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MATTER: EFFECT ON Zn-65 RELEASE

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Columbia River sediment was irradiated with ultraviolet light to
determine if organic material could be removed without altering the
sorptive properties of the hydrous oxides of iron and manganese.

A laboratory preparation of Zn-65 spiked hydrous ferric oxide
was subjected to ultraviolet irradiation in order to assess the photo-
chemical effect upon Zn-65 release. The photochemically induced
release of Mn-54 present on the Columbia River sediment was used
to assess the effect on the hydrous oxides of manganese.

The ultraviolet irradiation proved effective in removing up to
68% of the sedimentary organic material in 17 hours without causing
release of Zn-65 or Sc-46.

While the ultraviolet irradiation had no effect upon Zn-65
release from laboratory preparations of hydrous ferric oxides and
Zn-65 spiked montmorillonite, a significant release of Mn-54 resulted

from the photolysis treatment. The removal of Mn-54 was not accompanied by the release of sorbed Zn-65 or Sc-46 (nuclides expected to be sorbed by hydrous oxides), nor did there appear to be any permanent change in the nature of the Mn-54 on the sediment. Although it is possible that the hydrous oxides of manganese are affected by the ultraviolet treatment, it is likely that another species, such as the carbonate, is the species involved.

Photo-oxidation appears to provide a method of obtaining sediments with substantially reduced organic content without affecting the sorptive properties of hydrous oxides or clay minerals. This result should allow the use of uptake studies to determine the importance of organic material in trace metal sorption by sediments.

Photochemical Degradation of Sediment Organic
Matter: Effect on Zn-65 Release

by

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INTRODUCTION

General Statement

An understanding of the factors controlling concentrations of

trace metals in natural waters and sediments is of significance in main-

taining and improving the fertility of soils, in the understanding of the

areal incidence of certain diseases, and in the facilitation of water

treatment on industrial waste.

When an artificially induced radionuclide is introduced into the

aqueous environment it becomes fractionated among the solution,

sediment, and biotic phases. Knowledge of how radionuclides are

partitioned is essential to recognizing potential pollution reservoirs

and would aid in coping with them. Further, if the radionuclide is in

the same physical and chemical state as its stable analog, it may pro-

vide information on biogeochemical processes.

The Columbia River contains sediments labeled with several

radioisotopes. Low level wastes from the operation of plutonium

production reactors at Hanford, Washington, have been introduced

into the river since the mid-1940's. Zinc-65 from this source is one

of the most easily detected radionuclides of biological importance in

the Columbia River sediments. Its 245-day half-life makes Zn-65 a

useful tracer for processes which may occur with durations that

may run into several months.

Fixation of trace elements by sediments and soils has been extensively investigated by soil scientists. Several primary modes of zinc fixation have been theorized. Among these are the following: sorption on hydrous oxides; complexation by organic matter; lattice penetration and surface interactions with clay minerals; and precipitation as discrete oxides, hydroxides and carbonates.

Of the proposed controls, only hydrous oxides and organic matter adequately explain the existing data (Jenne, 1968). Conclusive evidence as to which, if either, of these is of primary importance has not been obtained.

Attempts to determine the mode of fixation of zinc in sediments have followed many lines. To date, the central problem regarding chemical methods is their inability to selectively attack any one fraction of the sediment. For example, hydrogen peroxide treatment of sediment to remove organic material is suspected of interacting with the hydrous oxides of manganese with the possible release of sorbed trace metals (Best, 1931). The citrate buffered dithionite treatment used to remove hydrous oxide coatings is argued to remove organically bound trace metals with the citrate buffer. Cutshall (1967) reported that portions of the Co-60, Zn-65, Mn-54, and Cr-51 were capable of being removed by either the organic treatment or the dithionite treatment, depending upon which treatment was applied first.

The purpose of this research was to investigate the effect of ultraviolet light on sediment species believed to be involved in heavy metal fixation. It was hoped to demonstrate that the ultraviolet irradiation would remove sediment organic matter without affecting the hydrous oxides or clay minerals. Such a result would allow the use of uptake studies to assess the extent of trace metal fixation due to organic matter. The organic carbon content of the sediment will be measured with a LECO total carbon analyzer before and after irradiation to determine the amount of organic material removed from the sediment.

The ultraviolet treatment could possibly interact with the hydrous oxides and clay minerals in such a manner as to affect their ability to fix heavy metals. To demonstrate that such effects do not occur, the effect of ultraviolet light on Zn-65 spiked montmorillonite and hydrous ferric oxides will be examined. The effect on the ability of hydrous oxides of manganese to sorb Zn-65 will be assessed by monitoring the Mn-54 present on the Columbia River sediments.

Finally, the physicochemical nature of the Zn-65 released during ultraviolet treatment will be examined to determine its source and the factors which cause Zn-65 release to and resorption from solution. If such zinc were associated with preformed organic material, it could be used to directly estimate a minimum organic contribution to zinc fixation.

In the background that follows, the relevant chemistry of zinc is discussed along with a brief description of the comparative chemistry of other trace metals having radionuclides exhibiting measurable activities in the sediment studied. The nature of zinc in the aqueous and sedimentary environments is also examined with emphasis on the most probable methods of zinc fixation by sediments.

Background Information

Chemistry of Zinc

Zinc, atomic number 30, is a blueish-white metal located in Group II-B of the Periodic Table. Zinc metal is not found free in nature, but rather, exists always in the divalent state.

Zinc comprises only 0.013% of igneous rock, but mineral deposits are widely distributed throughout the world. Marmatite zinc and the zinc sulfide mineral, sphalerite, are the most common zinc minerals. These and most other zinc minerals are usually associated with other base metal sulfides such as those of copper and lead.

A most outstanding property of zinc is its strong electropositive character, surpassed only by aluminium, magnesium, and the alkali metals.

Zinc exhibits divalency in all its compounds, so there is only one series of zinc salts. The chlorides, nitrate, sulfate, and acetate

are soluble in water; the remainder are readily dissolved in mineral acids.

Of special interest in aqueous media are the hydroxides and the carbonate of zinc as their limited solubility is often used to estimate saturation concentrations for Zn^{2+}.

$$Zn_{tot} = Zn^{+2} + \Sigma[mZn_m(OH)_n^{(2m-n)+}] + \Sigma[pZn_p(CO_3)^{(p-q)+}]$$

The hydroxide of zinc is amphoteric. Accordingly, a mixture of $Zn(OH)_2$ and water will contain the following mixture:

$$Zn^{2+} + 2(OH^-) = \frac{Zn(OH)_2}{H_2ZnO_2} = H^+ + HZnO_2^-$$
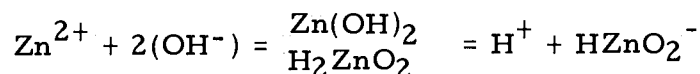
The solubility product for the hydroxide is given as 1.2×10^{-17} (Meites, 1961).

The carbonate of zinc is also rather insoluble having a solubility product of 1.4×10^{-11} (Meites, 1961). Krauskopf (1956) calculated a theoretical maximum concentration of zinc in seawater assuming saturation with respect to zinc carbonate.

Zinc, although a "post-transition" element, forms numerous complexes. Coordination compounds are interpreted as resulting from the use of available bonding orbitals on the metal for the formation of coordinate covalent bonds. The coordination number and configuration are determined by ionic size and charge in part, but

also to a great extent by the orbitals available for bonding.

"Stability" of a complex refers to the thermodynamic stability with respect to decomposition products. "Kinetic stability, " or inertness, implies a species exists only by virtue of its slow rate of decomposition.

Thus, stability constants normally given refer to thermodynamic stability and are related to free energy change for the formation of the complex. For a reaction:

$$M^{n+} + mX = MX_m^{n+}$$
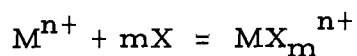
The formation constant is given by,

$$K_m = \frac{[MX_m^{n+}]}{[M^{n+}][X]^m}$$

where [ ] denotes thermodynamic activities. K_m is related to the change in free energy of the reaction by:

$$\Delta G^o = -RT \ln K_m$$

where ΔG is a function of binding energy and entropy changes:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Although the stability of complexes depends on the nature of both the metal and the ligand, coordination compounds of divalent transition and post-transition metals with many ligands follow a

consistent order of relative stability (Shaw, 1960). This order is widely referred to as the "natural order" or Irving-Williams order:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
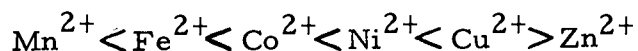
The major contribution to bond energy is electrostatic interaction, a function of size and charge. The natural order is thus not surprising except for the decrease of Zn^{2+}, although the magnitude of the actual differences in stability are much greater than expected on an electrostatic basis.

The decrease in stability of zinc and the actual magnitude of the differences is primarily due to the crystal field stabilization energy. Zinc, with its filled 3d orbitals, can gain no such stabilization.

Though zinc cannot gain ligand field stabilization, it may use its filled d-orbitals in "back pi bonding" with empty pi* molecular orbitals of the ligand. This "back bonding" increases the effective positive charge on the metal ion offsetting the accumulation of negative charge on the metal.

Zinc forms its most stable complexes with ligand atoms in the second period (N, O, F) due to their greater basicity, and prefers bonding to nitrogen over oxyacids. Bonds to chelate groups are more stable than those of unidentate ligands. The greater the number of chelate rings the greater the stability of the complex, with five and six member rings being the most stable.

Zinc in the Aqueous Environment

Goldberg (1965) reports an average zinc concentration of 10 ppb as an ocean average, and Buffo (1967) reports an average of 20 ppb along the Oregon coast. These values are not greatly different than those reported for the Columbia River, with 20 ppb being reported at McNary Dam (Kopp and Kroner, 1968).

Based upon the solubility of $ZnCO_3$, Krauskopf (1956) computed an undersaturation factor of 150-200 for Zn in sea water. Schindler (1967), however, noted that zinc may indeed be oversaturated in sea water if one considers $Zn(OH)_2$ and $ZnCO_3$ precipitates and assuming that ZnO is a minor constituent in solid solutions, such as occur in manganese nodules, where it would be in equilibrium with the meta-stable hydroxide. These two contrasting viewpoints indicate that some processes either keep zinc in solution or remove it from solution. A knowledge of how zinc occurs in the aqueous media is necessary to help answer this question.

Zinc is not likely to exist as free Zn^{2+} but rather in a coordinate complex form, whether merely hydrated or in inorganic or organic complexes. Zirino and Healy (1970) report that polarographic studies of sea water to which Zn, Pb, Cd, and Cu were added to bring their concentrations to 4×10^{-8} M and equilibrated for one hour, showed zinc was present in inorganic complexes probably as $ZnCO_3^{0}$ or

$Zn(OH)_2^0$ or both. They reported that the same pattern exists with sea water that was free of all organics.

Polarographic studies of zinc which is naturally present in sea water show a much different pattern (Piro, 1970). At various pH values 10-15% of the total zinc was found in the ionic form, 35-40% in the particulate fraction, and 50% was reported chelated with some organic substances. This work also showed that if ionic zinc is added to sea water it is distributed in the ionic and particulate form after a short time but does not appear in the organically complexed form even after three months.

Organisms possess the ability to produce organic-metal chelates via metabolic processes and release them to the environment either by excretion or degradation after death. Duursma (1965) reports an average for dissolved organic carbon of approximately 1 mg/l near the surface of the North Atlantic Ocean. In many fresh waters approximately ten times this concentration is normally reported.

Various reports can be found on the nature of dissolved organic compounds in sea water, but relative percents of organic classes such as proteins, lipids, vitamins, and carbohydrates for a single water mass are unknown. Independent reviews by Cooper (1965) and Duursma (1965) tabulate known information concerning organic matter in sea water.

Studies of organic matter in fresh water systems come primarily

from water management sources. Mueller et al. (1958) identified

organic acids and Rychman et al. (1961) characterized river water for

organic materials affecting taste and odor.

Zinc in the Sediment

Sediments are secondary products of rock weathering and have

been classified as follows: (1) residual oxides, (2) clays, (3) pre-

cipitates, (4) evaporites, and (5) residues of organic matter

(Degens, 1965). Sediments may be formed from any one or combina-

tion of these modes. Of these, the clay minerals, precipitates, and

organic matter are most often connected with heavy metal fixation.

The Zn-65 from the Hanford reactor shows a marked tendency

to be fixed in or on planktonic organisms and suspended clay-silt

particles. This zinc becomes concentrated in the sediment of the

Columbia River (Nielsen and Perkins, 1957), with the clay size

fraction showing the greatest relative concentration.

Johnson (1966) demonstrated that this interaction is more

specific than cation exchange. The process has been referred to as

"specific sorption." The dominant fraction of specifically sorbed

zinc is found to be "exchangeable" with certain of the transition

elements but not with Mg^{2+}, Ca^{2+}, and NH_4^+. The order of effective-

ness in displacing ability follows the so-called "natural order" or

Irving-Williams order (Evans, 1970).

Many of the clay particles are coated with a surface layer of hydrous oxides or strongly bonded organic matter (Bowen, 1966). Both of these factors make chemical analysis of clays difficult to interpret and have resulted in multiple theories for specific sorption of zinc on sediments. The most prominent binding theories implicate clay minerals, hydrous oxides, and organic matter. The proposed mechanisms of binding by these sites will be the subject of this section.

Fixation by Clay Minerals

Several modes of heavy metal fixation by clay minerals have been proposed, including lattice penetration, ion exchange, surface sorption, and surface complex formation.

Tiller and Hodgson (1962) note that specifically sorbed cobalt on montomorillonite consists of two main forms which are referred to as "exchangeable" and "nonexchangeable." The "exchangeable" form is dominant, and Hodgson (1960) reports the following order of effectiveness in displacing ability for these metals:

$$Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} = Mn^{2+}$$
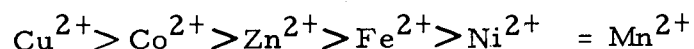
Tiller et al. (1963) demonstrates that fixation is not related to steric factors or cation exchange capacity. Rather, he suggests that chemisorption restricted to a monolayer appears to be involved, and proposes that broken bonds on the surface of the clay minerals expose

-OH groups which bind transition metal cations (Tiller et al., 1962).

It should be noted that the information presented above does not rule out the possibility that coatings of hydrous oxides or organic matter are the actual binding sites. Tiller et al. (1962) demonstrated that plots of sorption of 1.1×10^{-5} M $CoCl_2$ against pH for fifteen of sixteen soils of widely divergent minerology could be fitted to a single curve, and that the sixteenth varied by a constant. This would indicate a mechanism apart from cation exchange or clay mineral structure.

The theories of surface sorption or surface complex formation of heavy metals on clays seem doubtful, as Bingham et al. (1964) reports that the solubility product of $Cu(OH)_2$ and $Zn(OH)_2$ in aqueous suspensions of montmorillonite are nearly identical to those for distilled water containing the pure hydroxide.

Lattice penetration has also been proposed as a mechanism of fixation of non-exchangeable zinc (Tiller and Hodgson, 1962; Elgabaly, 1950). Elgabaly (1950) proposes that zinc could be fixed in the "holes" of the dioctahedral layer minerals and substituted for Mg^{2+} in trioctahedral minerals such as vermiculite and talc which have the octahedral layers of Mg^{2+}. Jenne (1968), noting the extreme conditions necessary to diffuse even small monovalent cations such as Li^{+}, labels such solid state diffusion as unlikely beyond a few atomic planes or at fractures. It thus seems most unlikely that lattice

penetration can explain the "exchangeable" specifically sorbed zinc.

Fixation by Hydrous Oxides of Mn and Fe

Hydrous oxides of manganese and iron are ubiquitous in soils (Carroll, 1958) and sediments (Jenne, 1968) both as coatings and as discrete oxide particles. Sorption by these hydrous oxide surfaces is proposed to be largely specific for heavy metals (Krauskopf, 1956; Morgan and Stumm, 1964; Jenne, 1968).

The general mode of occurence is as partial amorphous coatings on silicate minerals which allows activity far out of proportion to their concentration (Baars, 1950). Laboratory preparations are micro-crystalline with surface areas of up to 300 meters^2/gram for δ MnO$_2$ (Buser and Graf, 1955) and 230-320 meters^2/gram for α- and γ-FeOOH (as cited in Jenne, 1968). The area of surface coatings is expected to be on the order of those from laboratory preparations.

The amorphous hydrous oxides, such as are found in concretionary manganese and iron, are believed to be the most important species in fixation of transition metal ions by hydrous oxides. Such concretions contain large quantities of various metals (Harris et al., 1970; Taylor et al., 1964). Kolthoff et al. (1939) demonstrated that adsorption, rather than occlusion, is the principal cause of contamination of hydrous oxides of iron and that the Freundlich isotherm holds for Cu, Ni, and Zn adsorption over a wide range of concentrations.

The $-H^+$ and $-OH^-$ are potential determining for the MnO_2 series (Healy et al., 1966). Murray et al. (1968) reported that the transition metal ions Ni^{2+}, Cu^{2+}, and Co^{2+} exhibit marked specific adsorption as evidenced by finite adsorption of these ions but not Mg^{2+}, Ca^{2+}, or NH_4^+ at the zero point of charge.

Posselt et al. (1968) notes that for tensioactive organic material the electrostatic forces of attraction are the principle forces involved in sorption by MnO_2. Sorption of the cationic species was rapid and nearly complete, while both the anionic and neutral organic did not measurably adsorb on the MnO_2 despite the relatively large surface area of the oxide. Such data suggests that hydrous oxides of manganese and iron may be important not only in direct sorption of trace metals but may also be involved in fixation of organo-metallic complexes.

Fixation by Organic Matter

Evidence for complex formation or chelation of zinc and other metals by organic matter in the sediments has been deduced from three principal lines of reasoning: (1) the positive correlation often found between heavy metal content and organic matter content of soils, (2) the known chelating ability of certain organics, and (3) the reduction in fixing capacity by treatments which block or oxidize organic matter.

Organic control of zinc and other trace elements was first suspected due to the correlation often found between zinc content and organic content of soils and sediments. Rankama and Sahama (1950) report the zinc content of shales enriched in organic matter to range from 200 to 1000 grams/ton. Zinc is found in coal ash in quantities from 100 to 1000 grams/ton, and in the ash of asphalt and crude oil ranging between 100 and 2500 grams/ton.

In studies of the formation of zinc complexes with bog soil, Himes and Barber (1957) report that the humic acid fraction retained 59% of the zinc and the fulvic acid fraction 12%. Schnitzer and Skinner (1963, 1965) implicated the carboxyl groups and phenolic hydroxyls in chelation with humates by using acetylation, esterification, and methylation as blocking mechanisms for the functional groups. The affinities for metals followed the Irving-Williams order for the humates. Himes (1957) demonstrated similar results for carboxyl groups and active hydrogen groups in soil samples. Such results agree well with the known ability of zinc to form stable complexes with fulvic acid (Schnitzer and Skinner, 1966), tartrate (Tsimbler, 1956), citrate, oxzylate, and amino acids (as cited in Rankama and Sahama, 1955).

Oxidation of the organic matter with hydrogen peroxide has caused a marked reduction in the ability of soil samples to fix zinc (Baughman, 1956). Jenne (1968) argues that this may be due to

hydrous oxides of manganese catalyzing the decomposition of hydrogen peroxide, rather than actually being due to oxidation of organics.

Since sediments may contain the same organic constituents as soil, and possibly algae and phytoplankton as well, retention of Zn-65 as a coordinate complex with organic constituents of sediment seems plausible. Organic carbon in the Columbia River sediment averages 3 o/w. This small amount of organic matter may be important because it has a high exchange capacity and may selectively sorb certain ions (Haushild et al., 1966).

Other Elements Detectable in the Sediment

Radioanalysis of sediment samples also indicated the presence of Co-60, Mn-54, and Sc-46. Though these nuclides were not of primary interest in this study, their responses are of interest in the context of the comparative chemistries of these elements.

Cobalt-60

Cobalt is most similar to zinc in chemistry. Like zinc, cobalt is also a biologically essential element, performing a catalytic role. In the simple cobalt compounds, the divalent form is most stable. Cobaltous ion, Co^{2+}, is basic and is not easily hydrolyzed in aqueous solutions. It is not amphoteric. A few simple cobaltic, Co^{3+}, salts are known, but most simple Co^{3+} compounds are unstable because

Co^{3+} is a strong oxidizing agent and cannot exist in aqueous media.

The trivalent state of cobalt is stable relative to the divalent state only as complexes, of which there are a great many. The most numerous of these complexes, all of which are six coordinate, are those of ammonia and the amines, indicating that the most important donor atom is nitrogen. Carbon, oxygen, sulfur, and the halogens are also important donor atoms. In contrast, Co^{2+} has a coordinate number of either 4 or 6, and the Co^{2+} complexes are relatively unstable toward oxidation.

Manganese-54

Manganese is one of the most abundant heavy metals in the earth's crust and is widely dispersed. Manganese is also found in small quantities in animal tissue and is considered to be a required constituent functioning in a catalytic role.

Manganese can exist in valence states of +1 to +7, the most stable salts being of the divalent form and MnO_2 being the most stable oxide. The lower oxides are basic and the higher oxides acidic. MnO_2 is amphoteric but extremely insoluble.

Divalent manganese forms many complexes, but the equilibrium constants of their formation in aqueous solutions are not as high as those for Co^{2+} or Zn^{2+} because the Mn^{2+} ion is the largest of these and has no ligand field stabilization energy in its complexes (except

for a few low spin states).

Scandium-46

Scandium is much different than the other transition metals discussed in that only the Sc^{3+} state is stable (except for the metal). The chemical behavior is more like the trivalent rare earth elements or ferric iron than cobalt, manganese, or zinc. However, its size makes it very electropositive, and its oxides are decidedly more basic than aluminium.

Unlike the other metals noted, scandium does not appear to be biologically essential.

Scandium is known to be enriched in manganese nodules (Chester, 1965) and is believed to be associated with the hydrous oxides. The citrate buffered dithionite treatment removed over 80% of the Sc-46, along with the ferric oxides, on some sediments from the McNary reservoir (Cutshall, 1967).

METHODS AND MATERIALS

Sample Site

The Columbia River has been receiving radionuclides since the first Hanford Reactors began operating in 1944. Since the input levels were maintained over a long period of time, many radionuclides have approached equilibrium in the Columbia River water, sediment, and biota (Osterberg, 1965).

This inventory of radionuclides is not uniformly distributed through the length of the river. A major part is deposited in the reservoir behind McNary Dam, which provides the first slack water 120 km below the Hanford Reactors. Depletion calculations based upon effluent concentrations indicate 65% of the Zn-65 to be in the portion of the river between McNary Dam and Hanford (Nelson et al., 1966). Based upon Zn-65 activities from 1964, Nelson calculated the inventory of Zn-65 in this reach of the river to be 5500 Curies after decay corrections. With the reduced number of operating reactors just prior to the time of sampling, the activity was estimated to be approximately 1800 Curies in 1970.

Sampling and Storage

Samples of clay-silt sized sediments were taken in a near-shore area of quiet water. The average water depth was approximately

three meters. Samples were taken by a diver skimming a plastic

bucket along the sediment-water interface.

Samples were stored in plastic buckets under a layer of over-

lying river water. After arrival at the Corvallis laboratory, the

samples were stored at 12° C.

<div align="center">Preparation and Treatment</div>

General Method

Separation of sand and clay-silt size particles was made as soon

as possible to remove organisms and large debris from the sample.

The sand is arbitrarily defined as the fraction which settles through

a depth of 20 cm in twenty minutes, and the clay-silt fraction as that

which remained in suspension and could be centrifuged down at 1500

rpm in 15 minutes. This somewhat inexact method of fractionation

was used in order to avoid bringing the sample in contact with any

medium which might sorb or desorb zinc from the suspended particles

or which might subject the sediment to stresses that might alter the

mechanism of binding.

Four milliliter subsamples of the clay-silt fraction were taken

for ultraviolet treatment along with a second subsample which was

used to determine organic carbon content of the untreated sediment.

The 4 ml sample was analyzed for gamma-emitting nuclides and then

suspended in 750 ml of 0.01M $MgCl_2$ solution which had previously

been degassed and brought to pH 7.5 with NaOH. $MgCl_2$ was intended

to provide a constant ionic strength and to aid in flocculation during

centrifugation.

The sediment suspension was then irradiated with ultraviolet

light while being oxygenated in a closed loop system described below.

During the irradiation, the apparent pH was maintained between 6.8

and 7.2 by adding NaOH and HCl as needed.

Following irradiation, the sediment suspension was centrifuged

for one hour to separate the sediment. The supernatant liquid was

decanted, acidified, evaporated to 12 ml, and counted. The sediment

was recounted for gamma emitters, and then both irradiated sediment

and the control were analyzed for organic carbon content by the LECO

Carbon Analyzer.

Radioanalysis

All measurements of radioactivity were made by gamma-ray

spectroscopy. A lead shielded 5 x 5 inch NaI(Tl) well crystal coupled

to a Nuclear Data ND-130AT 512-channel analyzer calibrated at 10

Kev/channel provided the necessary instrumentation.

Sediments were counted for 40 to 100 minutes in a constant

geometry of 4 ml volume. Of over 60 different radionuclides present

in the effluent from the Hanford Reactors, four radionuclides (Mn-54,

Zn-65, Sc-46, and Co-60) were of sufficient activity and half-life to be detected under the conditions of this study. Spectra were reduced for Co-60, Sc-46, K-40, Zn-65, and Mn-54 by making corrections for interferences and counting efficiency.

Zinc-65 was selected for primary consideration largely because: (1) zinc is an essential trace metal, and (2) Zn-65 is most readily detectable with the sediment sample size and counting time used.

Solutions were analyzed at a volume of 12 ml and the data reduction done by computer. The same corrections were made for the simpler liquid medium which normally only contained Zn-65 and Mn-54 at detectable levels.

Ultraviolet Treatment

Ultraviolet Light for Organic Analysis

The use of ultraviolet photo-oxidation for analysis of organic material in fresh water and sea water is now accepted if not common practice. Beattie et al. (1961) observed that organic matter in fresh water could be oxidized to carbon dioxide on exposure of samples to radiation from a medium-pressure mercury vapor lamp. Armstrong et al. (1966) applied ultraviolet photo-oxidation techniques to the analysis of sea water. To assess the completeness of oxidation, they added various classes of organic compounds at concentrations of

1-2 milligrams of carbon/liter in artificial sea water. Samples were irradiated and the residual carbon determined. The following compounds were oxidized substantially to completion with a 2-3 hour irradiation period: pyridine, 2,2'-bi-pyridine, adenine, ethyl alcohol, methyl alcohol, glucose, glucosamine, acetic and oxalic acid, formic acid, palmitic acid, dimethylamine, casein, glycerol, phenylalanine, and "humic acid."

Basic Photochemical Mechanisms

Relating irradiation to chemical alteration necessarily leads to the need for a basic understanding of photoactivation. There are two basic laws of photochemistry: (1) only radiations which are absorbed by a reacting system are effective in producing chemical change, and (2) each molecule taking part in a photochemically induced reaction absorbs one quantum of radiation.

Photoactivation occurs by the absorption of a single photon or quantum of radiation (Pitt , 1946) with the energy of the photon expressed by Plank's Law, $E = hv$, where E is the energy in ergs, h is Plank's constant, and v is the frequency in $\sec^{-1}$. The proper wavelength of radiation for a photo-process corresponds to the energy difference between electronic orbitals of the reactant and the excited species (Cassano et al., 1967). Because of this, photochemical reactions can be highly selective.

Molecules absorbing radiation form a metastable excited state which is highly reactive and may lose this excess energy by a number of pathways. There are three primary modes of de-excitation: (1) loss of excess energy by transfer to another molecule, (2) loss of energy through radiation emission, and (3) formation of ground state products. Several types of photochemical reactions are: (1) elimination and decomposition, (2) addition and dimerization, (3) rearrangement, (4) substitution, (5) atom abstraction, and (6) chain reactions. The usual wavelength range for such reactions is between 200-700 nm (Necker, 1967).

The quantity of energy necessary for bond rupture of most organic molecules ranges from 1 to 5 ev (Necker, 1967). Because the photon energy is quantized, however, the molecular decomposition mode is greatly influenced by small differences in energy between molecular bond strengths.

Solvents influence the course of the reaction because molecular collisions are frequent when solvent molecules are present. Quenching and chemical reactions with the solvent are thus rapid. The sediment substrate may also act to quench the excited species. Further, the solvent also exerts a cage effect which favors recombination and reduces the likelihood of addition-type reactions in dilute media.

Photolysis System

The basic photolysis system (Figure 1) consisted of an ultra-violet lamp which is fitted in a double-walled quartz immersion well. Cooling water, which kept the sediment solution at $22^{o}C$, was circulated through the jacket in the immersion well. The solution irradiation vessel sealed around the immersion well with a ground glass joint. The sediment suspension was drawn from a 1.5 liter Nalgene holding bottle, past an oxygen bubble source, through the irradiation chamber, and then pushed back into the holding bottle by a centrifugal pump. (Equipment specifications are given in the Appendix.)

Sediment Organic Carbon Analysis

The organic carbon content of irradiated and non-irradiated sediment was measured using the LECO WR-12. The LECO total carbon analyzer quantitatively converts carbon present to CO_2 by combustion in a high frequency induction furnance. The CO_2 is selectively absorbed on a molecular sieve. It is later released by heating and measured by thermal conductivity. The output of the thermistor bridge is integrated and read directly on a digital voltmeter as the weight percent of carbon.

As the LECO instrument measures total carbon, the trace
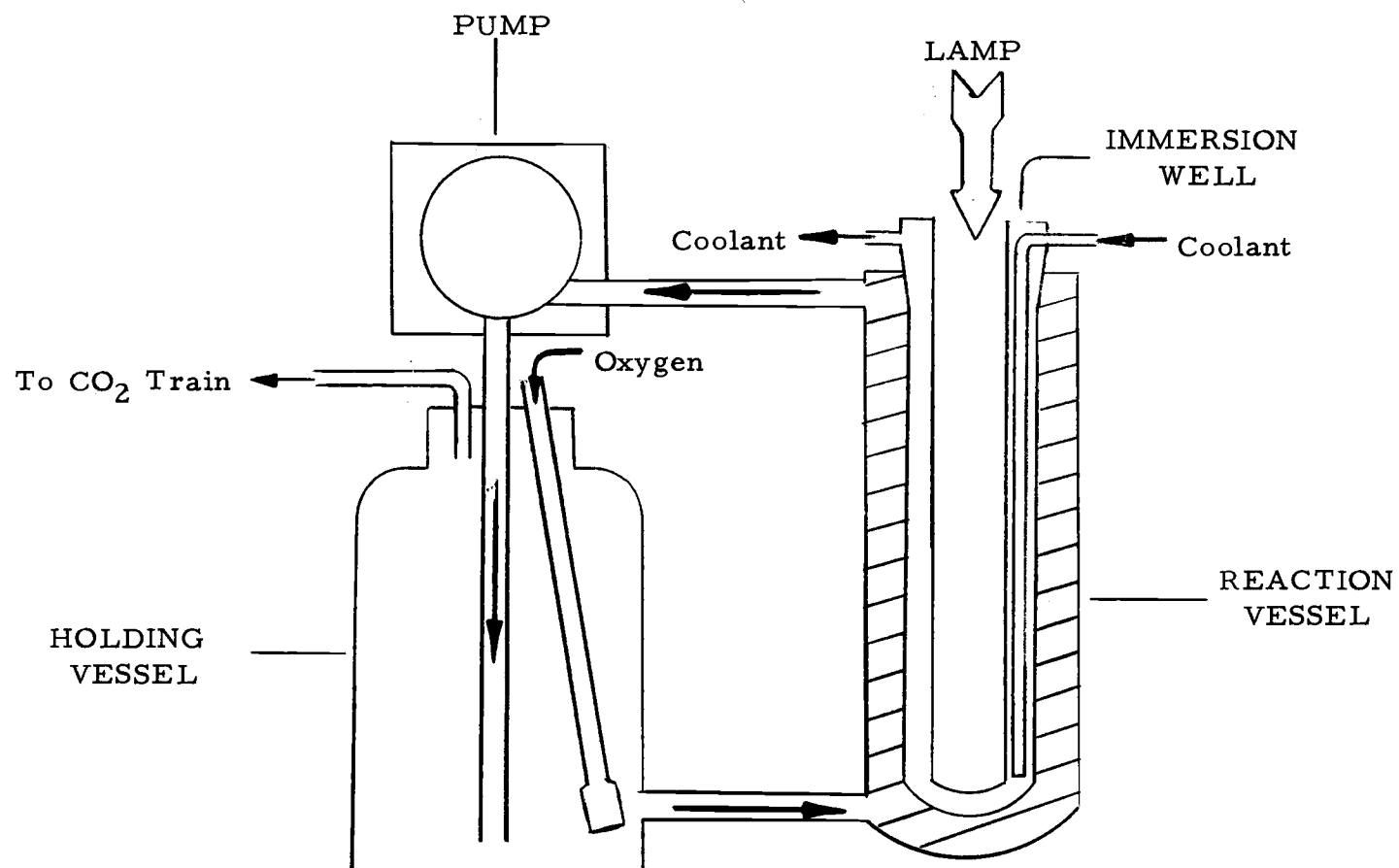
Figure 1. Photolysis Apparatus

amounts of carbonate carbon must be removed in sample preparation. The sediment samples are air dried and then kept at 100°C overnight. The samples are then weighed into preburned sample crucibles and placed on a hot plate at 55°C. Ten percent HCl is added drop-wise just wetting the sediment until carbonates have been removed. The samples are then washed five times with 5 ml of distilled deionized water, dried at 100°C, and analyzed.

RESULTS AND DISCUSSION

Effect of Ultraviolet Treatment Upon Sediments

Treatments

Two methods of ultraviolet irradiation of sediment were investigated. The first entailed continuous irradiation of a sediment sample suspended in 0.01M $MgCl_2$ solution. The duration of irradiation ranged from one to thirty-seven hours. At the end of the treatment, the suspension was centrifuged and the supernatant liquid and sediment were separated for analysis. Such a treatment procedure will be referred to as a continuous irradiation throughout this section.

The second method consisted of irradiating the sediment in suspension for a series of one hour runs. After each run, the sample was centrifuged, the supernatant solution was removed for analysis, and a new $MgCl_2$ solution was added as a suspending medium. Such a treatment procedure will be referred to as a series irradiation throughout this section.

During treatments by both methods, the change in pH was monitored and held between 6.8 and 7.1. The amount of acid or base added gave a measure of the acid formed or destroyed during the ultraviolet irradiation.

At the end of the irradiation period, the release of organic

carbon from the sediment and the release of radionuclides to solution were measured.
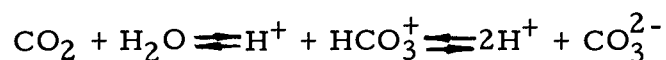
Effect of Continuous Irradiation

Figure 2 shows the pattern of Zn-65 release, organic carbon removal, and change in hydrogen-ion concentration, $[H^+]$, when sediment is subjected to some durations of ultraviolet irradiation.

The error bars represent the standard deviation where multiple samples were analyzed. No error bars were included where multiple samples were not run as the counting errors were insignificant in comparison to the standard deviation between samples. It was felt that indicating counting errors would be more misleading than informative.

The change in H^+ concentration is that of an individual sample run. Although the magnitude of the change in $[H^+]$ varied between samples, the increase ceased after 2-3 hours of irradiation in all runs. After 8-12 hours of irradiation, the H^+ concentration began to drop with the pattern noted in the graph.

The H^+ concentration pattern most likely results from alterations in the carbonate equilibrium caused by photo-oxidation of organic matter to CO_2.

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^+ \rightleftharpoons 2H^+ + CO_3^{2-}$$
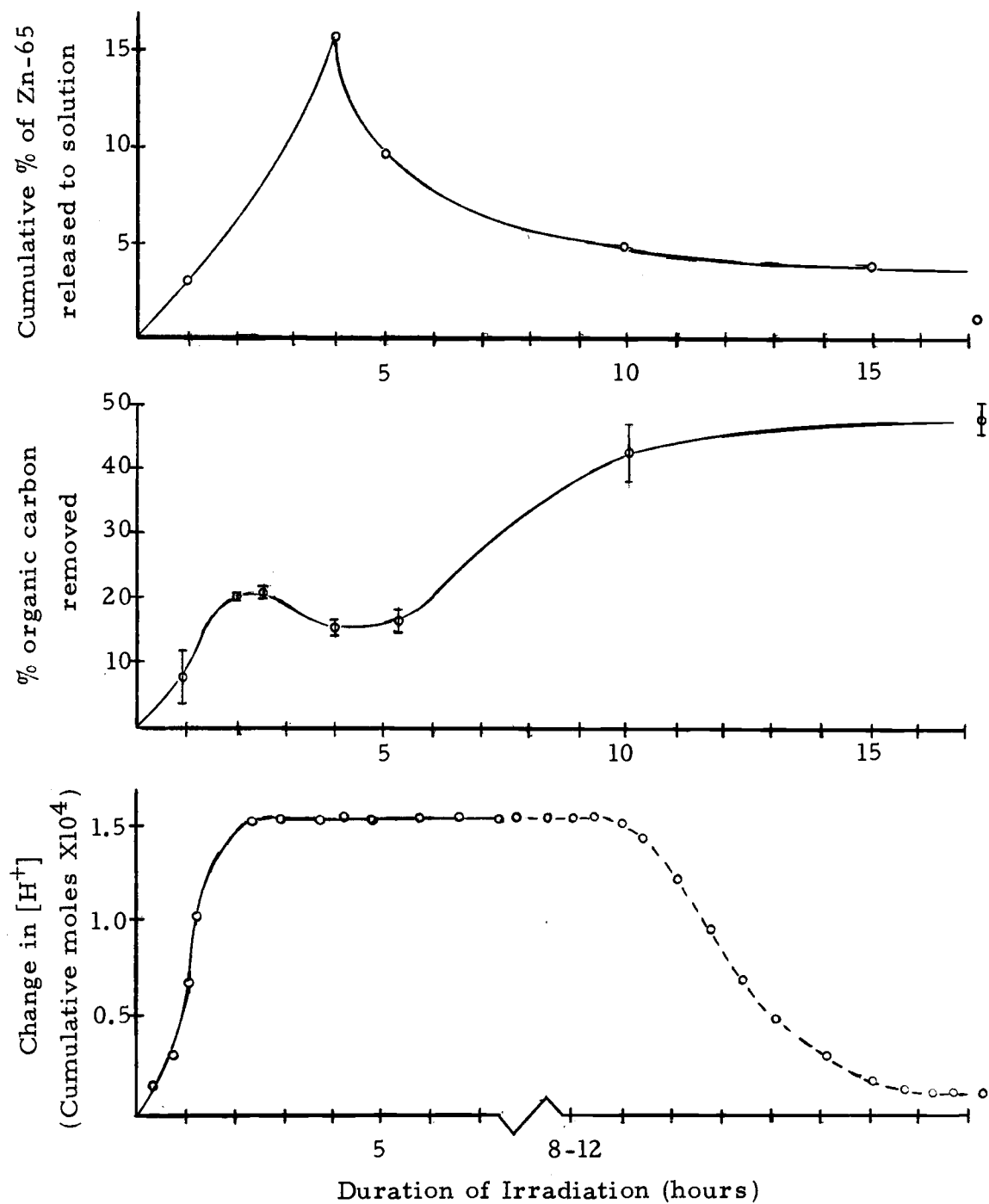
Figure 2. Effect of continuous irradiation. (1) Zn-65 release to solution. (2) Organic carbon removal from sediment. (3) H^+ concentration change.

An increase in CO_2 from photo-oxidation of organics displaces the equilibrium in favor of a more acid medium, causing the initial drop in pH. Once equilibrium is established, after 2-3 hours, the pH remains constant. When the organic content of the sediment has been sufficiently reduced to become the limiting reagent, the CO_2 equilibrium begins to be displaced back to the initial state, causing the rise in pH.

This explanation of pH change is consistent with the pattern of organic carbon release from the sediment. Furthermore, leveling off of the H^+ concentration curve and a possible break in slope of organic carbon release occur simultaneously.

The pattern of Zn-65 release to solution is striking in that it is initially released to solution and later resorbed by the sediment. The release of Mn-54 and Co-60 follow this pattern, while there is no release of Sc-46 from the sediment. The return of radionuclides to the sediment also coincides with the break in slope for H^+ concentration.

The carbonate and hydroxide systems are held to control the concentration of Zn in aqueous solution. As both H^+ and CO_2 concentrations are known to be affected by the ultraviolet treatment, it is likely that these systems are involved in the Zn-65 release pattern. Due to a paucity of data, however, no specific hypotheses are offered regarding how these systems may be involved.

The patterns noted in figure 2 could also be explained through photolytic release of organo-metallic complexes. This alternate hypothesis would have soluble organic acids formed as one of the photolytic degradation products of sediment organic matter. These organic acids would explain the pH change in the same manner as noted in the carbonate hypothesis. The pattern of Zn-65 release and resorption would be viewed as a case of transient equilibrium between release of organo-metallic complexes to solution and their degradation; organics in solution should be degraded more rapidly than those in the sediment due to quenching considerations, and those which are metal complexes should be further sensitized to photolytic attack by the bound metal.

Such a hypothesis is interesting as it could yield a direct means of assessing the contribution of organic material to trace metal fixation. If the soluble organic complexes were originally present as complexes in the sediment, the Zn-65 released to solution would be an estimated minimum organic contribution to zinc fixation by sediment.

Effects of Series Irradiation

Both of the hypotheses mentioned previously imply that equilibrium processes cause the pH and Zn-65 release patterns. To examine this possibility and the processes in action, series
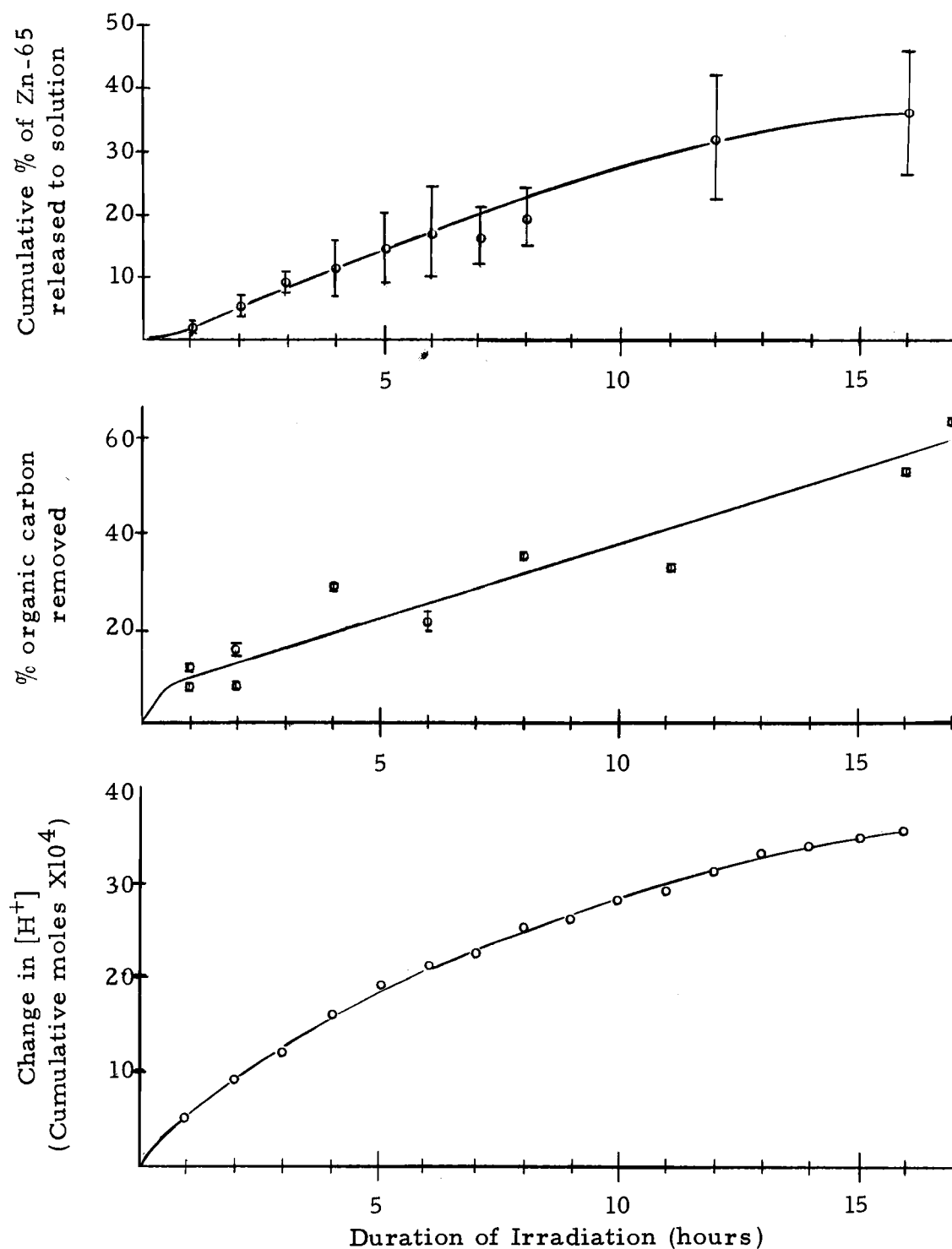
Figure 3. Effect of series ultraviolet irradiation. (1) Zn-65 release to solution. (2) Organic carbon removal from sediments. (3) H^+ concentration change.

irradiations were carried out with the sediments. This procedure would oppose the establishment of an equilibrium.

The plots of series irradiation effects (Figure 3) demonstrate a much different pattern than did the continuous irradiations. Again, the plot of H^+ concentration refers to a representative sample pattern. Zn-65 release is highly variable, as indicated by the bars marking the standard deviation, but any individual sample series followed the pattern indicated by the line plotted.

The release of Mn-54 and Co-60 followed the pattern of increasing cumulative release that was shown by the Zn-65. There was no detectable release of Sc-46.

Organic Carbon Removal From Sediments

Both the continuous irradiation of a single suspension and the series of one hour irradiations removed organic carbon from the sediment. The rate of removal was similar by both methods (see Table 1). This was contrasted to the control runs which showed a 4.0 $\pm$ 1.0% increase in organic carbon content in 16 hours of series irradiation. The increase is probably from organic material in the distilled deionized water.

There was no obvious change in appearance or texture of the sediment after the ultraviolet treatment. In contrast, hydrogen peroxide treatment, which removed 87.0 $\pm$ 0.4% of the organic carbon,

Table 1.   Organic carbon removal from the sediment by ultraviolet irradiation.

CONTINUOUS IRRADIATION		SERIES IRRADIATION	
Duration of Irradiation (hours)	Percent Organic Carbon Release	Duration of Irradiation (hours)	Percent Organic Carbon Release
1	8. 16 ± 0. 28	2	8. 24 ± 1. 40
1	11. 60 ± 0. 17	2	16. 88 ± 2. 36
2	20. 76 ± 0. 18	4	29. 57 ± 0. 98
2. 5	21. 50 ± 0. 52	6	21. 91 ± 0. 96
4	15. 70 ± 0. 54	8	34. 57 ± 2. 31
5	16. 95 ± 1. 74	11	32. 87 ± 0. 85
10	42. 73 ± 4. 45	16	52. 60 ± 0. 14
38	58. 77 ± 6. 26	17	62. 64 ± 4. 62

Each duration represents a single sediment sample that was analyzed in three aliquots.   The error term is the standard deviation of those aliquots.

altered the appearance of the sediment from a deep brown to a pale gray.

Measurement of carbon dioxide release during irradiation would be valuable in determining the fraction of organic carbon which might be present in solution and the fraction completely oxidized to carbon dioxide. An attempt was made to measure this, but the precision of the method was inadequate.

Effect of Ultraviolet Irradiation on Hydrous Oxides

Effect upon the Hydrous Oxides of Iron

To test the effect of ultraviolet light on the hydrous oxides of iron, a laboratory sample of Zn-65 labeled Fe_2O_3 was formed in a sterile medium following the method of Krauskopf (1956). The oxide was allowed several months to come to equilibrium.

The hydrous oxide sample was irradiated in the same manner as the sediment for a series of four one-hour runs. The supernatant solutions were pooled and analyzed for the presence of Zn-65. There was no Zn-65 released, nor was there any change in the appearance of the samples.

A second sample of spiked hydrous ferric oxide was irradiated in the presence of montmorillonite. Again Zn-65 was not released. On the other hand, spiked samples of the standard clay demonstrated

the same pattern of Zn-65 release as sediments.

The results indicate that ultraviolet irradiation does not cause desorption of Zn-65 from ferric hydrous oxides.

## Effect upon the Hydrous Oxides of Manganese

Because of the complexity of the manganese hydrous oxide system, it was decided to examine the effect of ultraviolet irradiation upon Mn-54 present in the sediment rather than attempting to use laboratory preparations.

The series of one hour irradiations indicated that Mn-54 was being released by the ultraviolet treatment. Though the control showed some release, Mn-54 release during irradiation was significantly greater than the control. This indicated that the hydrous oxides of manganese may have been affected by the ultraviolet treatment.

Best (1931) proposed that MnO_2 acted as a catalyst in the decomposition of hydrogen peroxide. The same process may occur during ultraviolet irradiation. Hydrogen peroxide can be photochemically produced by the reaction (Rollefson and Burton, 1939)

$$H_2O \overset{h\nu}{=\!=} H_2O_2 + H_2 \quad .$$
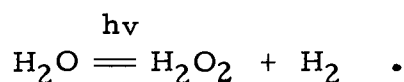
In neutral and alkaline suspensions the process proposed by Best is:

$$MnO_2 + H_2O_2 = Mn(OH)_2 + O_2$$

$$Mn(OH)_2 + H_2O_2 = MnO_2 + H_2O \quad ,$$
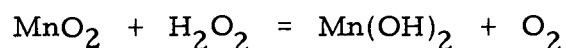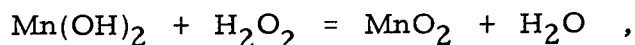
and in acidic media:

$$MnO_2 + H_2O_2 + 2H^+ = Mn^{2+} + 2H_2O + O_2 \quad .$$

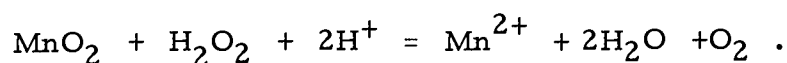To further investigate this possibility, sediments were treated with 30% hydrogen peroxide following the method used by Cutshall (1967). Peroxide treated sediments were then irradiated. In this instance, there was no pH change since little organic matter was present. The release of Mn-54 from both the control and the irradiated sample followed the pattern of release shown by the series irradiation of normal sediments. The hydrogen peroxide treatment and ultra-violet irradiation thus have a similar effect upon Mn-54 release.

It is doubtful, however, that hydrogen peroxide is the cause of photolytic Mn-54 release due to (1) the unlikelihood of sufficient hydrogen peroxide being present during photolysis, and (2) the inability of hydrogen peroxide effects to explain the pattern of Mn-54 release with continuous irradiation.

Though hydrogen peroxide may be produced during photolysis, it is unlikely to accumulate to significant levels. The H_2O_2 is highly unstable to photolytic decomposition (Rollefson and Burton, 1939). Beattie et al. (1961) reported that no hydrogen peroxide remained after two hours of irradiation of a 100 ml solution of fresh water to which

5 ml of 30% H_2O_2 had been added. It is unlikely that a system originally free of hydrogen peroxide would produce a significant amount of this product.

If hydrogen peroxide had developed in significant amounts, it still would not explain the pattern of Mn-54 release exhibited during continuous irradiation. If the Mn-54 release were from the catalytic decomposition of the hydrogen peroxide, the reaction should continue throughout the irradiation and resorption should not be observed.

To explain resorption, one must propose a physicochemical change in the Mn-54 species such that it is no longer affected by the process which initially released it. This does not appear to be the case, however. Upon re-irradiation of a sediment sample that had been previously subjected to a 37-hour continuous irradiation, there was a 12.0 ± 2.2% Mn-54 release; this is the same release exhibited by sediment irradiated for the first time.

There is no apparent change in the sorptive ability of the sediment accompanying the photolytic release of up to 60% of the Mn-54. Neither Sc-46 or Zn-65 showed any release in response to the ultraviolet treatment. While the release of Zn-65 was diminished by hydrogen peroxide treatment, there was no similar effect exhibited by the sediment subjected to ultraviolet irradiation.

The results of this investigation indicate that although Mn-54 is released by ultraviolet treatment, the sorption of other trace
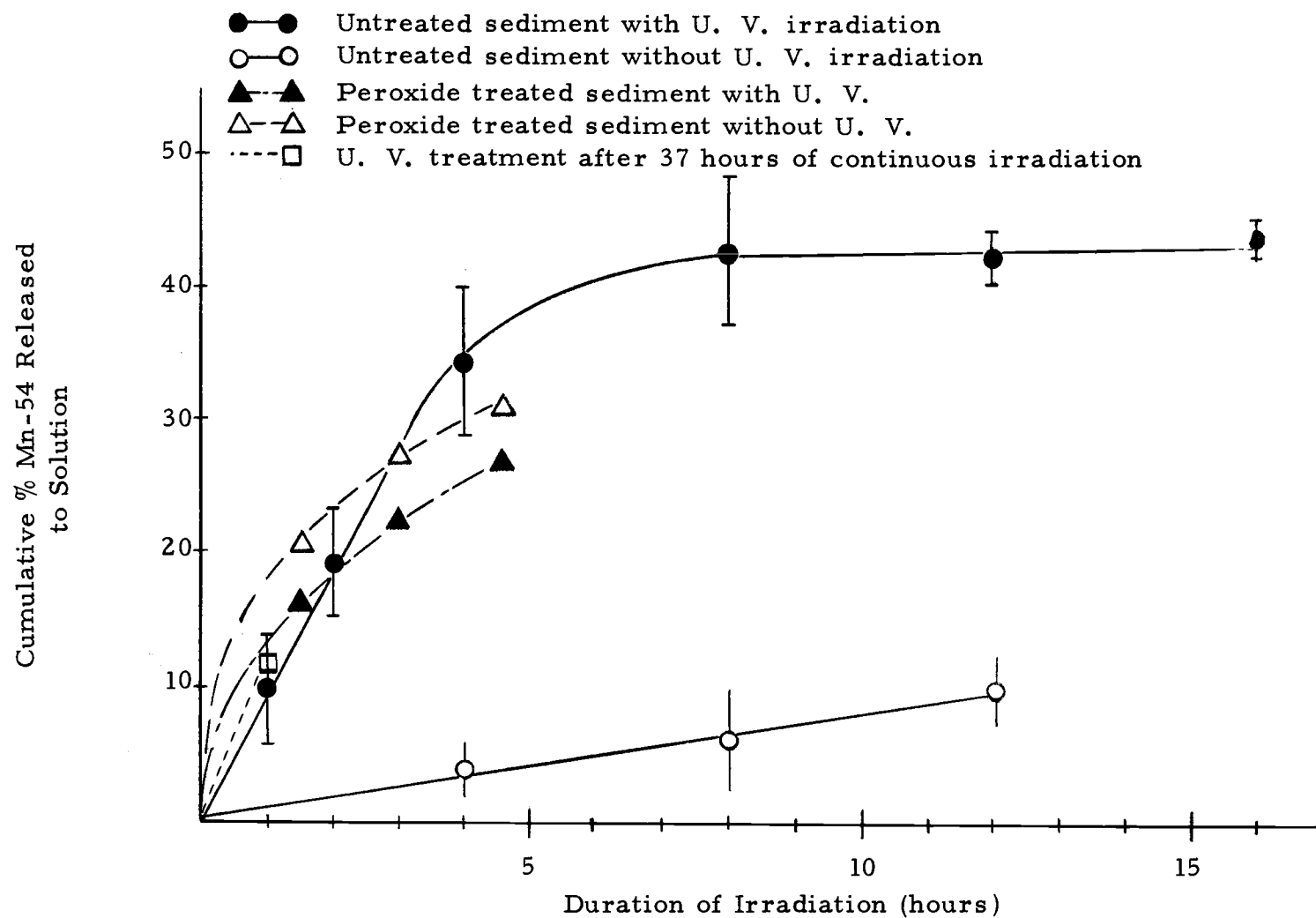
Figure 4. Release of Mn-54 to solution in response to ultraviolet
irradiation and peroxide treatment

metals does not seem to be affected. If the Mn-54 is from hydrous oxides, their disruption does not allow the release of Zn-65 or Sc-46. Further work is needed to determine the source of the Mn-54 released by ultraviolet irradiation.

Physicochemical Nature of Zn-65 Released to Solution

Introduction

The series of one hour irradiations showed a release of Zn-65 which increased monotonically with diminishing slope. This release is not a function of ultraviolet irradiation as the controls follow the same pattern.

The release of zinc to solution was not expected. Experiments by Johnson (1966) demonstrated that artificial sea water leached only $0.2 \pm 0.03\%$ of the Zn-65 from McNary sediments. Experiments using the sediment of this study demonstrated nearly quantitative uptake of 1-20 ppm Zn^{2+} from 250 ml of 0.05M $MgCl_2$ solution.

If the release were simply due to leaching, one would expect to observe a leveling out of Zn-65 release at some maximum if the cycling were allowed to continue over a long duration. This behavior is not exhibited, however.

These results raise questions as to how the Zn-65 was released from the sediments and as to the physicochemical nature of the Zn-65

in solution.

Size of Zn-65 in Solution

To determine if the Zn-65 was held in solution by some particulate or colloidal material, the solutions were filtered with a 0.45 micron millipore filter and dialyzed through a regenerated cellulose membrane with an average pore size of 48 Angstrom units. The Zn-65 passed through both pore sizes, demonstrating that it was neither particulate nor colloidal in character.

Solvent Effect

To determine if the Zn-65 release was dependent upon the $MgCl_2$ concentration of the suspending solution, the concentration of the solution was varied between 5.0×10^{-3} and 0.5 M. There was no significant change in Zn-65 release, as indicated in Table 2.

Table 2. Percent of Zn-65 released to solution with various concentrations of $MgCl_2$ in the suspending solution.

$MgCl_2$ concentration (moles/liter)	% Zn-65 released into solution
0.005	9.64 ± 0.56
0.01	11.27 ± 4.19
0.50	11.83 ± 0.59

The value for 0.01M $MgCl_2$ is the mean and standard deviation of all sediment series irradiations of four hours. The other concentrations are reported as % release on a single series run ± the counting error.

Charge on the Zn-65 Species

The work of Posselt et al. (1968) with sorption of tensioactive species on clays indicated that while cationic species were rapidly and nearly totally sorbed, there was no appreciable sorption of either neutral or anionic species. It was hypothesized that a charge effect might be involved in the solubility of the Zn-65.

To examine the charge of the Zn-65 released into a 5.0×10^{-3} M $MgCl_2$ solution during irradiation, the supernatant solution was passed through a 50 ml ion exchange column. There was no Zn-65 found on the Dowex 1-4X anion exchange resin, while the Dowex 50 cation exchange resin exhibited quantitative removal of the Zn-65 from solution.

These results do not prove that Zn-65 was cationic while in solution nor that it was not anionic or neutral. The Zn-65 could have been stripped from an anionic complex by the cationic exchange resin, or it could have been displaced from the anionic exchange resin. The results do indicate that if the Zn-65 is in an anionic or neutral complex, it is not highly stable.

Effect of U. V. Irradiation on Solution

The fact that the continuous ultraviolet irradiation of a single sediment suspension would release as much as 15-20% of the Zn-65 before resorbing all but a few percent, generated the hypothesis that some Zn-65 species was released to solution and remained there until photochemically decomposed.

To specifically test this possibility, the supernatant solution containing Zn-65 was irradiated in the absence of sediment for three hours. Following the irradiation, the solution was mixed with sediment for 15 minutes to allow resorption and was then centrifuged and counted.

The final supernatant solution showed no loss of activity. This indicates that the Zn-65 is not present in solution in a form which is decomposed by ultraviolet irradiation.

Effect on Zn-65 Spiked Sediments

To determine if Zn-65 released to solution belonged to a kinetically stable, preformed species or was merely related to the concentration of Zn-65 on the sediment, a 400 pico-curie Zn-65 spike of high specific activity was added to the sediment. This approximately tripled the specific activity of Zn-65 on the sediment.

The release of Zn-65 was proportional to the total activity of

the sediment in both irradiated samples and controls. This indicated that the Zn-65 released was ionic or in a form which is readily exchangeable with cationic zinc.

Effect of Removal of Organic Carbon on Zn-65 Release

Organic material was removed from the sediment by two methods: (1) photo-oxidation of organics, and (2) hydrogen peroxide treatment of the sediment. The samples were then irradiated to see what effect this had on Zn-65 release.

There was no change in the Zn-65 release for sediments that had been previously subjected to a 37-hour continuous irradiation with the removal of $58.8 \pm 6.3\%$ of the organic carbon. This is further evidence that the photo-oxidation of organic matter has no effect upon Zn-65 release.

The hydrogen peroxide treatment removed $87.0 \pm 0.4\%$ of the organic carbon. In this case, the availability of Zn-65 was significantly reduced in both the control and irradiated sediment. It appears that the hydrogen peroxide treatment interacts with the sediment in some manner that limits the availability of Zn-65. This interaction is probably more than just oxidation of organic matter.
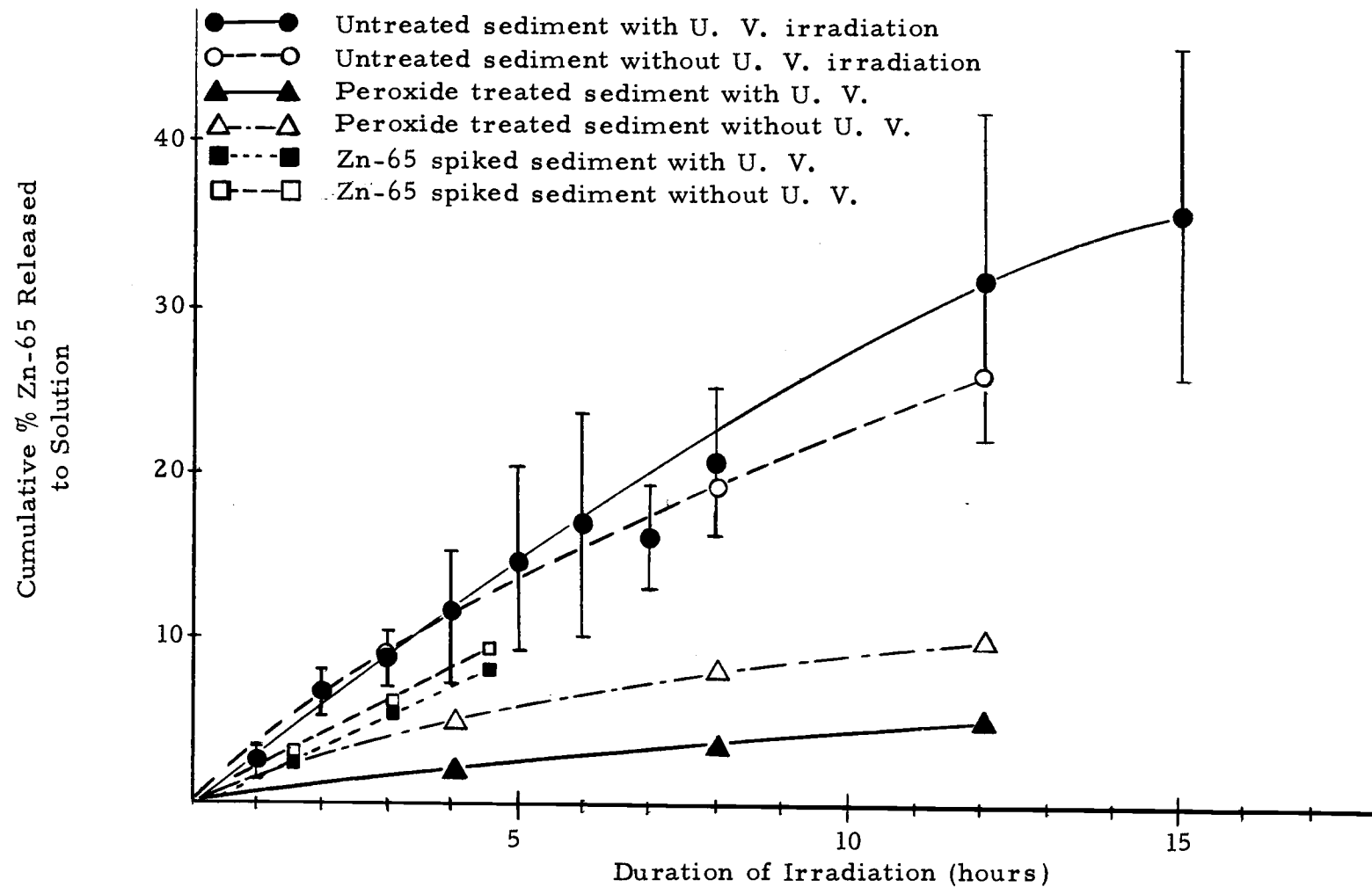
Figure 5. Release of Zn-65 to solution in response to ultraviolet irradiation of untreated sediments, peroxide treated sediments, and Zn-65 spiked sediment.

CONCLUSIONS AND RECOMMENDATIONS

The results demonstrate that a major portion of the sedimentary organic material can be removed photochemically without inducing the desorption of Zn-65, Co-60, or Sc-46. This does not prove that organics do not complex zinc or the other nuclides; ionic zinc released from the oxidation of organic complexes is expected to be substantially sorbed by other sediment species, even in the presence of Mg^{2+} to block non-specific sorption.

There appears to be no change in the ability of the other sediment species to bind zinc as a result of photo-oxidation of organic matter. This is contrasted to the effect of hydrogen peroxide which altered the appearance of the sediment and the release of Zn-65.

There is some question as to the effect of ultraviolet irradiation upon the hydrous oxides of manganese, as Mn-54 was released as either a direct or indirect result of the irradiation. The nature of this effect upon the release of manganese needs further consideration regarding the source of release. Both discrete hydrous oxides and carbonates should be investigated.

If it is established that the hydrous oxides of manganese are not destroyed by the ultraviolet irradiation, then such treatment may provide a means to examine the effect of organic matter on trace metal sorption. Ultraviolet treatment will selectively remove organic

material from the sediments. Uptake studies on such sediments

should yield information as to the effectiveness of organic material

in fixing trace metals when compared to untreated sediments.

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APPENDIX

APPENDIX

Photolysis Equipment

Ultraviolet Lamp

A type "A" medium-pressure 550 watt mercury-vapor lamp
(Model No. 673A-36, Engelhard-Hanovia Company, Newark, N. J.),
powered by a transformer (Model No. 20651-1, Hanovia Company) was
used. This lamp emits approximately 29 percent of its radiation
between 184.9 and 404.5 nm, 16 percent between 435.8 and 623.4 nm,
and 55 percent in the infrared region (Pitt, 1957).

Immersion Well

A double-walled quartz immersion well with a 60/50 male ground
glass joint was used to contain the lamp. This is essentially a copy of
the commercially available Model No. 19434 by Engelhard-Hanovia
Company. Coolant water was circulated through the double wall and
the irradiated solution was circulated around the outside of the well.

Reaction Vessel

The reaction vessel fits externally to the immersion well with a
60/50 ground glass female joint. The vessel with an inlet tube at the
bottom and an outlet tube at the top contained about 100 ml of solution

at any one instant.

Oxygenation System

Compressed oxygen gas (NCG) was passed through a needle valve and flow meter at a rate of 15 ml/min. The oxygen was then passed through a fine pore fritted glass dispersion tube which was located directly in front of the tube leading to the irradiation vessel.

Pump

A centrifugal polyethylene-housing pump circulated the sediment suspension through the system at a rate of 8 liters per minute.