and retain radionuclides following their disposal.

Many soils have the capacity to remove fission products from waste solutions by filtration, adsorption, and by ionic exchange. Fission products, especially the cations, are exchanged for various constituents of the clay fraction of the soil. This ability of soil to remove specific radionuclides is contingent on the type of ion, its valence state, ion concentration, and both the salt and chemical composition of the radioactive waste solutions. As such, the behavior, movement, and the biological availability of ruthenium in soil systems are directly affected by chemical transformations and reactions involving both the soil minerals and solutions.

Early investigations concerning the behavior of ruthenium in soils were conducted by Brown et al. (1956), Cowser and Parker (1958), Spitsyn et al. (1958), and Brown et al. (1958). All of these studies showed that ruthenium was quite mobile and indicated that further investigations were needed for a more adequate containment of ruthenium. For example, Brown et al. (1955) and (1958) found that when low-level liquid waste containing ruthenium-106 with a fairly high salt concentration of 80 grams per liter (g/1) was added to soils in disposal cribs, the downward movement of ruthenium-106 occurred at a much faster rate than other disposed of radionuclides. They also reported that the results of an ion exchange study involving ruthenium again demonstrated the rapid movement of this isotope in soils, as its movement was delayed only slightly through laboratory soil columns. Following the rapid movement of ruthenium-106 in a sodium nitrate solution through a sandy clay loam soil, Spitsyn et al. (1958) hypothesized that areas most favorable for radioactive waste sites would be those which have low-lying subsoil water with slow movement, and soils with both a low concentration of calcium ions and a generally low salt content.

As the supply of radioruthenium for disposal increased, reevaluation of existing waste sites and the development of methods for permanent containment were required. These investigations included the testing and evaluation of many different soils, in addition to a selected number of humic materials, for their retentive properties. One of these investigations, related to the disposal of low-level reactor waste into soils, was conducted by Bryant et al. (1961). Their study was designed to measure the fixation of ruthenium on clay soil, and also to determine if this containment could be retained more adequately in fermentable humic materials such as soil sawdust and soil peat mixtures. Since ruthenium exists in a variety of valence states, as cations, complex anions, and neutral oxides, it was anticipated by Bryant that the ruthenium compounds may become complexed with stable organic and microbial materials

4

during the soil-sawdust and peat decompositions. He further hypothesized
that nitrate ruthenium salts could be reduced by oxygen-consuming
bacteria under anaerobic conditions. Ruthenium chloride, complexed
with a nitric acid solution to simulate radiochemical waste, was
applied to soil columns containing clay and the soil-sawdust and soil-
peat mixes. At preselected times during a 120-day storage period, the
columns were leached with distilled water and then sampled. Their
results showed that the retention of ruthenium increased in time for
both sawdust and peat mixes. The amount of ruthenium retained exceeded
90% in both humic mixes. The degree of fixation was determined by
leaching selected columns with three different concentrations of sodium
nitrate. The sodium which competes for the available ion-exchange
sites did not have any effect on the ruthenium fixation. The clay mix
appeared to be the most effective medium for the retention of ruthenium.
This is probably due to the abundant ion-exchange sites found in clay
soils.

Another study, conducted by Lomenick (1963) using a different form of
ruthenium determined the degree of fixation on a silty clay loam soil
collected near the Oak Ridge National Laboratory. This soil, which was
contaminated with a mixture of nitrosylruthenium hydroxide and mononitrato
nitrosylruthenium that had seeped from nearby waste pits, was leached
with six different solutions. His results showed that less than 10% of
the ruthenium was removed by leaching with water, both tap and distilled,
and also, with low normality acidic and basic solutions. Nearly 45% was
removed by $KMnO_4$ at a pH of 8.8, while in excess of 60% was removed by the
three following solutions: NaOH at a pH of 11.3 and two acids, HCl and
$HNO_3$ having a pH of less than 1.0. It was suggested that, of the two
forms of ruthenium, the hydroxide is retained to a larger degree than the
mononitrato nitrosylruthenium which was essentially unadsorbed by the soil.

Similar studies using a variety of inorganic and organic compounds of
ruthenium were conducted by Spitsyn et al. (1958), Nishita et al. (1956),
van der Westhuizen and van Rensburg (1973) and Amy (1971). Spitsyn et al.
(1958), using inorganic radioruthenium in solutions of NaOH, $NaNO_3$ and
$Al(NO_3)_3$, found in laboratory experiments that the sorption of ruthenium
in soils was extremely low. Sorption from the alkaline solutions reached
several tenths of a millicurie per 100 grams (g) of soil when cationic
ruthenium was used. However, almost no ruthenium was adsorbed from the
acidic solutions and no anionic ruthenium was absorbed by the soils. The
non-absorption of anionic ruthenium was again shown by Spitsyn et al.
(1958), when they applied ruthenium-106 to field soil which was identified
as a sandy clay loam. To determine fixation and extractability,
ruthenium-106 as the cation in the chloride form, in a HCl solution, was
fixed in seven different soils by Nishita et al. (1956). These soils
included four loams having pH's of 4.6, 5.7, 6.5, and 6.6, one muck with
a pH of 3.9 and two clays, Bentonite pH 8.2 and Kaolinite pH 4.3, which
were leached with $NH_4Ac$ and distilled water. Their results indicated
that cationic ruthenium is also quite mobile as it, with few exceptions,
was leached from these soils in greater amounts than other tested radio-
nuclides. They also determined that the pH of leaching solutions may
affect the extractability of ruthenium from soils when they reported that,
when aliquots of acidic acid adjusted from a pH of 2.3 to a pH of 9.2 with
$NH_4OH$ were added to these soils, the amount of ruthenium-106 leached

decreased slightly with increasing pH up to a pH of 8.5 and then the amount of ruthenium leached increased.

The sorption of cationic ruthenium was again shown to occur when van der Westhuizen and van Rensburg (1973) added ruthenium to sandy soils. Their investigation was conducted using the jar method (Orcutt et al., 1956) to determine the movements of radionuclides through porous soils under the influence of ground water. The results showed that a downward movement of 1,000 meters by soil water through sandy soil would result only in a 2-meter movement of ruthenium. Because of the retardation of movement caused by the sorption of ruthenium in the sand, its relatively short half-life and the apparent dissipation of this element in sandy soils, they concluded that it would not present a serious environmental hazard.

Perhaps the most ambitious and revealing investigation was conducted by Amy (1971). His work was conducted in an agricultural soil environment that had been contaminated by irrigation water in which radioactive wastes from a nearby nuclear facility had been discharged. Of the radioactivity in the effluent being discharged, ruthenium-103 and ruthenium-106 contributed approximately 90% of this total. In addition to the soils under cultivation, a number of acidic and calcareous soils representative of this irrigated region were used in laboratory investigations for the determination of specific parameters which favor and/or inhibit ruthenium migration and sorption by soil (Tables 1 and 2).

TABLE 1. MECHANICAL AND CHEMICAL CHARACTERISTICS OF ACIDIC SOILS USED IN LABORATORY INVESTIGATIONS BY JEAN-PAUL AMY (1971)

| Soils | Levels | pH | Granulometry % | | | | Organic Matter | | | Absorbent Complex | | | Free Sesquioxide | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Clays | Fine Loams | Coarse Loams | Sands | C % | N % | C/N | S meq/100g | meq/100g | S/T | Iron | Alumi-num | Silica |
| Acidic Brown Soil From Rudlin | A₁₁ | 4.1 | 15.7 | 15.2 | 2.6 | 58.9 | 7.1 | 0.398 | 17.8 | 4.75 | 27.1 | 17.5 | 18.8 | 3.9 | 4.6 |
| | A₁₂ | 4.1 | 13.0 | 13.8 | 6.0 | 62.1 | 2.8 | 0.158 | 17.5 | 1.23 | 17.8 | 6.9 | 26.0 | 6.2 | 6.0 |
| | (B) | 4.1 | 10.8 | 14.4 | 5.2 | 68.3 | 1.9 | 0.113 | 17.2 | 0.87 | 15.5 | 5.1 | 23.2 | 6.9 | 5.0 |
| | (B)C | 4.2 | 9.2 | 6.5 | 4.3 | 72.0 | 1.3 | 0.071 | 18.3 | 0.70 | 14.2 | 4.9 | 21.4 | 6.5 | 5.1 |
| | C | 4.4 | 9.2 | 10.2 | 3.8 | 68.3 | 0.9 | 0.046 | 19.1 | 0.59 | 12.2 | 4.8 | 21.6 | 7.0 | 5.5 |
| Alkaline Brown Soil From Grande Fraize | A₁ | 5.4 | 22.6 | 40 | 22 | 4.5 | 2.68 | 1.14 | 10.7 | 12.02 | 16.5 | 73.2 | 32.1 | 6.5 | 6.8 |
| | A₂ | 4.25 | 29.1 | 25 | 18 | 26.5 | 2.10 | 0.25 | 16.1 | 4.20 | 15 | 28.0 | 34.5 | 6.8 | 9.7 |
| | B | 4.8 | 35.7 | 27 | 16 | 20 | 1.27 | 0.09 | 13.8 | 8.86 | 17.7 | 49.8 | 60.1 | 10.8 | 12.9 |

TABLE 2. MECHANICAL AND CHEMICAL CHARACTERISTICS OF THE CALCAREOUS SOILS USED IN LABORATORY INVESTIGATIONS BY JEAN-PAUL AMY (1971)

| Soils | pH | Granulometry (%) | | | | Organic Matter (%) | Absorbent Complex | | | | | Total Calc (%) | Active Calc. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Clays | Fine Loams | Coarse Loams | Sands | | Ca (meg/100g) | Mg (meg/100g) | K (meg/100g) | Na (meg/100g) | S/T | | |
| Miemar | 7.9 | 2.1 | 6.3 | 4.4 | 87.2 | 3.8 | 15.41 | 0.92 | 0.44 | 0.99 | sature | 25.1 | 6.2 |
| Codelet | 7.7 | 3.4 | 4.3 | 19.9 | 72.4 | 2.5 | 12.21 | 0.77 | 0.52 | 0.12 | " | 15.7 | 2.8 |
| Piboulette | 8.3 | 5.4 | 12.4 | 30.2 | 52.0 | 4.2 | 31.42 | 1.51 | 0.75 | 0.19 | " | 20.7 | 5.1 |
| Pichegu | 8.4 | 8.7 | 24.2 | 35.4 | 31.7 | 2.9 | 28.42 | 1.77 | 0.92 | 0.22 | " | 35.9 | 9.7 |
| Panier | 8.1 | 5.3 | 42.5 | 38.2 | 14.0 | 5.3 | 21.42 | 1.84 | 0.81 | 0.27 | " | 28.4 | 7.7 |
| Barthelasse | 7.2 | 2.8 | 28.4 | 26.1 | 42.7 | 12.5 | 26.49 | 2.21 | 1.03 | 0.34 | " | 34.1 | 3.1 |

Following the radioanalysis of soils collected at various depths in this irrigated area, it appeared that the mobility of ruthenium-106 was associated primarily with the soil texture and the percolation rate of the applied irrigation water. These preliminary conclusions were based on two findings: (1) Of the nitrosyl ruthenium complexes applied to the soil in the irrigation waters, only a small portion was found to be sorbed on either the irrigation canal sediments or on the irrigated soil itself, (2) Even though most of the ruthenium was associated in the top layers of the irrigated soils, due exclusively to the continual application of ruthenium contaminated water, it was commonly found to be evenly distributed at the lower depths in the soil profile. Amy, similar to van der Westhuizen and van Rensburg (1973), hypothesized that because of the mobility and even distribution of ruthenium in these soils, a favorable radioecological situation existed as there was not any large accumulation and also, because of the relatively short half-life of ruthenium, 368 days, the soil concentrations were always quite low.

Amy's laboratory experiments were conducted using three different ruthenium-106 solutions. Two of these were the nitronitrosyl ruthenium complexes, dinitro, $RuNO(NO_2)_2OH(H_2O)_2$, and nitrodinitrato, $RuNONO_2-(NO_3)_2(H_2O)_2$. These two compounds were selected because both are very stable and constitute 70% of the ruthenium form being released from nuclear facilities. The other compound used was ruthenium chloride.

The two laboratory experimental methods used by Amy were the percolation method and the agitation method. The percolation method consisted of filling a glass soil column measuring 30 centimeters (cm) in height and 4.5 cm in diameter with soil. The soil was then pre-moistened with distilled water via capillary action, followed by the addition of one of the ruthenium-106 tagged compounds. The amount of ruthenium solution applied to each column was approximately 1-liter with a total activity of 5 microcuries (μCi). The duration of the percolation varied depending on the texture of the soil used and ranged from 1 hour to more than 70 hours. After percolation, the soil column was dissected into nine equal sections, each then being analyzed for its ruthenium content.

The agitation method consisted of mixing 25 g of soil into a 1-liter ruthenium contaminated solution. This mixture was continually stirred, thereby keeping the soil in as near a homogenous suspension as possible. At predetermined times, 15 milliliter (ml) aliquots of this mixture were collected and then filtered. The soil and filtrate were then analyzed for ruthenium content.

As the behavior of ruthenium in soils is quite complex, because of its many changing chemical forms and its ability to form both cationic and anionic complexes, the ionic nature of these three solutions was determined. After passing these compounds through both anionic and cationic resins, the nitrodinitrato complex, $RuNONO_2(NO_3)_2(H_2O)_2$, was identified to have a cationic character, whereas the dinitro complex, $RuNO(NO_2)_2OH(H_2O)_2$, had an anionic character. The ruthenium chloride caused a predominance of anionic forms to appear which had previously been documented by Bhagat and Gloyna (1965). It was also reported by Amy

7

that these compounds can change in their ionic character as a function of time. As a result, the behavior of the ruthenium was studied in both the acidic and calcareous soils simultaneously.

Amy's percolation experimental results showed that all of the ruthenium compounds used were quite mobile. As expected, the movement of the anionic form through all of the soils tested exceeded both the ruthenium chloride and the cationic nitrodinitrato form. In fact, two of the soils, Miemar and Codelet, retained only 11% and 36% of the total anionic ruthenium, respectively. In contrast to the anionic form 38% to 80% of the cationic ruthenium was sorbed in the surface layers (0-4.5 cm in depth). Even though the retention in the surface layer was generally quite high, at no time did the cationic ruthenium fail to migrate throughout the soil column. The minimum amount retained in the bottom soil layer varied between 1% and 2%, with a minimum of 2% and a maximum of 33% being passed into the percolate.

The data also showed that generally ruthenium chloride was more mobile than the nitrodinitrato ruthenium complex, with 10% to 50% of the applied ruthenium being retained in the 0- to 4.5-cm surface layers. The amount of ruthenium chloride that passed into the percolate following its migration throughout the soil columns varied from a low of 3% to a high of 68% of the amount applied. The mobility of ruthenium chloride was found to be similar to the nitrodinitrato complex in three of the six soils tested, Piboulette, Pichegu, and Panier, with greater mobility, similar to the dinitro form, observed in the Miemar and Codelet soils. As is seen in Table 1, the former three soils are similar in both their mechanical and chemical makeup. The latter two soils exhibit a high permeability having an excess of 72% sand with less than 3.4% clay and 3.9% organic matter.

As is evident, the ionic nature of ruthenium is a very important parameter in its rate of migration. To augment the data obtained from these soil column migration studies, the rate of ruthenium sorption by the Piboulette soil as a function of time was determined by the agitation method. As is seen in Table 3, the nitrodinitrato complex with its cationic character corresponds to some extent to the high sorption rate of the cation cesium-137, whereas the sorption rate of the dinitro complex with its anionic character is relatively slow. However, irrespective of the three forms of ruthenium used, the rate of sorption is progressive, reaching 90% sorb after a 3-day period. Similar sorption percentages were observed by Bryant et al. (1961) during 120-day exposure of humic materials.

8

TABLE 3.  SORPTION PERCENTAGE OF CESIUM-137 AND THREE FORMS OF RUTHENIUM-106
BY PIBOULETTE SOIL AS A FUNCTION OF CONTACT TIME (AMY 1971)

| Radionuclides | Contact Time (min) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 min | 5 min | 10 min | 40 min | 100 min | 500 min | 1 day | 3 days | 7 days |
| Cesium-137 | 95.2 | 98.1 | 99.2 | 99.3 | 99.6 | 99.5 | 99.7 | 99.7 | 99.6 |
| Ruthenium-106 Complexes nitronidinitrato $RuNO\ NO_2(NO_3)_2(H_2O)_2$ | 49.2 | 60.0 | 64.9 | 73.2 | 80.3 | 88.4 | 94.4 | 98.1 | 97.4 |
| Ruthenium Chloride $^{106}RuCl_3$ | 7.9 | 9.4 | 12.4 | 21.9 | 36.1 | 85.7 | 94.0 | 97.4 | 97.5 |
| Dinitro $RuNO(NO_2)_2CH(H_2O)_2$ | 5.2 | 6.0 | 7.2 | 10.5 | 18.9 | 42.0 | 76.2 | 89.6 | 92.1 |

Other studies conducted by Amy showed that the effect of organic
matter and soil particle size on the sorption rate during ruthenium
exposures was quite variable.  For example, the Barthelasse soil, which
is fairly rich in organic matter, 12.5%, was exposed to the three
ruthenium compounds both before and after the destruction of its organic
matter.  The data showed that the presence of the organic matter
increased the amount of ruthenium sorbed in all three compounds with a
two-fold increase in the retention of the dinitro complex.  The effect
of the sorption rate, relative to the soil particle size, was determined
by separating the treated soil into various sizes ranging from clay to
sands.  He reported that the ruthenium content decreased as the particle
size increased.  The clays, which make up only 5.9% of the Piboulette
soil, sorbed in an excess of 84% of the ruthenium, whereas the sands, 52%,
sorbed less than 1%, the remainder being associated with the silt
fractions.

Following these investigations, Amy conducted a study to determine
if the sorption or fixation of the three forms of ruthenium resulted
from an ionic exchange phenomenon, or if a physical bonding occurred,
depending only on the surface characteristics of the soil particles.  Amy
concluded, following the data collection and analysis that the fixation
of the cationic form on the soil particle is a result of physical binding,
depending on both the particle's surface area and its physical character-
istics, whereas the anionic ruthenium compounds appear to be fixed
chemically.

Acidic soils appeared to enhance the rate of ruthenium migration
when compared to the migration rates in calcareous soils.  Amy reported
that, irrespective of a soil's texture and organic matter, the amount of
ruthenium sorbed by the acidic soils as a function of time was always
less than that sorbed by calcareous soils.  For example, depending on
soil type, the sorbtion of 50% of the radioactive ruthenium-106 applied to
the calcareous soils required from 1 to 4 minutes for the cationic form,
1.5 to 5.0 hours for the ruthenium chloride, and from 2.5 hours to 1.0 day
for the anionic forms, whereas for the acidic soils, the cationic form

took from 30 minutes to 2.5 hours, ruthenium chloride 1 minute to 3 days, and for the fixation of the anionic form, 3 minutes to 7 days. He also found that the maximum amount of ruthenium sorbed occurred between a solution pH of 7-8. This finding agreed in large part with the data reported by Nishita et al. (1956) when they found that an increase in the soil sorption rate occurred up to a pH of 8.5.

The sorption of ruthenium-106 by three different soils was investigated by Klechkovsky (1958). His method, similar to Amy's agitation technique, consisted of mixing 0.5 g of each of the following soils: red earth, black earth, and turf podzol, with a 10-ml solution containing ruthenium-106. After stirring and allowing the soil to settle, aliquots of the solution were taken and analyzed. A direct comparison of his results with those of Amy's unfortunately cannot be made, as neither the form of ruthenium used nor the physical or chemical identity of the three soils was presented. His data did show, however, that between 30% and 50%, depending on soil type, was sorbed on the soils. A limited effort to determine if the ruthenium could be replaced by calcium was accomplished by adding $CaCl_2$ to the ruthenium-contaminated soils. These results showed that the calcium was ineffective in replacing the ruthenium. Two conclusions can possibly be drawn from Klechkovsky's data: ruthenium under proper conditions can reach a sorption equilibrium with selected soils in a relatively short time, perhaps less than 2 hours, and once fixed, the attraction, if ionic, is quite strong as ionic $Ca^{++}$ can replace most other ions. In 1958, Klechkovsky repeated the $CaCl_2$ desorption treatment using two additional soils. His results were identical to those obtained in 1957.

A limited number of investigations has been initiated concerning the effect of various complexing and chelating agents on the mobility of ruthenium in soils and its uptake by plants. Some of the original work was conducted by Essington et al. (1963) when they applied and mixed the chelating agents, cyclohexane-1, 2-diaminetetraacetic acid, (CDTA), diethylenetriaminepentaacetic acid (DTPA), and ethylenediamine di(O-hydroxyphenylacetic acid) (EDDHA), into a Sorrento loam soil that had been previously contaminated by ruthenium-106. After watering, the soil was stored for a 2-week period and then planted. The degree of fixation and solubility of the ruthenium in the soil as a function of the addition of each of the chelating agents was indicated by the amount of plant uptake. A comparison of ruthenium concentration in the plants grown in uncontaminated soil versus those grown in the soils treated with the chelating agents showed virtually no difference in tissue concentrations. They concluded that as a cation, the ruthenium may have been strongly sorbed on the soil colloids and thus be relatively unavailable for chelate formation. This hypothesis is probably correct in view of the rate of ruthenium fixation with time as reported by Amy (1971) and Bryant et al. (1961) on a variety of soils and humic materials. They further suggested that if the ruthenium was chelated, it may have become fixed on the soil colloids in such a manner as to remain unavailable for plant assimilation.

Another study to determine the effect of soil amendments on the movement of ruthenium in soils was conducted by Essington and Nishita (1966). They prepared and applied leaching solutions consisting of DTPA,

EDDHA, and CDTA to soil columns containing 260 g of uncontaminated soil covered with a ½-inch layer of ruthenium-contaminated soil. After leaching, the columns were fractioned into ½-inch increments and analyzed for their ruthenium content. The results showed that the effects of the chelating agents in leaching the ruthenium were in the following order: DTPA > EDDHA > CDTA. A control, leached with 30 inches of distilled water, removed only 6% of the ruthenium from the zone of contamination with 0.030% of the applied ruthenium occurring in the leachate where only 9.5% was removed using the same amount of DTPA, with 0.042% occurring in the leachate. They concluded that as only cationic metal ions are chelatable, this small chelate effect may have been related to a low concentration of ruthenium cations in the soil solution.

The transfer, mobility, and biological availability of ruthenium in soils may be enhanced by soil microorganisms. For example, it is common knowledge that soil microorganisms aid in plant assimilation of various minerals by chemically altering their form. A study by Au (1974) showed that plutonium was assimilated and taken up by the common fungus, Aspergillus sp., from a plutonium-contaminated malt agar. His work, along with Auerbach and Olson (1963), indicates that other pollutants, including ruthenium, may become more soluble and mobile in soil systems following microbial action. Unfortunately, there does not appear to be any conclusive data in the literature concerning microbial effects on the soil mobility of ruthenium.


RUTHENIUM IN PLANT SYSTEMS

In 1955, Rediske et al. indicated that the majority of the radioactive pollutants that became incorporated into biological systems have entered via plants. One means of incorporation is by the interception and retention of airborne contaminants by aerial portions of plants with subsequent transport between the different trophic levels. Another method is the deposition of contaminants on soils with eventual root absorption.

With its tendency to be mobile in most soils, ruthenium is readily taken up and translocated in a variety of plant species. However, ruthenium belongs in a group of metals identified by Menzel (1965) which include iron, cesium, and beryllium, and which apparently become less concentrated in plant tissues than that in the surrounding media.

Several studies have shown that ruthenium can be incorporated into the aerial organs of plants following exposures to airborne ruthenium in both the particulate and gaseous forms. In addition to the numerous surveys which have reported a variety of ruthenium concentrations in both plants and soils, related directly to airborne radioactive fallout, a number of local studies have been conducted. For example, Culver (1960) reported that growing grass, which had become exposed to an accidental release of particulate ruthenium, contained over twice the amount of ruthenium per gram than did other environmental samples (litter, root mat, and subsurface and surface soil) collected in the same area.

Another study conducted by Hungate et al. (1960), following a simulated reactor burnup, reported that vegetation had become contaminated

by both ruthenium-103 and ruthenium-106 following an aerial exposure. Their data showed that initial retention of ruthenium on the vegetation was only 0.3% to 0.7% of the total radioactivity applied. However, the binding of these contaminants on the leaf tissue appeared to be quite weak, as after washing the plants with water only half the deposited ruthenium remained. This apparently slow permanent binding characteristic of ruthenium on leaf tissue was also indicated by Russell (1965). He reported that growing cabbage treated with a soluble form of ruthenium-106 lost nearly 90% of the original ruthenium deposited after 28 days. Another 27% of this was removed by washing in water for a relatively short period of 90 seconds. The fairly long period in which this soluble contaminant was being lost from the leaves is evidence that much of this material remained superficially on the leaf surface. This conclusion is supported by the fact that, even after 28 days, an appreciable fraction of the contamination remaining on the leaves could still be removed by washing with water. Based on these data, Russell hypothesized that from the viewpoint of a ruthenium radiation dose to the biota, the extent of absorption by leaves is of small importance as compared with the extent of its retention.

The absorption and retention of ruthenium into both seeds and fleshy fruits were reported by Wittwer et al. (1956) following an aerial exposure to radioactive fallout. This accumulation of ruthenium in the reproductive organs is quite small, however, as most of the ruthenium entering the above-ground portions concentrate mainly in the vegetative organs (leaves and stems) (Klechkovsky, 1956).

As with the early investigations concerning the behavior of ruthenium in soils conducted in the vicinity of the Oak Ridge National Laboratory, studies were in progress to determine if this contaminant was being taken up by the local flora. Auerbach and Olson (1963) reported from their previous investigations that concentrations of ruthenium-106 from $10^{-1}$ to $10^{-3}$ microcuries per gram ($\mu$Ci/g) of dry weight were found in trees growing in known seepage areas near the National Laboratory. A similar study reported by Olson (1960) indicated that ruthenium is readily translocated into various plant parts. His data showed that ruthenium-106 was the main component of the radioactivity in both the hulls and nuts collected from the local walnut, Juglans nigra, having concentrations of 117 x $10^{-6}$ and 31 x $10^{-6}$ $\mu$Ci/g dry tissue weight, respectively.

Obviously, plant uptake of ruthenium by root absorption via a soil exposure can be affected by soil treatments. This should not be surprising in respect to the complex soil chemical behavior exhibited by this element. The soil makeup, changes in pH, additions of various organic humic materials, and/or complexing agents, can become associated with ruthenium forming various cationic or anionic compounds which may serve to limit or facilitate its availability.

Many of the early investigators attempted to identify the form of ruthenium used in "controlled" soil-plant kinetic studies, but neglected to identify and investigate its chemical behavior once mixed in soil. This fact is probably due to the extreme difficulties encountered in

12

qualitative analysis of its many complex forms; however, as a result, most of the data reported is quantitative in nature.

A study conducted by Auerbach (1957b) showed that the concentration of ruthenium-106 was greater in the leaves and roots than in the stems of bean plants, Phaselus vulgaris, grown in pots filled with shale soil and watered with ruthenium-containing wastes. The form of the ruthenium contamination was thought to be nitrosyl ruthenium complexes from wastes which had been derived from nitric acid treatments of fuel elements. Similar data were obtained following a series of root uptake studies by Klechkovsky (1956) using wheat, Triticum persicum, exposed to ruthenium-106. He also found that the majority of ruthenium was accumulated in the roots. His data showed that between 88% to 95% of the ruthenium, depending on the development stage of the plant at the time of exposure, accumulated in this plant organ. Mature plants accumulated far less ruthenium in both stem and leaf tissue (1.9% and 1.5%, respectively), whereas both stem and leaf tissues of younger plants each contained approximately 4.9%.

Other studies, which have contributed to an understanding of the root uptake and retention of ruthenium by plants, have been conducted by Klechkovsky and Gulyakin (1958), Goss and Romney (1959), Mills and Shields (1961), Neel et al. (1953), Romney et al. (1957) (1966), and Ng and Thompson (1966). Most of these investigators used crop plants in their studies as indicators of the possible hazards associated with human consumption of cultivated species following their exposure to soils contaminated with radioruthenium. Generally, the results of these studies, similar to those reported previously, showed that the greatest amount of ruthenium incorporated by the plants occurred in the roots. The largest amount of ruthenium found in the roots occurred in carrots, whereas red bromegrass, Bromus rubens, which had been germinated and grown on soils contaminated by a nuclear detonation, had the greatest amount of ruthenium in the leaf and stem organs. It also appears from the data of these investigators that ruthenium is taken up in much smaller quantities than either strontium or cesium. The reason for this is perhaps related to the fact that whereas strontium and cesium are closely related to the plant micronutrients, calcium and potassium, ruthenium apparently lacks any relationship with nutrient elements.

All of these studies have shown that ruthenium is taken up and translocated into a variety of plant species. However, it is abundantly evident that, of the quantity of ruthenium incorporated in the plant, the majority is retained in the root system. The amount of ruthenium that becomes fixed, either by chemical or mechanical means, on the root surface versus that which becomes biologically incorporated into the root tissues, however, was not fully investigated.

A greenhouse study to determine if the amount of ruthenium-106 extracted from soils could be used in assessing the biological availability of this isotope was conducted by Schulz and Babcock (1974). Basically, their method involved planting five different soils that had been previously mixed with ruthenium-106 in the chloride form, with ladino clover. At 2-month intervals throughout a 10-month period, the clover was harvested and regrowth allowed. The soils were then extracted with the following solutions: water, $1\underline{N}$ $NH_4OAc$, $1\underline{N}$ $NaOAc$, and $1\underline{N}$ $CaCl_2$. Their

study, unfortunately, did not show any conclusive pattern as to the availability of ruthenium. However, it did indicate that exposure of plants to ruthenium for a considerable length of time does not necessarily result in an increase in tissue concentration as a function of time. This is contrary to other reported data, such as by Romney et al. (1970) who found that a consistent increase of other radionuclides in plant leaf tissue occurred during an alfalfa cropping study. This lack of an increase in ruthenium uptake as a function of time is probably related to its ability to become strongly fixed with soil colloids with time, thereby becoming biologically unavailable.

The use of ruthenium-106 as a tracer in translocation investigations was recently reported by Handley and Babcock (1970, 1972). Ruthenium-106, in the form of $^{106}RuCl_3$, was applied in some cases to the foliage, and in other cases to hydroponic solutions containing a variety of crop plants and woody shrub species. Following these treatments, the ruthenium content of roots, and both old and newly formed plant tissue, was determined. Their results showed that in excess of 99% of the ruthenium applied to the foliage remained fixed on the treated area. Of the amount translocated, no evidence of preferential movement into new growth was observed. The results of the hydroponic treatment were similar to those obtained in the foliage treatment with an excess of 99% of the ruthenium being retained on the roots. Over 80% was found in newly formed tissue of corn. From these results, even though translocation is evident, ruthenium in the chloride form at least becomes bound very rapidly to surface tissues, thereby reducing its availability.

The effects of ruthenium on plants have apparently received very limited study. One study in plant nutrition was conducted by Menzel and Brown (1959). They found that ruthenium at 0.0018 and 0.18 micrograms per milliliter in hydroponic solutions had no effect on the metabolism of iron by red clover, Trifolium protense.

The need for an adequate supply of water, and the relatively easy means of disposing of radioactive wastes into aquatic environments, have led to the construction of many nuclear power facilities along both fresh water and marine shorelines. As a result of reactor effluent being dis- charged into these environments, studies to determine the fate and behavior of ruthenium in aquatic biota are being initiated.

A comparison between the biological behavior of nitrosylnitrato ruthenium-106, and complexes of nitrosyl ruthenium-106 occurring in waste effluents commonly discharged into the sea, was conducted by Jones (1960). His data showed that the accumulation of the synthesized complex, nitrato ruthenium, was always greater on marine algae than were the other two ruthenium complexes. He also found that the majority of the accumulated ruthenium on the algae was due to a surface binding characteristic rather than to actual incorporation. Desorption of 60% of the accumulated ruthenium on the algae occurred after a 1-hour emergence in clean sea water. Contrary to the relatively weak binding on the algae, he found that ruthenium-106 which became fixed on particles of marine sediments was not easily removed. For example, less than 7% was removed by washing in sea water or in water adjusted to pH's of 2, 4, or 6. However, a solution of 50% nitric acid, or 5% solution of potassium hydroxide and potassium periodate, removed over 80%. He concluded that the adsorption on the

14

particles was predominantly the result of a chemical binding rather than mechanical. His data further indicated that marine diatoms were as efficient as fine particles of sand in removing ruthenium-106 from solution in sea water. The mode of binding appeared to be about the same for both collecting media.

A similar study by van der Borght and van Puymbroeck (1970), using the same synthesized ruthenium complex as Jones (1960), also found that ruthenium could be removed from marine algae fairly easily. Their data showed that the marine algae Fucus, spp. lost 15% to 20% of the bound ruthenium-106 after six changes of water within a 10-day period.

A number of other studies, such as by Burkholder (1963), Beninson et al. (1965), and Simek et al. (1967), along with a study by Hampson (1967), who used the common seaweed Porphyia umbilicalis as an indicator species, have shown that marine flora will accumulate ruthenium. However, these studies, being more quantitative in nature, serve to illustrate the need for additional investigations concerning the adsorption and fixation of defined complexes of ruthenium on biological surfaces.

LITERATURE CITED

Amy, Jean-Paul, "Study of $^{106}$Ru Migration in Soils," Thesis (CEA-R-4168), in French, translated, RFP-TRANS-140, Nancy University (France), Faculte des Sciences (1971).

Au, F. H. F., "The Role of Soil Microorganisms in the Movement of Plutonium," The Dynamics of Plutonium in Desert Environments, Nevada Applied Ecology Group Progress Report, NVO-142, pp 135-141 (1974).

Auerbach, S. I., "Waste Pit Area Studies: Uptake of Fission Product Seepage by Vegetation," Health Physics, Annual Progress Report for Period Ending July 31, 1957, Oak Ridge National Laboratory, USAEC Report ORNL-2384, pp 27-37 (1957a).

Auerbach, S. I., "Uptake of $^{106}$Ru and $^{60}$Co From Seep Water by Bean Plants," Health Physics, Annual Progress Report for Period Ending July 31, 1957, Oak Ridge National Laboratory, USAEC Report ORNL-2384, pp 37-40 (1957b).

Auerbach, S. I., and Olson, J. S., "Biological and Environmental Behavior of Ruthenium and Rhodium," Radioecology, The American Institute of Biological Sciences, Oak Ridge National Laboratory, pp 509-519 (1963).

Beninson, D., E. Vander Elst, and D. Cancio, "Incorporation of Fission Products by Fresh-Water Plants," Fifth Inter-American Symposium on the Peaceful Application of Nuclear Energy, Washington, D. C., pp 227-232 (1965).

Bhagat, S. K. and Gloyna, E. F., "Radioactivity Transport in Water: Transport of Nitrosylruthenium in an Aquatic Environment," USAEC Report TID 22.870 (1965).

Booth, R. S., "A Compendium of Radionuclides Found in Liquid Effluents of Nuclear Power Stations," USAEC Report ORNL-TM-3801, Oak Ridge National Laboratory, Oak Ridge, TN, pp 22 (1975).

Brown, R. E., Parker, H. M., and Smith, J. M., "Disposal of Liquid Wastes to the Ground," Proceedings of the Intern. Conf. on the Peaceful Uses of Atomic Energy, United Nations, Geneva, Vol 9, pp 669-675 (August 1955).

Brown, R. E., Pearce, D. W., de Laguna, W., Struxness, E. G., Horton, J. H. Jr., and Patterson, C. M., "Experiments in the Disposal of Radioactive Wastes to the Ground," Prepared for the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, pp 13 (A/Conf. 15/P/1767). (1958).

Bryant, G. F., O'Connor, J. T., and Wintner, I., "Studies of Ruthenium and Cesium Retention in Soil-Sawdust and Soil-Peat Mixtures," NYO-7834, Publication of John Hopkins Sanitary Engineering and Water Resources Division, Baltimore, MD, pp 45 (June 1961).

Burkholder, P. R., "Radioactivity in Some Aquatic Plants," Nature, 188, No. 4880, pp 601-603 (1963).

Cowser, K. E. and Parker, F. L., "Soil Disposal of Radioactive Wastes at ORNL: Criteria and Techniques of Site Selection and Monitoring," Health Physics, 1, No. 9, pp 152-163 (1958).

Crockett, A. B., Personal Communications, U. S. Environmental Protection Agency, Las Vegas, Nevada (1975).

Crossley, D. A. Jr., "Comparative Movement of $^{106}$Ru, $^{60}$Co, and $^{137}$Cs in Arthropod Food Chain," Proceedings of the Second National Symposium, Ann Arbor, Michigan, May 15-17, 1967 Conf. 670503 Sec. 11, pp 687-695 (1967).

Culver, H. N., "Activity Releases at Oak Ridge National Laboratory," Nuclear Safety, 1, No. 4, pp 83-88 (1960).

Essington, E. H. and Nishita, H., "Effect of Chelates on the Movement of Fission Products Through Soil Columns," Plant and Soil, 24, No. 1, pp 1-23 (1966).

Essington, E., Nishita, H., and Wallace, A., "Effect of Chelating Agents on the Uptake of $^{91}$Y, $^{106}$Ru, $^{144}$Ce, and $^{147}$Pm by Beans Grown in a Calcareous Soil," Soil Science, 95, No. 5, pp 331-337 (1963).

Fletcher, J. M., Jenkins, I. L., Lever, F. M., Martin, F. S., and Powell, A. R., "Nitrato and Nitro Complexes of Nitrosyl Ruthenium," Inorganic Nuclear Chemistry, 1, No. 6, pp 378-401 (1955).

Goss, J. A. and Romney, E. M., "Effects of Bicarbonate and Some Other Anions on the Shoot Content of Phosphorus-32, Calcium-45, Iron-59, Rubidium-86, Strontium-90, Ruthenium-106, Cesium-137, and Cerium-144 in Bean and Barley Plants," Plant and Soil, 10 pp 233-241 (1959).

Hampson, B. L., "Restricted Dispersion of $^{95}$Zr and $^{96}$Nb after Release to the Sea in Nuclear Fuel Reprocessing Effluent," Health Physics, 13, No. 13, pp 1093-1103 (1967).

Handley, R. and Babcock, K. L., "Translocation of Carrier-Free $^{85}$Sr, $^{137}$Cs, and $^{106}$Ru in Woody Plants," Radiation Botany, 10, pp 577-583 (1970).

Handley, R. and Babcock, K. L., "Translocation of $^{85}$Sr, $^{137}$Cs, and $^{106}$Ru in Crop Plants," Radiation Botany, 12, pp 113-119, (1972).

Hungate, F. P., Stewart, J. D., Uhler, R. L., and Cline, J. F., "Decontamination of Plants Exposed to a Simulated Reactor Burn," Hanford Atomic Products Operation, General Electric Co., USAEC Report HW-63173, pp 1-23 (1960).

Jones, R. F., "The Accumulation of Nitrosol Ruthenium by Fine Particles and Marine Organisms," Limnology and Oceanography, 5, No. 3., pp 312-325 (1960).

Klechkovsky, V. M., "On the Behavior of Radioactive Fission Products in Soil: Their Absorption by Plants and Their Accumulation in Crops," USAEC Translation Series AEC-TR-2867, pp 227 (1956).

Klechkovsky, V. M. and Gulyakin, I. V., "Behavior of Microquantities of Strontium, Cesium, Ruthenium, and Zinc in Soil and Plants," Pochvovedenie, 3, pp 1-15 (1958).

Lomenick, T. F., "Movement of Ruthenium In the Bed of White Oak Lake," Health Physics, 9, pp 835-845 (1963).

Matsunami, T. A., Mizohata, A., and Mamura, T., "Isotopic Ratios of Radioruthenium and Radiocerium in Rain Water at Asaka in Relation to Nuclear Explosions During the Period of Late 1969 to 1972," J. Radiat. Res., 15, pp 96-102 (1974).

Menzel, R. G., "Soil-Plant Relationships of Radioactive Elements," Health Physics, 11, No. 12, pp 1325-1332 (1965).

Menzel, R. G., and Brown, I. C., "Ruthenium (III) and Iron Uptake by Red Clover from Nutrient Solution," U.S. Dept. of Agriculture, Agricultural Research Service Bureau of Plant Industry, Soils and Agricultural Engineering, Division of Soil and Plant Relationships, Beltsville, Maryland, USAEC Report M-7126, pp 1-4 (1959).

Mills, H. L. and Shields, L. M., "Root Absorption of Fission Products by Bromus Rubens From the AEC Nevada Test Site Soil Contamination by an Underground Nuclear Explosion," Radiation Botany, 1, No. 1, pp 84-92 (1961).

Mishra, U. C. and Sadasivan, S. "Fallout Radioactivity in Indian Soil," Health Physics, 23, No. 7, pp 55-62 (1972).

National Committee on Radiation Protection, "Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air and in Water for Occupational Exposure," U.S. National Bureau of Standards, Washington, D.C., Handbook 69, viii, pp 95 (1959).

Neel, J. W., Olafson, J. H., Steen, A. J., Gillooly, B. E., Nishita, H., and Larson, K. H., "Soil-Plant Interrelationships with Respect to the Uptake of Fission Products," UCLA-247, USAEC Technical Information Service, Oak Ridge, Tennessee, pp 4-44 (1953).

Ng, Y. C., and Thompson, S. E., "Prediction of the Maximum Dosage to Man From the Fallout of Nuclear Devices, II. Estimation of the Maximum Dose From Internal Emitters," UCRL-50163 (1966).

Nishita, H., Kowalewsky, B. W., Steen, A. J., and Larson, K. H., "Fixation and Extractability of Fission Products Contaminating Various Soils and Clays: $^{90}Sr$, $^{91}Y$, $^{106}Ru$, $^{137}Cs$, and $^{144}Ce$," Soil Science, 81, No. 4, pp 317-326 (1956).

Olson, J. S., "Forest Studies," Health Physics, Annual Progress Report for Period Ending July 31, 1960. Oak Ridge National Laboratory, USAEC Report ORNL-2994, pp 167-185 (1960).

Orcutt, R. G., Kaufman, W. J., and Klein, G., "The Movement of Radio-strontium Through Natural Porous Media," AECU-3608, University of California, Berkeley, Sanitary Engineering Research Laboratory, pp 58 (1956).

Plummer, G. L., and Helseth, F., "Movement and Distribution of Radionuclides on Granetic Outcrops Within the Georgia Piedmont," Health Physics, 11, No. 12, pp 1423-1428 (1965).

Rediske, J. H., Cline, J. F., and Selders, A. A., "The Absorption of Fission Products by Plants," USAEC Report HW-36734, pp 1-17 (1955).

Ritchie, J. C., Clebsch, E. E. C., and Rudolph, W. K., "Distribution of Fallout and Natural Gamma Radionuclides in Litter, Humus, and Surface Mineral Soil Layers Under Natural Vegetation in the Great Smoky Mountains, North Carolina - Tennessee," Health Physics, 18, No. 5, pp 479-489 (1970).

Romney, E. M., Mork, H. M., and Larson, K. H., "Persistence of Plutonium in Soil, Plants, and Small Mammals," Health Physics, 19, pp 487-491 (1970).

Romney, E. M., Neel, J. W., Nishita, H., Olafson, J. H., and Larson, K. H., "Plant Uptake of Strontium-90, Yttrium-91, Ruthenium-106, Cesium-137 and Cesium-144, From Soil," Soil Science, 83, No. 5, pp 369-376 (1957).

Romney, E. M., Steen, A. J., Wood, R. A., and Rhoades, W. A., "Concentration of Radionuclides by Plants Grown on Ejecta From the Sedan Thermonuclear Cratering Detonation," Radioecological Concentration Processes, Proceedings International Symposium Stockholm, pp 25-29, April 25-29, 1966.

Rudstam, G., "Studies on Nitrosylruthenium Complexes in Nitric Acid Using Repeated Extractions," Acta Chem. Stand., 13, No. 11, pp 1480-1501 (1959).

Russell, R. S., "Interception and Retention of Air-Borne Materials on Plants," Health Physics, 11, No. 12, pp 1305-1315 (1965).

Schulz, R. K. and Babcock, K. L., "Note on the Availability of Carrier-Free $^{106}$Ru from Soils," Soil Science, 117, No. 3, pp 171 - 172 (1974).

Selders, A. A., "The Absorption and Translocation of Several Fission Elements by Russian Thistle," HW18034 (1950).

Simek, J. E., David, J. A., and Day, C. E. III., "Sorption of Radioactive Nuclides by Sargassum Fluitans and S. Nutons," Proceedings of the Second National Symposium on Radioecology, May 15-17, 1967, CONF-670503, pp 505-508 (1967).

Spitsyn, V. I., Bauukova, V. D., Noumova, A. F., Gromou, V. V., Spiridonov, F. M., Vetrov, E. M., and Grafov, G. I., "A Study of the Migration of Radioelements in Soils," Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Sept. 1-13, 1958, Vol. 18, Waste Treatment and Environmental Aspects of Atomic Energy, pp 439-448 (1958).

Tikhomirov, V. K. and Petrukhin, N. V., "The Determination of Radioactive Ruthenium in the Environment," Hygiene and Sanitation, 32 (10-12) pp 99-105 (1967).

van der Borght, O., and S. van Puymbroeck, "Initial Uptake, Distribution and Loss of Soluble $^{106}$Ru in Marine and Freshwater Organisms in Laboratory Conditions," Health Physics, 19, No. 12, pp 801-811 (1970).

van der Westhuizen, H. J., and van Rensburg, H. A. J., "Movement of Some Nuclear Fission and Activation Products in Duinefontein Soil," Pelindaba Pretoria Republic of South Africa, PEL 226, pp 5-14 (February, 1973).

Wittwer, S. H., Tukey, H. B., Tuebaer, F. G., and Long, G., "Current Status of Nutritional Spraying as Revealed by Radioactive Isotopes," California Hort. Society, 17, pp 50-57 (1956).

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*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. EPA-600/3-76-019 | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| 4. TITLE AND SUBTITLE RUTHENIUM: ITS BEHAVIOR IN PLANT AND SOIL SYSTEMS | | 5. REPORT DATE February 1976 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) K. W. Brown | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring & Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Las Vegas, NV 89114 | | 10. PROGRAM ELEMENT NO. 1FA083 |
| | | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS Same as Above | | 13. TYPE OF REPORT AND PERIOD COVERED Final |
| | | 14. SPONSORING AGENCY CODE EPA-ORD, Office of Health and Ecological Effects |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The information published concerning the behavior of ruthenium in plant and soil systems is reviewed and areas needing further investigation are identified. Studies in the literature indicate that ruthenium is one of the most chemically complex elements, thereby challenging the initiative and investigative abilities of both physical and biological scientists.

Ruthenium can become extremely mobile in soils at one time, and then become tightly bound the next. The retention and binding of ruthenium on soil colloids and other environmental media have been demonstrated to be both a physical and chemical phenomenon; however, these binding mechanisms have largely remained unidentified and uninvestigated.

Evidence indicates that ruthenium can become incorporated into plants through either a root or foliar exposure. Mechanisms of vegetative incorporation and retention of ruthenium are still not fully understood, thereby requiring continued study.

| 17. | KEY WORDS AND DOCUMENT ANALYSIS | | |
|---|---|---|---|
| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Ruthenium          Soil physics Absorption (biology)  Radioisotopes Plant metabolism Radioactive tracers Leaching Agronomy Soil chemistry | | Ruthenium uptake Plant systems Soil systems | 06F 07E 08M 18B |
| 18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC | | 19. SECURITY CLASS *(This Report)* Unclassified | 21. NO. OF PAGES 28 |
| | | 20. SECURITY CLASS *(This page)* Unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)