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Fate of Corrosion Products Released From Stainless Steel in Marine Sediments and Seawater

Part 2: Sequim Bay Clayey Silt

Ronald L. Schmidt
Marine Research Laboratory
Sequim, Washington

April 1982

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FATE OF CORROSION PRODUCTS RELEASED FROM STAINLESS STEEL IN MARINE SEDIMENTS AND SEAWATER

Part 2: Sequim Bay Clayey Silt

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April 1982

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SUMMARY

The physicochemical speciation of corrosion products released when stainless steel is subjected to selected environmental conditions is the subject of a series of laboratory experiments at the Pacific Northwest Laboratory. This report describes laboratory experiments in which neutron-activated 347 stainless steel specimens were exposed to clayey silt from Sequim Bay, Washington. The properties and trace metal geochemistry of the sediment and the amounts of corrosion products that were released under oxic and reduced conditions and their distribution among different chemical fractions of the sediment are discussed.

The distributions of Cr, Mn, Fe, Ni and Cu among different chemical forms in the Sequim Bay sediment show that DTPA removed <10% of extractable Cr, Fe and Mn, ~20% of extractable Ni and ~30% of extractable Cu. The inorganic fraction (material soluble in 2.5% acetic acid) accounted for ~30% of total extractable Mn and ~10% or less of Cr, Fe, Ni and Cu. Major portions of Cr and Cu, and a large amount of Fe were in the organic fraction. Extractable Mn, Fe and Ni were associated with hydrous oxides likely as coatings on the mineral substrate of the sediment. No Co was detectable in any of the extracts.

Neutron-activated 347 stainless steel specimens were exposed to slurries of Sequim Bay clayey silt under aerated and non-oxygenated conditions for a period of 90 days. The redox potentials for the air-sparged and N_2, CO_2-sparged sediment slurries were +420 and -140 mv, respectively. In aerated sediment the estimated corrosion rate was 6.3 micrograms per year per square centimeter of stainless steel surface area; greater than four times that amount, 28.3 micrograms per year per square centimeter, were released under anoxic conditions. Relatively labile substances constituted about half of the ^{60}Co activity released in aerated sediment. Adsorbed ^{60}Co soluble in DTPA and ^{60}Co associated with sediment organic matter were the most predominant. A substantial amount (49%) of the ^{60}Co activity was released as, or converted to, relatively inert substances requiring rigorous treatment to dissolve.

The distribution of ^{60}Co released to anoxic Sequim Bay clayey silt among various extracts show that relatively labile substances constituted about 95% of the ^{60}Co released. The largest quantity was in the organic fraction. In the absence of O_2 the association of ^{60}Co with the refractory (oxidic) fraction was inhibited and only ~5% of the ^{60}Co activity was in relatively inert forms.

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INTRODUCTION

This report is the second of a series describing the physicochemical speciation of corrosion products released from stainless steel upon exposure to selected environmental conditions in laboratory experiments. A previous report (Schmidt, 1982) discussed the corrosion products released to aerated coastal seawater and aerated and non-oxygenated North Pacific pelagic red clay. In that study the distribution of corrosion products among various selected chemical forms was different between aerated and non-oxygenated red clay. In addition, the amount of corrosion products released under aeration exceeded that under non-oxygenated conditions. This result is anomalous with other experiments that have shown that anoxic conditions accelerate the corrosion of stainless steel (La Que, 1975). However, the oxidic nature of the pelagic red clay is apparently such that lowered redox potential was not attained in the absence of O_2.

In order to determine the physicochemical forms and amounts of corrosion products which might be released under lowered redox potential, neutron-activated 347 stainless steel specimens were exposed in laboratory experiments to clayey silt from Sequim Bay, Washington. Previous studies have shown that in this sediment lowered Eh measurements were produced in the absence of O_2 (Schmidt et al., 1974). An additional objective was to examine the effect of the chemical properties of sediment on the amounts and forms of corrosion products. The presence of organic matter and hydrous oxides have important influences on the geochemistry of indigenous trace metals in sediments (Jenne, 1977; Schmidt, 1978). Sequim Bay clayey silt has an organic C content about 4-fold greater and a Mn content about 20 times less than the red clay used previously. The differences in organic C and Mn content between the two sediments were expected to influence the distribution of corrosion products among the various components of the sediments. It can be expected that lowered redox potential will cause dissolution of hydrous Mn-oxides (Ehrlich, 1975) removing this material as an adsorbent for soluble corrosion products. Thus, under reduced conditions, sediment organic matter may assume a more predominant role for adsorbing corrosion products.

This report 1) describes the properties and trace metal geochemistry of the Sequim Bay clayey silt used for the corrosion product release experiments and 2) discusses the amounts of corrosion products that were released from neutron-activated stainless steel 347 under oxic and reduced conditions and their distribution among different chemical fractions of the sediment. Radioanalysis of ^{60}Co in solutions derived from sequential extraction of the sediment was used to determine the chemical speciation of the corrosion products. This study was sponsored by the Department of Energy under the auspices of the Knolls Atomic Power Laboratory and was performed at the Pacific Northwest Laboratory operated by Battelle Memorial Institute. The laboratory experiments were conducted at the Battelle Marine Research Laboratory, Sequim, Washington.

MATERIALS AND METHODS

SEDIMENT AND SEAWATER

The sediment used in this study was collected from the lower end of Sequim Bay, Washington (48° 02'N, 123° 00.5'W) (Figure 1) using a PTFE-coated Birge-Ekman dredge. Surface sediment (0-5 cm) was collected for use in the corrosion studies. Seawater used for preparing the sediment slurry was from the unfiltered laboratory supply which is taken from the bottom (~10 m depth) of the entrance channel to Sequim Bay. The salinity of the seawater was ~30 parts per thousand.

ANALYTICAL METHODS

Sediment was subjected to analysis by X-ray fluorescence spectroscopy (XRF) for trace metals and microcombustion for total and organic C concentrations. The precision of measurement of sediment components by XRF is indicated by the following coefficients of variation: Ti, 4%; Cr, 12%; Mn, 6%; Fe, 5%; Ni, 8%; Cu, 8%; Zn, 6%. The accuracy of measurement was determined by comparing XRF analysis of standard reference materials with certified concentrations. To determine Co concentration, sediment samples were analyzed by neutron activation.

SEQUENTIAL EXTRACTION

Aliquots (~2.0 g dry weight equivalent) of undried sediment taken from the Sequim Bay sampling site were treated sequentially with 50 ml each of reagents selected to determine the chemical forms of the trace metals. Each of the reagents listed on Table 1 and Figure 2 was agitated vigorously with the sediment for a period of 3 or 4 days at 10°C. The slurry was then centrifuged at 5000 RPM for 30 min and the supernatant liquid was decanted. Trace metals were determined by AAS using standard additions to reagent blanks. Detailed rationale for this extraction procedure was discussed in previous reports (Schmidt, 1979; 1982).

METAL CORROSION STUDIES

Neutron-irradiated 347 stainless steel specimens, having dimensions of about 5 x 1 x 0.05 cm, were suspended in exposure medium consisting of 300 g wet sediment (100 g dry weight equivalent) diluted with seawater to 1 liter in a cylindrical glass vessel. The media were held at 10°C and gently sparged with air or N_2 containing 350 ppm CO_2. After 90 days of exposure the metal specimens were removed and the sediment slurries were sampled for ^{60}Co radioassay and chemical extraction. The chemical forms of ^{60}Co activity associated with the sediment slurries were determined using the sequential extraction protocol described in Table 1 and Figure 2. Thirty ml aliquots (~1 gm dry weight equivalent) of well-mixed slurry were treated with the reagents at 10°C for 3 or 4 days. Following centrifugation and decantation, the quantity of ^{60}Co in each extractant was measured.

Gamma-ray spectroscopic measurements of the irradiated metal specimens indicate that ^{60}Co is the major gamma-emitting isotope. Sufficient time has elapsed (>5 yr) since activation to have allowed decay of shorter-lived isotopes. Aliquots of sediment slurry or extracts were pipetted into glass vials and ^{60}Co activity was determined using a NaI crystal mounted horizontally and connected to a 4000-channel pulse height analyzer. Integration of 25 channels on each side of the 1.33 Mev ^{60}Co peak was performed and compared to the assay of a known standard for estimating ^{60}Co activity. Background samples of unexposed sediment slurry were also counted. Counting times varied from 2 to 24 hours depending on activity.

To verify the accuracy of the ^{60}Co radioassays, a set of sediment extracts and slurry samples was prepared and sent to Knolls Atomic Power Laboratory for analysis as an independent check on the Pacific Northwest Laboratory results. The results, shown in Table 2, indicate that the measured ^{60}Co activity in a counting standard prepared at PNL is 98 ± 2.5% of the activity measured at KAPL. The mean ratio of ^{60}Co activities in 4 samples, as determined by the two laboratories is 0.99. The 95% confidence limits are 0.89 and 1.09; thus, the mean ratio is not significantly different from 1.00. To further ensure the accuracy of results, Knolls Atomic Power Laboratory participates in a quality assurance program that includes the Environmental Protection Agency's Environmental Radioactivity Laboratory Intercomparison Studies Program and the Quality Assurance Program of the Department of Energy Environmental Measurements Laboratory.

RESULTS AND DISCUSSION

SEDIMENT CHEMISTRY

The sediment from Sequim Bay used in these experiments was a clayey silt consisting of 44% clay, 53% silt and 3% sand. The concentrations of selected components in the sediment, Table 3, were calculated from analysis of sediment cores collected bimonthly for one year for an unrelated research task. The measurements of standard reference materials are within the range for analytical variability. The concentrations of trace metals are typical of those for many nearshore sediments (Calvert, 1976). Although the organic C content of Sequim Bay clayey silt (3%) is relatively high compared to deep-sea sediments, other coastal sediments contain like quantities of organic matter (Calvert, 1976; Schmidt, et al., 1978).

With respect to the North Pacific pelagic red clay used in the previous experiments (Schmidt, 1982), Sequim Bay clayey silt contains about 4 times more organic C, similar quantities of Ti, Cr, and Fe, markedly less Mn (<5%), and less Co, Ni and Cu (~25% each). The differences in Mn and trace metal contents may be related to several causes: 1) dilution by terrestrial materials in the coastal sediment, 2) differences in particle size, 3) deep-sea sediment undergoes longer exposure to seawater and adsorption of soluble metals may occur during and following deposition, 4) hydrothermal sources in the deep-sea, or 5) diffusion of dissolved metal from reduced buried sediments. The most likely causes for the increased metals in the deep-sea sediment appear to be hydrothermal sources and/or diffusion from buried sediments (Corliss, et al., 1978; Calvert and Price, 1972).

The distributions of Cr, Mn, Fe, Co, Ni and Cu among different chemical forms in the Sequim Bay sediment are presented in Table 4. Two sets of samples were extracted in replicate according to the treatment protocol described in Table 1 and Figure 2. One set was initially treated with diethylenetriaminepentaacetic acid (DTPA) in seawater and then extracted through the remaining treatment sequence in parallel with another set which was initially treated with seawater only. The results (Table 4) show that at the low concentration of Co in Sequim Bay sediment, no Co was detectable in any of the extracts. As shown on Table 5, treatment with DTPA (sorbed fraction) removed <10% of extractable Cr, Fe and Mn, ~20% of extractable Ni and ~30% of extractable Cu. DTPA-extractable Ni and Cu are about equally associated with sediment organic matter and Mn and Fe oxides (Table 4) and are likely adsorbed cationic forms of the elements which are readily desorbed by a strong complexing agent (Lindsay and Norvell, 1978).

The inorganic or weakly complexed fraction (material soluble in 2.5% acetic acid) accounts for ~30% of total extractable Mn and 10% or less of Cr, Fe, Ni and Cu (Table 5). Mn in this fraction may result from the desorption of Mn(II) from MnO_2 under reduced pH. Data presented by Morgan and Stumm (1964) indicated that the sorption capacity of MnO_2 for Mn(II) is about 1.0 and 0.2 moles of Mn(II) per mole of MnO_2 at pH 8 and pH 4.5, respectively. Prior treatment with DTPA removed almost 50% of the 2.5% acetic acid-extractable Mn fraction. Most of this fraction of Mn apparently did not remain associated with the complexing agent, but became oxidized during DTPA treatment. This is evident because the oxidic (reductant-soluble) fraction of Mn increased when preceded by DTPA treatment.

Major portions of Cr and Cu, and a large amount of Fe are in the organic fraction (Table 5). Most of the organic Cu and Fe were readily removed with 0.1 $\underline{M}$ sodium pyrophosphate, indicating that this fraction in the sediment consists of hydroxylated Fe species bound to humic acid which contain coprecipitated (occluded) or adsorbed transition elements (Aleksandrova, 1967; Schnitzer and Khan, 1972). Removal of organic Cr required treatment with an oxidizing agent, NaOCl.

Extractable Mn, Ni and Fe (Table 5) were, to a large extent, removed by treatment with an acidic reducing agent (1 $\underline{M}$ hydroxlamine hydrochloride in 25% acetic acid) indicating that they are present in hydrous oxide forms likely as coatings on the mineral substrate of the sediment (Jenne, 1977). The amount of Mn in the reductant-soluble fraction increased following DTPA treatment indicating that some of the Mn which was removed by DTPA from the inorganic or weakly complexed and organic forms appeared to oxidize to MnO_2. Acidic reducing conditions were then required to extract this material.

Table 5 also shows the comparative distribution among chemical forms of Cr, Mn, Fe, Co, Ni and Cu present in the sediment from Sequim Bay used in the current study and in the Northeast Pacific pelagic red clay used in a previous study (Schmidt, 1982). These data show strong parallels as well as contrasts. The distribution of Cr between the two sediments is quite similar except for the presence of greater amounts of Cr adsorbed or complexed by organic matter in the Sequim Bay sediment.

In spite of a more than 20-fold greater concentration of Mn in the pelagic sediment, its distribution in the two sediments is quite similar (Table 5). The major differences are the proportions of extractable Mn removed by DPTA (sorbed fraction) and weak acid treatment (inorganic fraction). Organic substances apparently act as stronger adsorbents for Mn(II) than does MnO_2 (van den Berg and Kramer, 1979). Thus, the removal of the adsorbed fraction of Mn by DTPA from the relatively high amount of organic matter in Sequim Bay sediment was not as efficient as from pelagic clay which contains little organic matter and a larger amount of MnO_2. Treatment with 2.5% acetic acid appeared to extract Mn from the organic matter in the Sequim Bay sediment.

The distributions in the two sediments of Fe, of Ni and of Cu are remarkably similar (Table 5); the major differences are the increased amounts of inorganic, or more likely, weakly complexed Fe, and organic Cu in the coastal sediment. The correlations between the percentage distributions among extractable forms of Fe, Ni and Cu in the two sediments are statistically significant at $P < 0.01$ ($r = 0.989$, 0.993, and 0.975, respectively), whereas those of Cr and of Mn are not significant at $P < 0.01$ ($r = 0.651$ and 0.747, respectively).

CORROSION PRODUCT DISTRIBUTION

Neutron-activated 347 stainless steel specimens were exposed to slurries of Sequim Bay clayey silt under aerobic and non-oxygenated conditions for a period of 90 days. The conditions of exposure and total amounts of ^{60}Co released from the metal are given in Table 6. The redox potentials for the air-sparged and N_2, CO_2-sparged sediment slurries were +420 and -140 mv, respectively. The non-oxygenated system was reduced very nearly to the point where SO_4^{2} was being converted to S^{2} (Breck, 1974; Morris and Stumm, 1967). The pH of the aerated system was reduced from pH 7.6 for freshly acquired sediment to about 7.2 after 90 days likely due to the oxidation of sulfides and organic matter. The absence of O_2 in this sediment produced a marked effect on the amount of corrosion products released. In the aerated sediment the estimated corrosion rate was 6.3 μg per year per square centimeter of stainless steel surface area; greater than four times that amount or 28.3 $\mu g/y/cm^2$ was released under anoxic conditions (Table 6).

Aerated Sediment

Samples of sediment slurry containing corrosion products were subjected to sequential extraction according to the procedure outlined in Table 1 and Figure 2. The results of ^{60}Co assay of the extracts are presented in Table 7 and summarized in Table 9 and Figure 3. Fractions 1 through 8 (Table 7) are relatively labile substances and, as shown in Table 9, constitute about half of the ^{60}Co activity released in aerated sediment. Adsorbed ^{60}Co soluble in DTPA and ^{60}Co associated with sediment organic matter were the most predominant, each accounting for ~40% of the labile material. As shown on Table 7, the DTPA-soluble, or sorbed, fraction appears to be derived about equally from the inorganic or weakly complexed (Fraction 3), organically-complexed (Fractions 4-6), and reductant-soluble oxidic materials (Fractions 7 and 8). Only a small fraction (6%) of the ^{60}Co activity is in the reductant-soluble, or oxidic, fraction. Table 9 shows that a substantial amount (49%) of the ^{60}Co activity was released as, or converted to, relatively inert substances requiring rigorous treatment to dissolve. The HCl-soluble, or refractory, material is likely freshly-formed Fe oxide resulting from oxidation of corroded Fe^{3+} and contains adsorbed or coprecipitated (occluded) ^{60}Co. The residual fraction may be metal particles.

Non-oxygenated Sediment

The distribution of ^{60}Co released to anoxic Sequim Bay clayey silt among various extracts is listed in Table 8 and summarized in Table 9 and Figure 3. As shown on Table 9, relatively labile substances constitute about 95% of the ^{60}Co released under anoxic conditions. The distribution of labile ^{60}Co activity is similar to that in aerated Sequim Bay sediment: the largest quantity was in the organic fraction. Cobalt-60 associated with labile material was likely released in ionic form which then became associated with various sediment components.

In the absence of O_2 the association of ^{60}Co with the refractory (oxidic) fraction was inhibited in the Sequim Bay sediment (Table 9). This is likely due to the dissolution of Mn-oxides under reduced conditions and/or the lack of formation of Fe-oxides from corroded Fe^{3+}. At the redox potential of this experiment (-140 mv), the formation of Mn and Fe oxides is not likely (Stumm and Morgan, 1970). Consequently, the association of ^{60}Co with organic matter was enhanced. Only ~5% of the ^{60}Co was relatively inert, i.e., either not soluble in the extraction reagents or only soluble in 1:1 HCl.

Influence of Sediment Chemical Properties on Corrosion Product Distribution

The differences in organic C and Mn content between the two sediments investigated in this program to date present implications relative to the distribution of trace metals and corrosion products in deep-sea sediments. Organic material in the sediments in this study was extracted by sodium pyrophosphate, a reagent which is used to remove substances from soils known as humates (Aleksandrova, 1967). The humate fraction of soils contains organomineral complexes consisting of chelated hydrous oxides of principally Fe and Al (Schnitzer and Kahn, 1972). Although Co and Ni will also form organomineral complexes with humic substances (Kahn, 1969), the stability of these chelates varies inversely with increasing ionic strength (Schnitzer and Hansen, 1970). Thus, they are not likely to form to a large extent in marine sediments. However, stable complexes are formed by the interaction between Fe^{3+} and humic substances. These substances have a coagulant nature at the ionic strength and pH of seawater (Picard and Felbeck, 1976) with the possible structure, $RCOOFe(OH)_2$ (Schnitzer and Kahn, 1972).

In sediments from both Sequim Bay and the Northeast Pacific, the amounts of indigenous Fe apparently associated with humic substances are both about 2 mg/g (4-5% of total Fe) (Table 4, this paper; Table 7, Schmidt, 1982). Indigenous Co and Ni present in the humate fraction of the sediments may have resulted from their direct adsorption to Fe-humate complexes or to hydrous oxides that are scavenged by, or carried with, coagulated organic material (Jenne, 1977). In the deep-sea clay the quantities of indigenous Co and Ni associated with the humate fraction are about equal; the weight:weight ratio for both Fe:Co and Fe:Ni is about 100-150:1. Since the concentrations of soluble Co and Ni in deep seawater are about 20 and 800 ng/l (Young, 1982), the Fe-humate complex appears to have a greater effect on the adsorption of Co than on Ni.

With respect to interaction of corrosion products with the humate fraction of sediment, only 4-5% of the corrosion products released to deep-sea red clay became associated with this material (Table 10). In contrast, in organic-rich clayey silt under aerobic and anoxic conditions, respectively, 23% and 53% of the corrosion products became associated with the organic fraction, either by adsorption or complexation.

In addition to a greater concentration (4-fold) of organic C in the clayey silt compared to the red clay, the relative state of degradation of the organic matter may also influence trace metal distribution. The organic matter in surficial sediment from shallow waters (10-15 m) likely consists of detritus undergoing the initial stages of decomposition and contains a large fraction of degradable non-humic material. On the other hand, in deep-sea red clay, organic matter is much more humic in nature and relatively resistant to further microbial degradation (Parsons, 1975).

It might be expected that decomposition of less refractory organic matter may lead to the release of adsorbed or complexed trace metals (corrosion products) from the sediment to the overlying seawater. It should be noted, however, that the distribution of relatively labile corrosion products (^{60}Co activity) released in aerated clayey silt (Table 9) correlates somewhat with the distribution of indigenous Cu among extracted fractions in this sediment (Table 5). The close geochemical analogy of corrosion products to indigenous Cu in the sediment indicates that, under aerobic conditions, the corrosion products will likely remain incorporated in a sediment receiving a continuous influx of organic detritus.

The geochemical implications of corrosion products associated with Mn oxides in the sediments can be inferred from the differences in distribution among chemical forms between aerated and non-oxygenated sediments (Table 10). In the deep-sea sediment, lack of O_2 lowered the production of refractory (oxidic) corrosion products from 45% to 19%. In turn, more of the corrosion products in the non-oxygenated sediment became adsorbed to sediment oxides compared to aerated sediment. Lack of O_2 likely hindered the formation of refractory oxidic corrosion material and, thus, the fraction of ionic corrosion products that became adsorbed to the sediment was increased.

Under sufficiently reduced conditions, it is possible that loss of Mn oxide from the sediment could occur and, thus, the amount of corrosion products adsorbed or associated with the oxidic fraction may be lowered and the soluble fraction could increase by as much as an order of magnitude. For example, Takematsu (1979) measured distribution coefficients of Co and Ni on hydrous Mn and Fe oxides of 5-200 x 10^4 and 1-30 x 10^4, respectively. Takematsu found that a red clay treated to remove Mn and Fe oxides with an acidic reducing agent similar to treatment 7 and 8, Table 1, had much lower distribution coefficients; 600 and 300 for Co and Ni, respectively. However, with regard to the organic-rich clayey silt, reduced conditions sufficient to dissolve Mn-oxides did not produce an increased amount of soluble corrosion products. Apparently, sufficient organic matter was present to provide an alternative adsorbent. Further corrosion experiments are planned utilizing sediment from the reduced layer (below 15 cm) from the Northeast Pacific site. This sediment has a lower MnO_2 content than the surficial sediments from that area.

CONCLUSIONS

The presence of increased amounts of organic matter and reduced amounts of Mn-oxide in the sediment had a major influence on chemical forms of corrosion products resulting from stainless steel in these experiments. Organic matter was important both in its direct reaction with the corrosion products as well as its role as a reducing agent in absence of oxygen. For example, in organic-rich Sequim Bay clayey silt in the absence of O_2, anoxic conditions were produced and about 7 μg of metal per cm^2 of specimen surface area were removed from a neutron-activated 347 stainless steel specimen in 90 days (Table 6). This is about 4 times more corrosion products than were removed under aerobic conditions. The fractions of corrosion products which became associated with the relatively labile fractions of the sediment constituted 51% and 95% of the total corrosion products released under aerobic and anoxic conditions, respectively (Table 9).

As shown on Table 9, a small fraction (2% or less) of the corrosion products were released in soluble or easily dissolved forms under either aerobic or anoxic conditions. Corrosion products assumed to be adsorbed to sediment components and removed by treatment with diethylenetriaminepentaacetic acid (DTPA) constituted 17% and 44% of corrosion products released under aerobic and anoxic conditions, respectively. The DTPA-soluble fraction was likely cations that had become adsorbed to materials otherwise inferred as inorganic or weakly complexed, organically complexed, and oxidic sediment fractions. Exposure to aerated organic-rich clayey silt produced fractions of corrosion products, with respect to total corrosion products released, which were associated with the following sediment components: inorganic or weakly complexed, 12% (of which 45% was DTPA-soluble); organically complexed, 23% (15% DTPA-soluble) and oxidic, 14% (56% DTPA-soluble). Under anoxic conditions, the respective fractions were: inorganic or weakly complexed, 17% (53% DTPA-soluble); organically complexed, 53% (29% DTPA-soluble); and oxidic 23% (84% DTPA-soluble). The remaining corrosion products were refractory (oxidic) and residual materials. These constituted, respectively, 35% and 15% in aerated sediment and 2% and 3% in anoxic sediment.

With respect to the total ^{60}Co activity in the metal specimens, the approximate ratios of the quantities of corrosion products removed under anoxic conditions to those under aerobic conditions are: soluble, 2:1; easily dissolved, ~5:1; DTPA-soluble (sorbed), 12:1; inorganic or weakly-complexed, ~6:1; organically complexed, ~9:1; oxidic, ~3:1; refractory (oxidic), ~0.3:1, residual, 0.7:1; and total, 4.4:1. The ratio of relatively labile materials is about 8:1. These ratios show that the amount of corrosion in a fairly organic sediment was increased by the lack of O_2 and the proportion of corrosion products released in relatively labile form was also greater.

Table 10 compares the distribution of corrosion products among chemical forms released to two different sediments: 1) Sequim Bay clayey silt which contained 28 mg/g organic C and ~30 µg/g oxidic Mn, and 2) Northeast Pacific pelagic red clay which contained 8 mg/g organic C and ~5000 µg/g oxidic Mn. For aerated sediments, the major differences in the quantities of corrosion products occurred in the relatively labile sediment fractions. The amount of relatively labile substances is defined by the sum of all fractions except the refractory and residual. As shown on Table 10, these quantities were nearly identical in aerated Sequim Bay sediment and red clay, constituting 51% and 48% of the amount of corrosion products (^{60}Co activity), respectively. The major difference in the distribution of corrosion products in the labile fractions for these two sediment types was in the organic vs. the oxidic or reductant-soluble fractions. The higher content of organic matter in the clayey silt appeared to induce the association of corrosion materials with the organic fraction of the sediment and precluded the formation or occlusion of a fraction of the corrosion products into reductant-soluble or oxidic materials.

For non-oxygenated conditions, the comparison of the distribution of corrosion products (^{60}Co activity) among chemical forms between exposure to organic-rich clayey silt and pelagic red clay, Table 10, indicates major differences similar to those under aerobic conditions: 1) the association of corrosion products with organic materials in the clayey silt, and 2) the association of corrosion products with the oxidic fraction in pelagic red clay. The absence of O_2 resulted in lowered redox potential in the clayey silt and possible dissolution of Mn oxides and, thus, inhibited the association of corrosion products with the oxidic fraction.

The association of corrosion products (^{60}Co activity) with certain components of the sediments seems to arise from the same properties which also appear to govern the distribution of trace metals among different chemical forms. Figure 4 shows two correlation matrices depicting the comparisons of the percent distribution of indigenous metals and corrosion products in sediment among four chemical forms: adsorbed, inorganic, organic and oxic. For Sequim Bay clayey silt, the distribution of corrosion products (^{60}Co activity) was not strongly affected by redox conditions and, as noted above, followed somewhat the distribution of indigenous Cu, an element which was almost 80% extractable by the reagents employed and was largely controlled by adsorption and organic chelation in this sediment. The lack of influence of hydrous Mn and Fe oxides as controls in both Cu and ^{60}Co activity in Sequim Bay clayey silt is evidenced by the absence of or negative correlation between Mn or Fe and these two variables.

In contrast, the chemical fractions of corrosion products released to aerated Northeast Pacific red clay were closely correlated with Mn and with Ni fractions. Strong chelation to sediment organic matter had little effect on the association of corrosion products with this sediment. In the O_2-deficient system, a larger fraction of the ^{60}Co activity was present as adsorbed cations in comparison to the indigenous trace metals which accounts for the lack of significant correlations.

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Table 1. Treatment scheme for selective extraction of trace metals and corrosion products in sediments.

Treatment[1] step	Extracting reagent	Expected form of trace metal or corrosion product in extractant
1	-	Soluble.
2A	Seawater	Easily dissolved.
2B	0.005 M diethylenetriaminepentaacetic acid (DTPA), pH 8	Adsorbed, readily complexed.
3	2.5% Acetic acid	Inorganic or weakly complexed.
4	0.1 M Sodium pyrophosphate	Strongly organically complexed.
5	Repeat 4.	
6	5% Sodium hypochlorite	Residual organically bound.
7	0.1 M Hydroxylamine hydrochloride in 25% acetic acid	Reductant soluble or oxidic (Mn- and Fe-oxide associated).
8	Repeat 7.	
9	1:1 HCl	Refractory oxidic or mineral occluded.
10	-	Residual.

---

[1] Sediments are sequentially treated with the reagents at 10°C for 3 or 4 days. Extractants are separated from sediment by centrifugation.

Table 2. Comparison of Pacific Northwest Laboratory (PNL) and Knolls Atomic Power Laboratory (KAPL) determinations of ^{60}Co activity in sediment extract and slurry samples.

Sample	Matrix	Activity, pCi/ml PNL[1]	Activity, pCi/ml KAPL[2,3]	Ratio, KAPL/PNL
^{60}Co Standard	-	34.0 (calc.)	33.2 (meas.)	0.98
023-21-03	Seawater + DTPA	0.09	ND[4]	--
023-21-04	2.5% Acetic acid	0.52	0.50	0.96
023-21-08	1M $NHOH_2 \cdot HCl$ in 25% HOAc	5.20	6.00	1.15
023-21-10	1:1 HCl	7.90	8.00	0.99
023-21-11	Residue	1.30	1.10	0.85
Total		15.01	15.60	0.96

Notes:

[1] NaI detector.

[2] Ge(Li) detector.

[3] To prepare the samples for Ge(Li) analyses at KAPL, 10 ml aliquots of sample material were transferred from ~20 ml counting vials to ~2" diameter Petri dishes and dried.

[4] ND = not detectable.

Table 3. Concentrations of selected components in surface (0-6 cm) clayey silt from Sequim Bay.

	Organic C	Ti	Cr	Mn	Fe
	-----mg/g-----		-----μg/g------		mg/g
Mean[1]	28	4.6	110	392	43.3
Std. Dev.	3	0.2	11	15	1.4
Std. Ref. Materials:					
USGS W-1		6.5(6.4)[3]	124(114)	1330(1300)	79(78)
Std. Soil SO-1		4.6(5.3)	163(160)	875(890)	59(60)
Analytical Method[2]	M	X	X	X	X

	Co	Ni	Cu	Zn	Rb
			μg/g		
Mean	11	53	42	109	48
Std. Dev.	1	3	4	6	2
Std. Ref. Materials					
USGS W-1	45(47)	78(76)	116(110)	85(86)	23(21)
Std. Soil SO-1		96(94)	68(61)	142(146)	124(144)
Analytical Method	A	X	X	X	X

---

[1] Data are means of 6 samples collected bimonthly.

[2] M - Microcombustion.
X - X-ray fluorescence.
A - Neutron activation.

[3] Certified or recommended value.

Table 4. Chemical forms of Cr, Mn, Fe, Co, Ni, and Cu in Sequim Bay clayey silt as inferred from selective extraction.

Chemical Form	Cr	Mn	Fe	Co	Ni	Cu
	----µg/g----		mg/g	-------µg/g-------		
Adsorbed to organic matter	2	2	1	<1	1	5
Adsorbed to sediment oxides	<1	<1	<1	<1	3	5
Inorganic or weakly complexed	2	14	1	<1	2	2
Organically complexed	11	1	2	<1	3	13
Oxidic	6	32	6	<1	12	7
Sum	21	49	9	<1	21	32
Total	110	392	43.3	11	53	42
% Extracted	19	12	21	<9	40	76

Table 5. Distribution of extracted Cr, Mn, Fe, Co, Ni, and Cu among different forms in two contrasting sediments.

	Cr		Mn		Fe		Co		Ni		Cu	
	S[1]	W[2]	S	W	S	W	S	W	S	W	S	W
	% Total extracted											
Sorbed	8	<1	4	28	9	5	<1	4	18	16	30	29
Inorganic	8	17	29	1	10	<1	<1	4	10	13	7	15
Organic	54	33	3	3	25	27	<1	53	14	11	41	36
Oxidic	30	50	64	68	56	68	<1	38	58	60	22	20

---

[1] S, surficial clayey silt from Sequim Bay.

[2] W, surficial red clay from Area W-N, Northeast Pacific Ocean (Schmidt, 1982).

Table 6. Experimental conditions, ^{60}Co activity of stainless steel specimens, and quantity of corrosion products released during laboratory exposure of irradiated 347 stainless steel to clayey silt from Sequim Bay.

A. Experimental conditions:

Experiment	Atmosphere	Final pH	Final Eh, mv
5	air	7.17	+420
6	N_2, CO_2	8.15	-140

B. ^{60}Co activity of S/S specimens:

Experiment	Specimen	Weight, g	Area, cm^2	^{60}Co, S/S specimens	
				Total µCi	µCi/g
5	4/2-3	0.923	5.2	820	889
6	5/9-10	0.884	5.0	1047	1184

C. Quantity of corrosion products released:

Experiment	^{60}Co released, µCi	Estimated loss from S/S		Estimated corrosion product release rate µg/year/cm^2
		µg	µg/cm^2	
5	7.2×10^{-3}	8.1	1.6	6.3
6	41.3×10^{-3}	34.9	7.0	28.3

Table 7. Distribution of corrosion products (^{60}Co activity) released from 347 stainless steel exposed to aerated clayey silt from Sequim Bay.

Treatment step (Table 1)		Sample			
		A[1]	B	A	B
		^{60}Co, nCi		%	
1	Centrifugation	<0.01	0.08	<0.10	0.90
2A	Seawater	0.09	-	1.04	-
2B	Seawater + DTPA	-	1.58	-	17.81
3	2.5% Acetic acid	0.99	0.57	11.48	6.43
4	Sodium pyrophosphate	0.76	0.97	8.82	10.94
5	Repeat 4.	0.70	0.31	8.12	3.49
6	Sodium hypochlorite	0.54	0.49	6.26	5.52
7	Hydroxylamine hydrochloride	0.70	0.36	8.12	4.06
8	Repeat 7.	0.21	0.19	2.44	2.14
9	1:1 HCl	3.30	3.11	38.28	35.06
10	Residual	1.33	1.21	15.43	13.64
Σ		8.62	8.87	100	100

---

[1] Sample A was initially extracted with seawater; sample B, with seawater + DTPA.

Table 8. Distribution of corrosion products (^{60}Co activity) released from 347 stainless steel exposed to anoxic clayey silt from Sequim Bay.

Treatment step (Table 1)		Sample A[1] ^{60}Co, nCi	Sample B ^{60}Co, nCi	Sample A %	Sample B %
1	Centrifugation	0.10	0.09	0.22	0.20
2A	Seawater	0.65	-	1.42	-
2B	Seawater + DTPA	-	20.44	-	45.93
3	2.5% Acetic acid	7.79	3.64	16.99	8.18
4	Sodium pyrophosphate	7.95	10.78	17.34	24.22
5	Repeat 4.	5.78	3.89	12.60	8.74
6	Sodium hypochlorite	10.52	2.39	22.94	5.37
7	Hydroxylamine hydrochloride	7.83	1.35	17.07	3.03
8	Repeat 7.	1.52	0.32	3.31	0.72
9	1:1 HCl	2.13	0.93	4.64	2.09
10	Residual	1.59	0.67	3.47	1.51
Σ		45.86	44.50	100	100

---

[1] Sample A was initially extracted with seawater; sample B, with seawater + DTPA.

Table 9. Chemical forms of corrosion products (^{60}Co activity) released from 347 stainless steel in Sequim Bay clayey silt as inferred from selective extraction.

	Treatment			
	Aerated sediment		Anoxic sediment	
Chemical Form	A[1]	B[2]	A	B
Relatively labile fraction:				
Soluble	0.5	0.01	0.2	0.02
Easily dissolved	1.0	0.02	1.4	0.10
DTPA-soluble from inorganic, weakly complexed fraction	5.2	0.08	9.0	0.63
Adsorbed to organic matter	3.6	0.06	15.5	1.08
Adsorbed to sediment oxides	8.0	0.12	19.5	1.36
Inorganic or weakly complexed total	6.4	0.10	8.1	0.57
Organically complexed	19.7	0.31	37.9	2.65
Oxidic	6.2	0.10	3.7	0.26
Σ - Relatively labile fractions	50.6	0.80	95.4	6.67
Refractory (oxidic)	34.8	0.54	2.1	0.14
Residual (metallic)	14.6	0.23	2.5	0.17
Σ - All fractions	100	1.57	100	6.98

---

[1] A - % of total ^{60}Co released.

[2] B - Estimated quantity of corrosion products, μg/cm^2 of specimen exposed.

Table 10. Comparison of distribution of chemical forms of corrosion products (^{60}Co activity) between Sequim Bay clayey silt and Northeast Pacific red clay.

	Treatment			
	Aerated sediment		Non-oxygenated sediment	
Chemical form	S[1]	W[2]	S	W
	%		%	
Relatively labile:				
Soluble	0.5	<0.1	0.2	3.0
Easily dissolved	1.0	<0.1	1.4	2.4
DTPA soluble from inorganic, weakly complexed fraction	5.2	<0.1	9.0	<0.1
Adsorbed to sediment organic matter	3.6	<0.1	15.5	<0.1
Adsorbed to sediment oxides	8.0	9.9	19.5	36.4
Inorganic or weakly complexed	6.4	<0.1	8.1	<0.1
Organically complexed	19.7	4.2	37.9	5.5
Oxidic	6.2	33.9	3.7	23.0
Σ - Relatively labile fractions	50.6	47.9	95.4	70.3
Refractory (oxidic)	34.8	45.0	2.1	19.4
Residual (metallic)	14.6	7.0	2.5	10.3

---

[1] S - Sequim Bay clayey silt, this report.

[2] W - Northeast Pacific red clay (Schmidt, 1982).

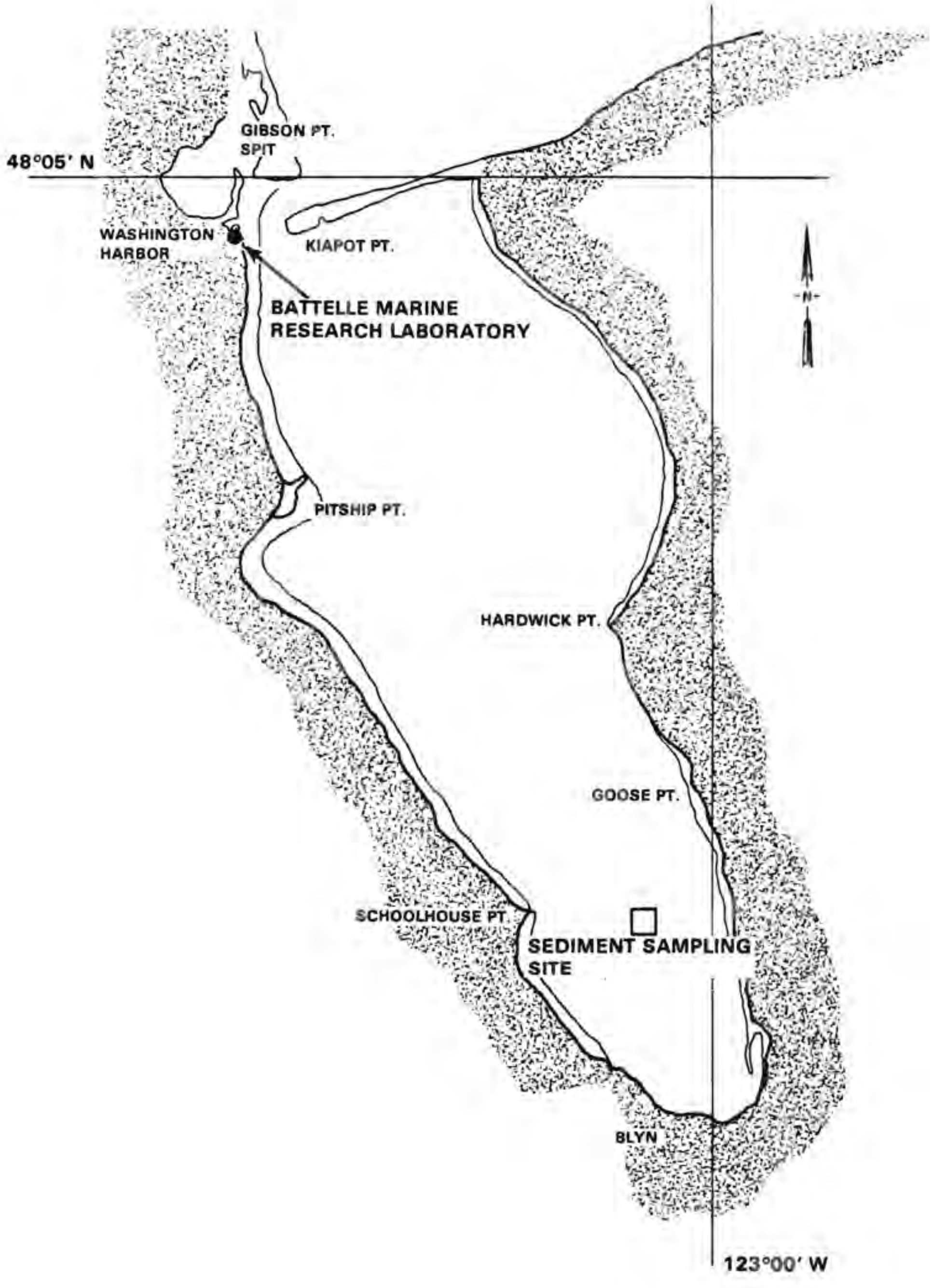

Figure 1. Sequim Bay, Washington. □ designates sediment sampling site.

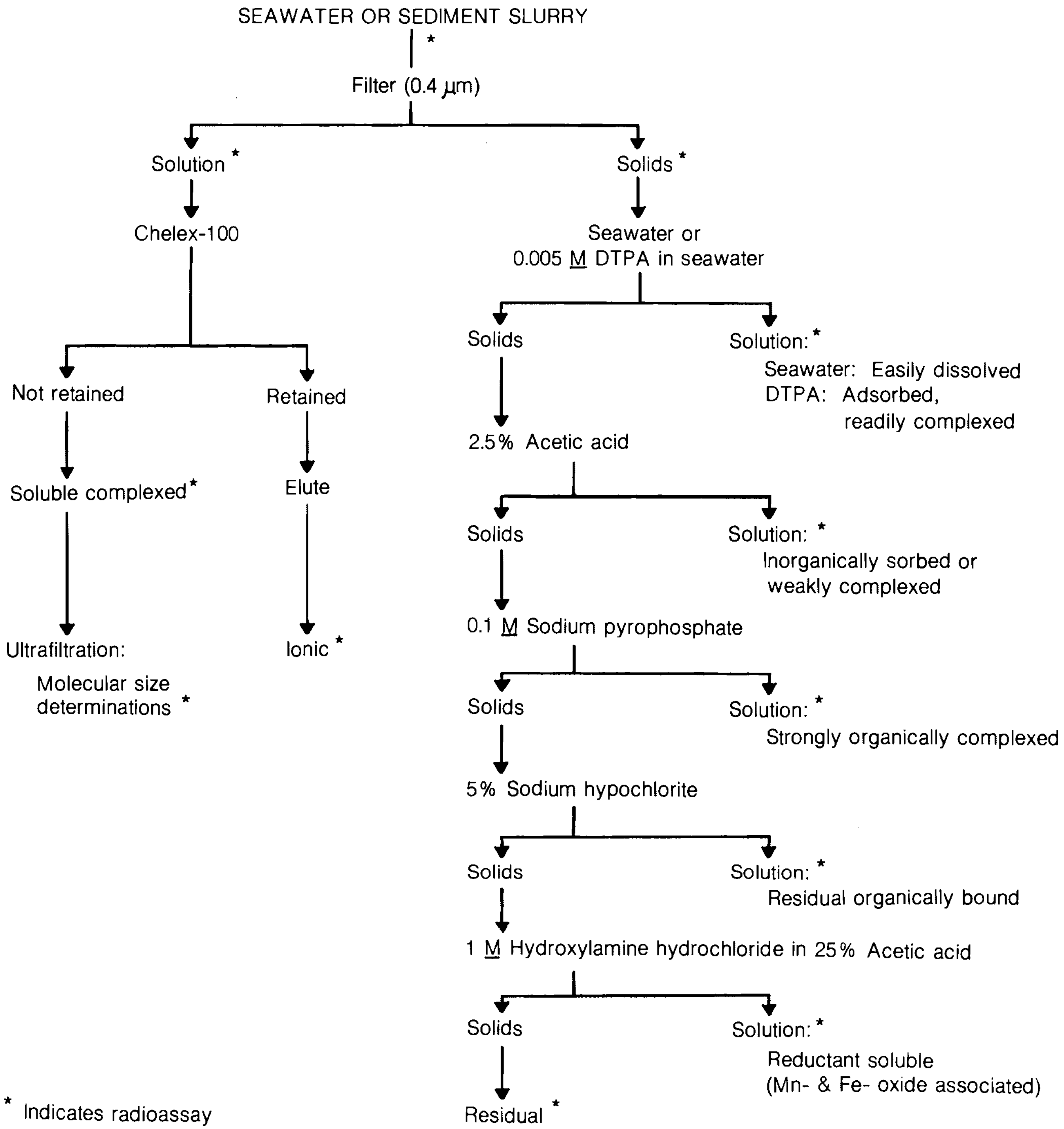

Figure 2. Sequential extraction of trace metals and corrosion products from sediments and suspended material.

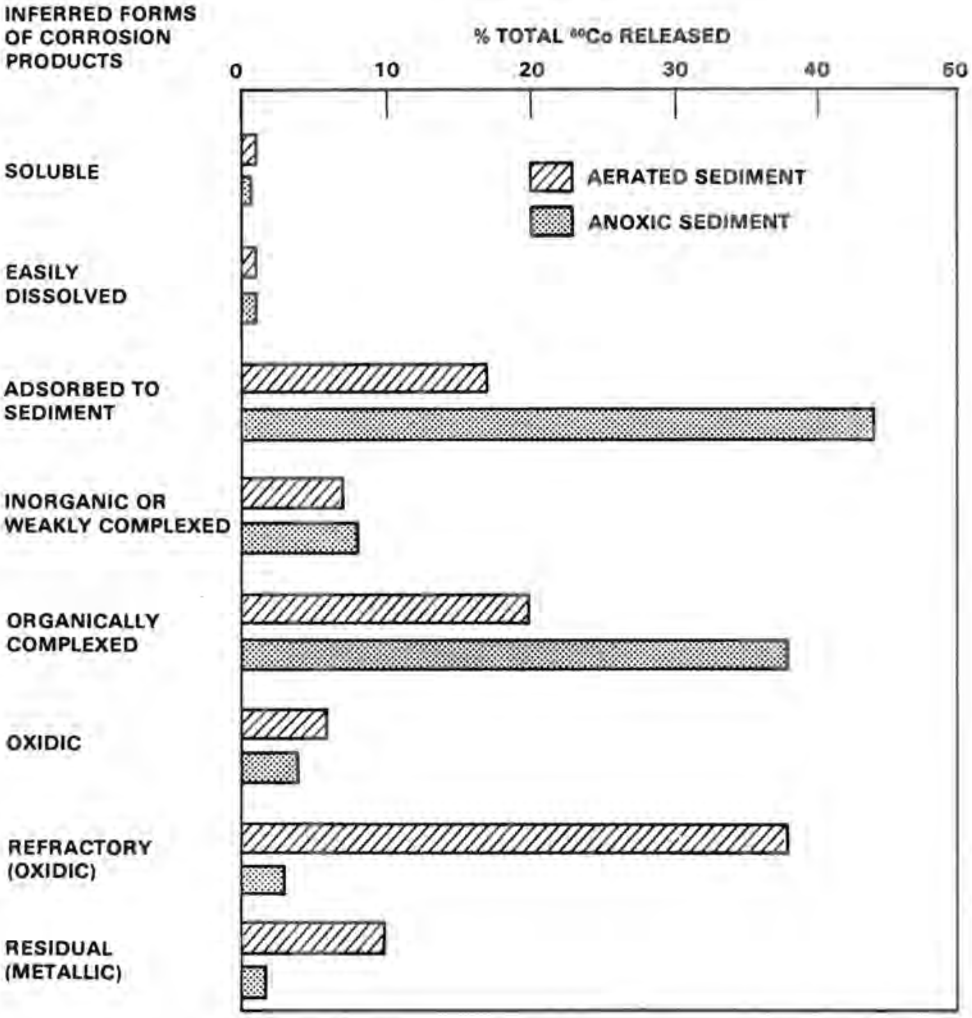

Figure 3. Distribution of corrosion products among chemical forms in organic-rich clayey silt as inferred from selective extraction (Table 1 and Figure 2).

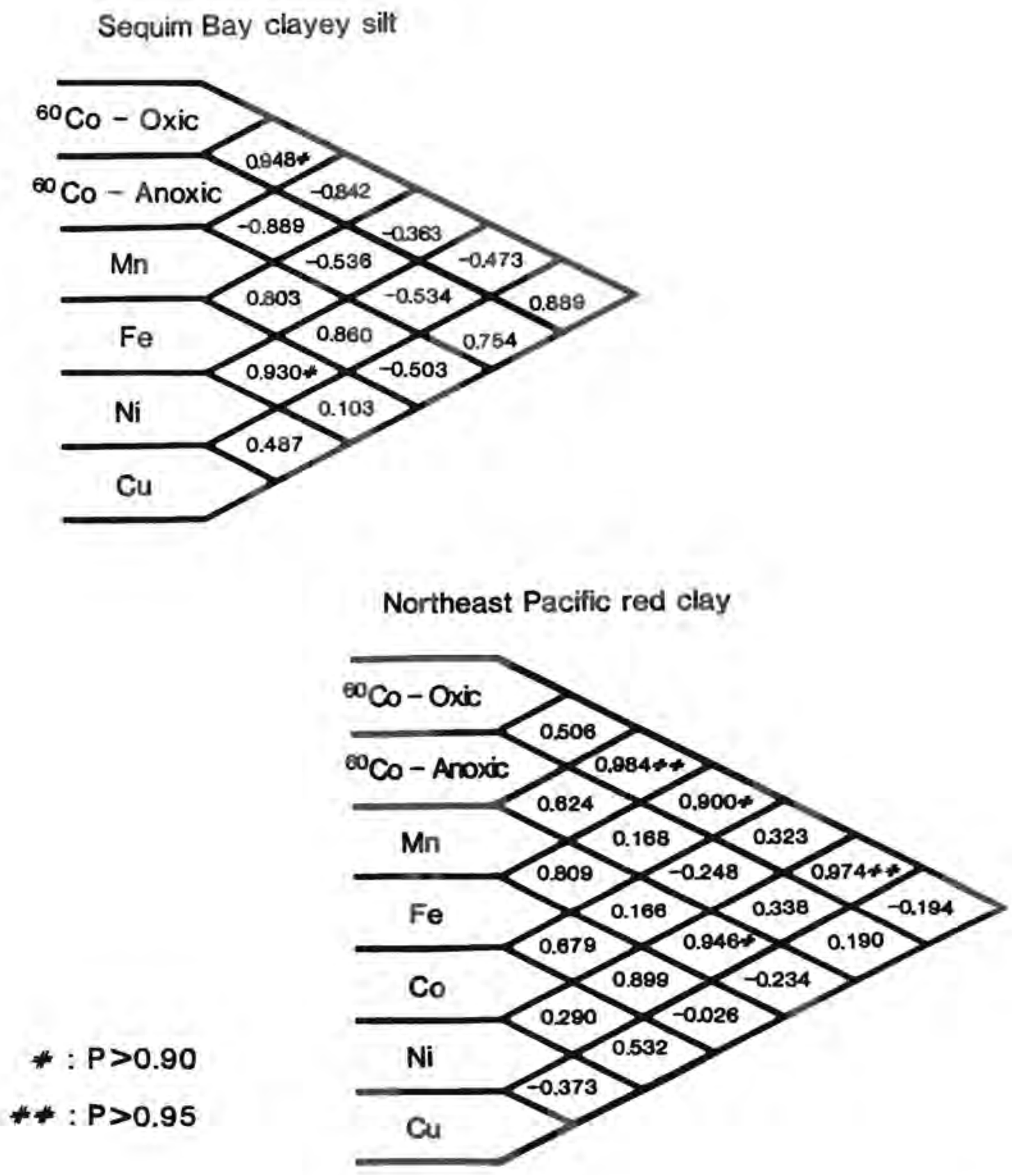

Figure 4. Correlation matrices comparing percent distribution among relatively labile chemical forms of ^{60}Co activity released from neutron-activated 347 stainless steel and indigenous trace metals in two contrasting sediments.

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