HUMIC AND FULVIC ACIDS AS INDICATORS OF SOIL AND WATER POLLUTION

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Abstract. Humic substances are the major organic components of soil and sediments, but little is known on how they are affected by environmental and industrial pollution. To find out whether such effects could be recognized, a number of analytical characteristics were compared of humic and fulvic acids extracted from unpolluted and polluted soils and sediments.

The main differences were that, per unit weight, polluted humic and fulvic acids contained more N, S and H but fewer CO₂H groups, and were more aliphatic than unpolluted samples. Unusually high N and S contents of humic materials appear to be the most valid indicators of pollution. Humic acids are preferred to fulvic acids as indicators of pollution because the former are more readily separated and purified.

1. Introduction

Pollution studies of soils and waters usually focus primarily on the nature and concentrations of the water-soluble and water-insoluble inorganics in these systems. Most investigators pay little attention to organic constituents which often control many chemical reactions that occur in aquatic and terrestrial environments.

It has been estimated (Schnitzer, 1978) that 65 to 75% if the organic matter in predominantly inorganic soils and most likely also in sediments consists of humic materials, that is, humic acid (HA), fulvic acid (FA), and humin. The remainder is composed mainly of polysaccharides and protein-like substances (Flaig et al., 1975; Schnitzer, 1978). Humic substances are amorphous, dark colored, hydrophilic, acidic, partly aromatic, chemically complex substances which can form water-soluble and water-insoluble complexes with metal ions and hydrous oxides and which interact not only with clays and other minerals but also with organic compounds such as alkanes, fatty acids, dialkyl phthalates, pesticides, herbicides, carbohydrates, amino acids, peptides and proteins (Schnitzer, 1978).

Of special concern is the formation of water-soluble complexes of FA with toxic metals and organics which can increase the concentrations of these constituents in soil solutions and natural waters to levels that are far in excess of their normal solubilities.

Based on their solubility in alkali and in acid, humic substances are usually partitioned into three main fractions: (1) humic acid (HA), which is soluble in dilute alkali but is precipitated by acidification of the alkaline extract; (2) fulvic acid (FA), which is that humic fraction which remains in solution when the alkaline extract is acidified, that is, it is soluble in both dilute alkali and in dilute acid; and (3) humin,

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which is that humic fraction that cannot be extracted from the soil or sediment by dilute base or acid.

From analytical data published in the literature (Schnitzer and Khan, 1972; Schnitzer, 1978), it becomes apparent that chemically, the three humic fractions are similar, but that they differ in molecular weight, ultimate analysis, and functional group content, with FA having a lower molecular weight but higher content of oxygen-containing groups (CO₂H, OH and C =O) per unit weight than the other two fractions.

There is increasing evidence (Schnitzer and Khan, 1972) that the chemical structure and properties of the humin fraction are similar to those of HA, and that its insolubility in dilute base and acid arises from the firmness with which it combines with inorganic soil and water constituents. One characteristic exhibited by all humic materials is their relatively high resistance to microbial degradation.

Two relatively simple methods that are often used for the characterization of humic materials are elemental and functional group analyses. Elemental analysis provides information on the distribution of the major constituent elements (C, H, N, S and O). Functional group analyses shed light on the occurrence of the major functional groups (CO₂H, phenolic and alcoholic OH, ketonic and quinonoid C =O) in humic materials. The major functional groups in humic substances are rich in oxygen and are often referred to as oxygen-containing functional groups. It is through these groups that humic materials react with metals, minerals and organic compounds.

Over the years, large numbers of elemental and functional group analyses on purified HAs and FAs, extracted from soils and sediments from widely differing locations on the Earth’s surface, have been done in our laboratory.

Recently, we computed from these data mean values for each constituent element and for each functional group which gave us the composition of the mean HA and FA. Aside from each mean value, the maximum and minimum range and the variance were also calculated. We wondered whether elemental and functional group analyses data for HA’s and FA’s extracted from polluted soils or sediments would differ significantly from similar data for HAs and FAs extracted from non-polluted soils and sediments, provided that the same methods of extraction and characterization were used. Would this relatively simple approach permit us to differentiate between polluted and unpolluted soils and sediments? To what extent does environmental and/or industrial pollution affect the analytical characteristics of humic materials? It was to provide answers to these questions that we undertook this investigation.

2. Materials and Methods

2.1. Polluted Samples

Four grab samples (Nos. 1, 5, 6 and 9) of the top 15 cm of sediment were taken with the aid of an Ekman dredge in the Altrhein river near Ginsheim, West Germany. The Altrhein is a cut-off channel of the Rhein river near Mainz, West Germany, and is located in one of the most highly populated and industrialized regions in Europe. The Altrhein river is an