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Copper in the Sea - A Bibliography

by
R. L. Schmidt

April 1977

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COPPER IN THE SEA - A BIBLIOGRAPHY

INTRODUCTION

Life in the sea is vulnerable to the influx of trace metals resulting from man's activities. Although many pollutants introduced to the sea eventually degrade to less harmful forms, trace metals accumulate in sediments and have a continued potential for effect on biota. Copper has a toxic potential exceeding all other metals due to the quantity discharged and its toxicological effect. Fortunately, copper in the oceans is rendered less bioavailable or less toxic by its ready interaction with the complex chemical components of seawater.

The toxicological effects of copper have been well documented, and literature on this subject is not included in this bibliography. Less easily measured and little investigated are subtle effects that slight increases in copper in the marine environment may have on the biota. Adaptation by marine sediment microbiota to increased Cu levels may have ramifications on biological and chemical processes that these organisms control and lead to an impact on the entire ecosystem.

This bibliography was prepared to illustrate the status of current knowledge of the biogeochemistry of copper and to aid the development of research programs to define the effects of copper discharged to the marine environment. The references are categorized to aid the reader to locate literature concerning specific aspects of the biogeochemistry of copper. A brief comment describing the important findings in each category is given. Although this bibliography is not exhaustive, the listed references are likely representative of current knowledge. A review of most of the references listed has been submitted to CRC Critical Reviews in Environmental Control at the publishers' request.

INORGANIC FORMS OF CU IN SEAWATER

Copper in seawater appears to be saturated with respect to CuO . The principal soluble inorganic species is likely $\text{CuCO}_3(\text{aq})$. Adsorption and precipitation appear to be the primary processes that maintain the geochemical balance of Cu in the ocean.

References

9, 19, 53, 70, 82, 85, 95, 123, 169, 193, 220, 226-229, 232, 238, 249, 274, 278, 291, 363, 373, 383, 399, 409, 489, 534, 583, 584, 591, 608, 618, 652, 667, 676, 677, 684-686, 693, 740, 783.

COPPER-ORGANIC MATTER INTERACTIONS

ORGANIC MATTER IN THE OCEANS

The sea contains an extensive variety of classes of organic compounds having functional groups capable of forming complexes with Cu. A lignin-type material, Gelbstoff, appears to exert a dominant influence on organo-Cu interactions in seawater.

References

23, 33, 41, 79, 80, 81, 110, 170, 186, 201, 212, 219, 275, 307, 332, 337, 358, 367, 386, 397, 426, 472, 506, 522, 524, 529, 567, 586, 588, 591, 604, 612, 616, 645, 648, 660, 668, 683, 698, 720, 735, 756, 757, 759-762, 775.

ORGANIC-COPPER COMPLEX FORMATION

The formation of stable Cu complexes has a major influence on the biogeochemistry of Cu. The association of Cu with organic materials may prevent precipitation, adsorption, or biological uptake of the metal.

References

8, 12, 29, 38, 39, 50, 51, 55, 56, 70, 92, 93, 104-106, 111, 140, 141, 159, 161, 165, 169, 183, 191, 192, 198, 233, 238, 262, 263, 280, 322, 325, 345, 346, 375, 377, 384, 385, 388, 391, 403, 412, 413, 417, 420, 421, 428, 449, 450, 452, 461, 468, 469, 481, 485, 494, 499, 507, 516, 517, 527, 546, 562, 563, 566, 574, 589, 619, 623, 625-633, 653, 674, 675, 677, 684, 692, 705, 736, 746, 755, 771, 772.

ORGANO-COPPER COMPLEXES IN THE SEA

Soluble Cu in nearshore seawater appears to exist primarily as organic complexes. Stable chelates may hinder the removal of Cu from solution and may provide a mechanism for continued recycling of the element through the food chain.

References

14, 19, 44, 47, 62, 108, 167, 168, 179, 182, 187, 188, 194, 201, 258, 312, 336, 347, 376, 378, 394, 398, 415, 419, 433, 448, 449, 451, 455, 456, 477, 479, 480, 489, 493, 501, 504, 506, 516, 520, 544, 545, 558, 565, 569-572, 606, 610, 624, 645, 649, 658, 659, 685, 690, 703, 752, 758, 760.

EXTRACTION AND ANALYTICAL METHODS

SAMPLING, SAMPLE PRESERVATION AND CONTAMINATION

Analysis of Cu at environmental concentrations is hindered by possible contamination or unknown chemical changes during sampling and analysis. Sample collection, storage, separation, and concentration techniques and analytical methods must be selected to minimize these problems.

References

60, 90, 234, 245, 341-343, 362, 457, 533, 540, 543, 589, 594, 598, 599, 608, 609, 614, 635, 647, 654, 657, 659, 671, 729, 730.

EXTRACTION OF CU FROM MARINE SAMPLES

Seawater

Preconcentration of Cu in sea water is required prior to analysis by commonly used methods. Chelation/solvent extraction, resin column chromatography, and coprecipitation are the concentration methods generally employed.

References

2, 3, 5, 10, 47, 59, 89, 102, 120, 124, 125, 137, 157, 178, 181, 191, 234, 249, 350, 361, 391, 394, 395, 400, 422, 427, 439, 441, 453, 496, 508, 543, 547, 550, 554, 589, 593-595, 605, 608, 656, 657, 659, 677, 678, 680, 681, 695, 718, 761, 780.

Sediment

Total Cu is usually removed from sediment by extraction with strong oxidizing acids. Selective chemical fractionation is useful for defining the forms of Cu present in sediments.

References

6, 7, 37, 77, 78, 93, 108, 119, 126, 139, 153, 205, 210, 216, 225, 257, 302, 305-306a, 309, 355, 362, 369, 388, 391, 401, 416, 418, 425, 444, 453, 467, 469, 503, 522, 531, 543, 545, 575, 580, 595, 596, 608, 622, 656, 682, 723, 778.

Biotic Material

A mixture of nitric and perchloric acids is the reagent most commonly used for mineralization of biotic samples prior to analysis for trace metals.

References

16, 143, 260, 299, 309, 330, 392, 543, 554, 592, 595, 729.

Isolation and Characterization of Organo-Cu Complexes

Ultrafiltration and gel permeation chromatography are often used to initially fractionate organo-Cu compounds. Other techniques including thin-layer electrophoresis and high pressure liquid chromatography are useful for characterizing these materials.

References

47, 52, 130, 159, 196, 285-288, 355, 361, 382, 387, 394, 423, 435, 451, 454, 471, 512, 548, 550, 568, 569, 571, 594, 633, 648, 657, 666, 691a, 706, 742, 747-749, 778.

ANALYTICAL TECHNIQUES

The appropriate analytical method for Cu is selected on the basis of the sensitivity, selectivity, species differentiation and precision required. Available sample quantity, cost, and time are also important factors.

References

245, 405, 463, 727, 754.

Spectrophotometric Methods

Sensitive and precise spectrophotometric methods are available for analyzing Cu in circumstances such as aboard ship where more sophisticated techniques are unavailable or not practicable.

References

14, 27, 90, 157, 239, 270, 308, 427, 453, 543, 589, 594, 595, 608, 671, 677, 681, 706, 754, 773.

Emission Spectroscopy

While emission spectroscopic techniques are less sensitive and less accurate than other methods, they are useful for determining quickly and economically the gross chemical composition of sediments.

References

77, 124, 207, 283, 441, 462, 501, 543, 582, 589, 594, 621, 754.

Atomic Absorption Spectroscopy

The response specificity of atomic absorption spectroscopy for Cu together with its capacity to analyze large numbers of samples have made this method the most popular technique for Cu analysis. Flameless atomization in conjunction with preconcentration by chelation/solvent extraction offers the greatest sensitivity for determining Cu in seawater.

References

11, 15, 16, 45, 67, 74, 86, 98, 107, 108, 119, 124, 128, 137, 139, 177, 178, 215, 234, 241, 297, 309, 362, 374, 381, 400, 402, 405, 432, 439, 545, 547, 561, 589, 592, 611, 636, 637, 639, 640, 656, 661, 689, 697, 733, 754.

Ion Selective Electrode

Lack of stability and sensitivity limits the use of the ion selective electrode for the direct measurement of Cu at normal seawater concentrations. However, the method is useful for investigating the interaction between ionic Cu and complexing ligands.

References

72, 140, 360, 364, 442, 482, 562, 563, 603, 664, 667, 722, 737, 754.

Anodic Stripping Voltammetry

Anodic stripping voltammetry is a sensitive and selective method for determining trace Cu levels in water which requires little chemical pretreatment of the samples and permits concurrent analysis of other metals.

References

1, 5, 46, 99, 100, 128, 238, 242, 248-251, 268, 273, 330, 431, 440, 464, 478, 482, 509, 510, 519, 589, 647, 663, 666, 753, 754, 781, 782.

Other Methods

Neutron activation as a means of determining Cu in environmental samples offers good sensitivity, but the short half-lives of the unstable Cu isotopes and need for extensive sample pretreatment limit its usefulness. X-ray fluorescence techniques are particularly applicable to trace metal analysis of sediments and biological samples.

References

17, 35, 123, 131, 221, 224, 225, 256, 257, 270, 333, 372, 391, 395, 422, 460, 465, 482, 589, 657, 659, 725, 754.

SOURCES OF CU TO THE SEA

Fluvial discharge of Cu to the world's oceans appears to exceed all other sources by about two orders of magnitude. However, point source discharges of industrial and municipal wastewater may lead to enrichment of Cu in local sediments and overlying waters.

References

30, 63, 112, 132, 142, 184, 190, 207, 247, 281, 309, 319, 357, 390, 436, 498, 515, 523, 537, 600, 601, 646, 679, 694, 700, 711, 715, 763, 777.

COPPER IN THE MARINE ATMOSPHERE AND SURFACE MICROLAYER

Atmospheric transport of dust from the continents is a source of Cu to the ocean. Marine atmospheric particulates appear to be enriched in Cu compared lithic materials. The surface microlayer of the sea contains a higher concentration of Cu than the water directly beneath it.

References

43, 44, 63, 66, 84, 129, 147, 199-201, 217, 237, 276, 327-329, 365, 408, 535, 536, 544, 564, 700, 732, 763, 766, 784.

COPPER CONTENT OF SEAWATER

SURFACE WATERS OF THE OPEN OCEAN

Until recently, the Cu concentration of seawater generally accepted as representative was 3 µg/l. However, current data indicates a value of near 1 µg/l and perhaps as low as 0.5 µg/l is more realistic.

References

58, 88, 89, 94, 97, 107, 148, 158, 206, 241, 252, 392, 400, 554, 583, 590, 591, 594, 634, 659, 669, 670, 706, 758.

COASTAL AND NEARSHORE WATERS

Nearshore waters on the average contain about twice as much Cu as open ocean samples. Freshwater runoff, atmospheric transport and terrestrial pollution are the likely sources for this enrichment.

References

3-5, 14, 27, 28, 91, 94, 107, 114, 127, 138, 148, 158, 167, 168, 208, 247, 250, 252, 253, 266, 267, 290, 309, 319, 321, 360, 392, 427, 431, 439, 496, 511, 553, 590, 593, 595, 610, 657-659, 663, 669, 670, 688, 753, 758.

SUBSURFACE WATERS

The copper content of seawater generally decreases with increasing depth. However, at about 500-1000 m below the surface, there is an increase in Cu content which might be related to the release of Cu from decaying organic materials. In some waters, the presence of an anoxic zone at depth produces lower soluble Cu concentrations due to CuS formation.

References

96, 97, 120, 158, 208, 241, 252, 253, 267, 518, 590, 634, 658, 659, 667, 669, 670, 706.

SEASONAL VARIATIONS

Seasonal variations of Cu in surface waters are related to several interacting factors including fluvial discharges, phytoplankton productivity, history of the water mass and upwelling. In general, soluble Cu exhibits a maximum concentration in early fall and a minimum in early spring.

References

3, 28, 158, 258, 392, 491, 492, 669.

FORMS OF CU

A large proportion of Cu in seawater is in organically complexed and particulate forms.

References

14, 59, 60, 96, 223, 258, 491, 492, 655, 657-659, 670, 758.

SUSPENDED PARTICULATES

Suspended particulates are nonuniformly distributed at the ocean's surface, increasing near the coast and in upwelling zones. The Cu concentration of suspended particulates is in the range of 25-100 µg/g.

References

3, 22, 49, 57, 75, 96, 146, 149, 163, 166, 203, 240, 359, 366, 379, 518, 537, 542, 555, 556, 620, 668, 710, 711, 751.

COPPER IN MARINE SEDIMENTS

NEARSHORE SEDIMENTS

Coastal sediments from industrialized areas invariably have higher Cu levels than sediments from less developed coasts. Although man's activities directly contribute Cu via industrial and municipal waste discharge, the presence of higher levels of organic matter may lead to the formation of organic-mineral aggregates which aid the nearshore deposition of fine Cu-laden particles.

References

26, 42, 77, 78, 91, 112, 115, 127, 132, 145, 156, 158, 165, 204, 209, 256, 269, 272, 304, 305, 309, 310, 312, 313, 318, 324, 366, 369, 380, 398, 407, 447, 459, 487, 523, 539, 545, 549, 552, 577, 580, 607, 621, 622, 638, 642, 665, 682, 696, 699, 701, 702, 723, 764, 774.

DEEP-SEA SEDIMENTS

Copper in deep-sea sediments is derived from continental lithic material, authigenic processes, or from biogenic sources. Magmatic and volcanic processes may contribute Cu to sediments at some locations. The average abundance of Cu increases from nearshore to pelagic clays and is higher in Pacific than in Atlantic sediments.

References

24, 61, 69, 76, 83, 122, 144, 150-152, 156, 171, 213, 230, 236, 294, 303, 348, 396, 398, 521, 549, 573, 581, 615, 650, 691, 712, 713, 726, 745.

FERROMANGANESE MINERALS

The abundance of Cu in pelagic ferromanganese nodules exceeds that of surrounding sediments by about an order of magnitude. This phenomenon likely results from adsorption of Cu on oxidized Mn. Both metals may diffuse from the sediment after dissolution under anoxic conditions.

References

123, 154, 172-174, 214, 293, 296, 300, 331, 344, 351, 396, 434, 446, 465, 466, 495, 513, 555, 557, 558, 576, 597, 745.

ANCIENT SEDIMENTS

The distribution and forms of Cu in ancient sediments appear to be little different from recent deposits. The diagenetic processes controlling Cu may occur soon after sedimentation.

References

31, 113, 231, 237, 378, 415, 438, 486, 501, 743, 744.

INTERSTITIAL WATERS

The concentration of Cu in interstitial waters is strongly influenced by oxidation-reduction reactions occurring in the buried sediments. Anoxic conditions may cause the release of Cu associated with oxidic minerals. Organic substances may stabilize Cu in interstitial water through formation of organo-Cu complexes.

References

52, 101, 102, 108, 202, 222, 264, 444, 458, 506, 551, 552, 609, 614, 651, 651a.

COPPER IN MARINE BIOTA

Several organisms tend to accumulate Cu in amounts directly proportional to the Cu concentration of their environment and have been proposed as suitable indicators of Cu contamination. Dietary uptake is the most important means of Cu accumulation for most marine animals, and the metal is generally concentrated in the digestive organs. The blood of mollusks and arthropods contains hemocyanin, a Cu-protein respiratory pigment.

References

13, 24, 32, 40, 54, 64, 65, 71, 87, 109, 114-118, 164, 175, 176, 197, 208, 235, 244, 255, 256, 259-261, 265, 270, 279, 291, 292, 294, 295, 299, 301, 309, 314, 315, 317, 318, 320, 321, 335, 336, 339, 340, 351-353, 370, 371, 376, 392, 406, 410, 429, 436, 437, 443, 470, 479, 480, 490, 492, 493, 502, 528, 530, 541, 550, 553, 554, 559-561, 578, 579, 581, 592, 602, 613, 641, 658, 662, 673, 686, 687, 702, 707, 708, 719, 724, 728, 738, 739, 741, 752, 770, 775, 776, 780.

PROCESSES AFFECTING CU IN COASTAL WATERS

Adsorption appears to be the dominant process controlling Cu added to the sea from freshwater sources. Organic matter and hydrous metal oxides are likely the principal adsorbents. Copper enters the sediment by deposition of lithic materials and biotic debris and by adsorption from the water column. The uptake of soluble Cu by plankton and ingestion of Cu-containing nonbiotic particulates are the major pathways for entry of Cu in the marine food web. Copper may be mobilized from suspended matter and sediments by oxidation or reduction reactions which are strongly influenced by marine microbiota.

References

3, 20, 21, 25, 26, 62, 64, 68, 73, 82, 85, 95, 96, 103, 114, 116, 122, 133, 134, 135, 136, 142, 155, 160, 162, 179, 185, 189, 190, 195, 203, 204, 207, 210, 211, 218, 222, 228, 229, 232, 243, 246, 254, 257, 258, 279, 281, 289, 295, 296, 311, 315, 316, 319-321, 331, 334, 349, 357, 363, 379, 380, 389, 393, 399, 404, 407, 410, 411, 414, 430, 433, 445, 460, 466, 468, 475, 477, 483-485, 488, 489, 495, 497, 500, 514, 525, 526, 530, 532, 534, 538, 551, 560, 576, 578, 584, 585, 587, 600, 601, 607, 608, 610, 617, 643, 644, 662, 667, 670, 672, 675, 686-688, 701, 709, 710, 713, 714, 726, 741, 746, 750, 751, 764, 765, 767-769, 777, 779.

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