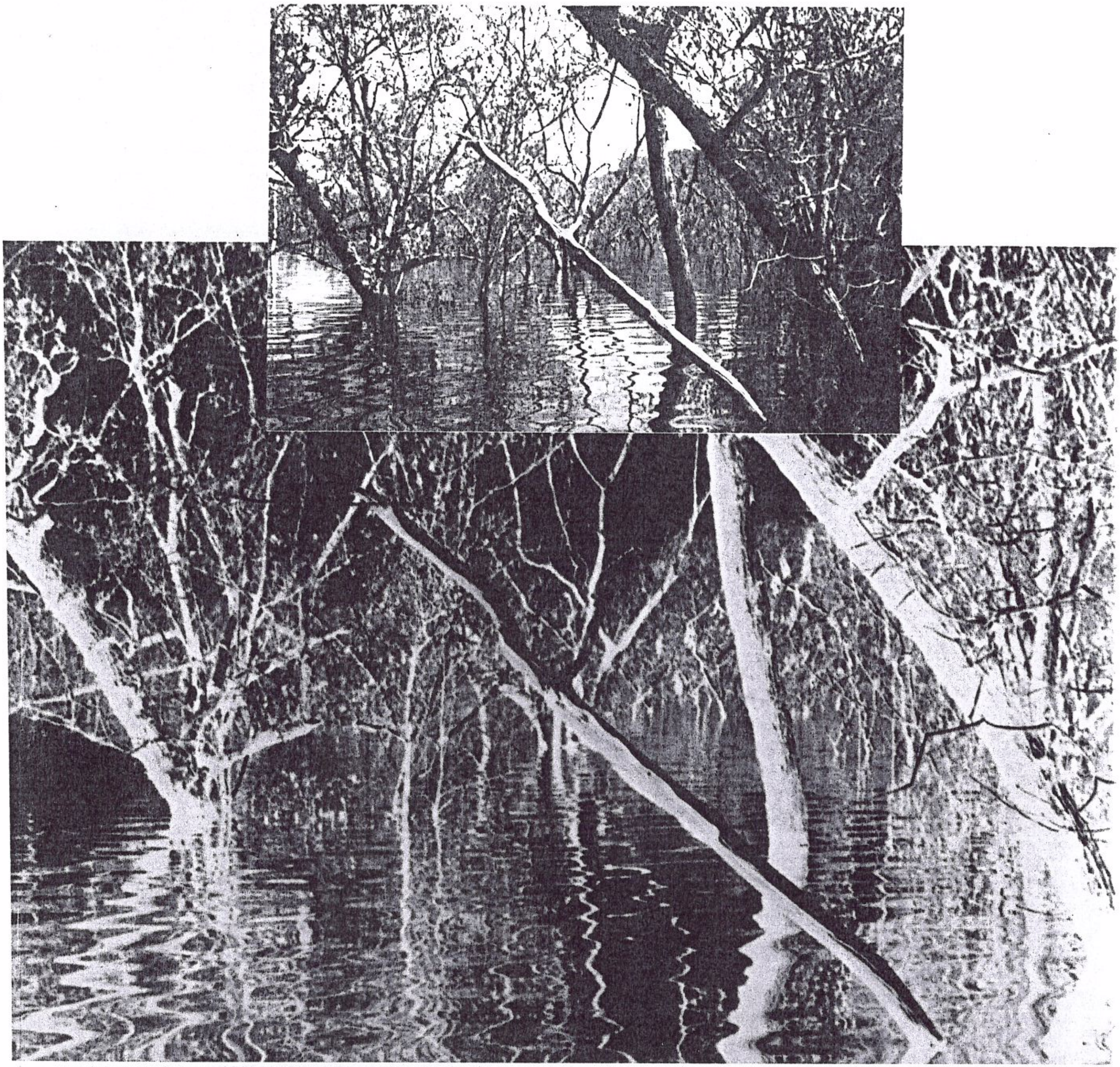

Hydropower Plants and Greenhouse Gas Emissions

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Planejamento Energético

HYDROPOWER PLANTS AND GREENHOUSE GAS EMISSIONS

Proceedings of
INTERNATIONAL WORKSHOP ON GREENHOUSE GAS EMISSIONS FROM HYDROELECTRIC RESERVOIRS
ELETROBRÁS, Rio de Janeiro, Brazil
11-12 SEPTEMBER, 1996

and

"*GREENHOUSE GASES FROM HYDROELECTRIC RESERVOIRS: PRODUCTION, FATE, AND MEANS OF STUDY*"
Universidade Federal do Pará, Santarém, Pará, Brazil
01-04, FEBRUARY, 1997

Supporting material prepared for consideration by Intergovernmental Panel on Climate Change and international expert community.
This material has not been subject to formal IPCC review process.

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FINANCIAL SUPPORT
ENERGE - ENERGY STUDIES CENTER
PPE/COPPE/UFRJ
MINISTRY OF SCIENCE AND TECHNOLOGY/CNPq
ELETROBRÁS - ENVIRONMENTAL DEPARTMENT

The Degradation Process of Organic Matter in Reservoirs

I. Bianchini Jr. [1]

This paper is aimed at discussing a number of aspects associated with the degradation of organic matter in reservoirs. In general, in this type of environment the detrital organic matter is originated from three sources: 1.phytomass that was drowned during the filling operation; 2.particulate and dissolved detritus carried through tributaries and from rain (allochthonous sources); 3.detritus from the processes of primary production in the reservoir itself (autochthonous sources). The fundamental knowledge of the kinetics for the systemic modeling of degradation processes in reservoirs is discussed using information from detritus sources, and from different forms of carbon and their properties.

O PROCESSO DE DEGRADAÇÃO DA MATÉRIA ORGÂNICA EM RESERVATÓRIOS. Este trabalho visa discutir aspectos relacionados com a degradação de matéria orgânica em reservatórios. Em geral, nestes ambientes a matéria orgânica detrital origina-se de três fontes: 1ª. fitomassa afogada durante a operação de enchimento; 2ª. detritos particulados e dissolvidos carreados através dos tributários e das enxurradas (fontes alóctones) e 3ª. detritos originados dos processos de produção primária do próprio reservatório (fontes autóctones). Com base no conhecimento das fontes de detrito, das formas do carbono orgânico e de suas propriedades, apresentam-se os fundamentos cinéticos que podem ser utilizados para descrição sistêmica dos processos de degradação da matéria orgânica em reservatórios.

1. Introduction

Today about $25x10^9$ tons of CO_2 are released to the atmosphere per year. No other commodity in the world is handled on this scale. For example, annual world food production and steel production are 1-2 orders magnitude smaller (MADDOX, 1990). In addition to the burning of fossile fuels to maintain facilities of modern society (e.g.: electric power, food production), decomposition of organic matter may also be an important source of CO_2 as well as of other gases. If issues related to the greenhouse effect are to be addressed effectively, knowledge is required of biogeochemical and physical machinery that cycle carbon in the global system. Also required are models of the carbon cycle to predict the effects of increasing CO_2 in the atmosphere (DUCKLOW & FASHAM, 1994). In aquatic ecosystems, in particular, the efficacy of the cycle of detrital organic matter depends on several factors such as: oxireduction conditions, temperature, specific community composition of decomposers, the amount and quality of detritus. In

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this context, this paper is aimed at discussing some aspects of the decay of organic matter in the aquatic ecosystems, with emphasis on artificial reservoirs. The paper comprises three items: in the first one the main forms in which the detrital organic carbon can be found are presented. It also includes the main origins of the organic carbon and some of its interactions with the aquatic communities. The kinetics of the decomposition processes is conceptually described in the second part. Some driving functions (abiotic factors) and their effects on the detritus cycling are presented. The third part is related with the kinetics concepts usually employed in the mathematical modeling of the processes involved. It should be stressed that this study is not aimed as a comprehensive review of the issues addressed. Rather, its aim is to discuss the basic elements involved in the processes of CO_2 and other gases generation during the decay of organic detritus in aquatic systems.

2. *Detrital Organic Carbon: forms, sources and properties.*

In aquatic ecosystems the main fraction of carbon is found in its inorganic form, in equilibrium with carbonic acid products. Just a little amount is present as organic compounds and still a smaller one as a biota constituent (WETZEL, 1983). In addition to a constituent of organisms, carbon could also be found in particulate material: in the live fraction (plankton) and in detritus. In the inorganic forms of the detritus, the carbon is found in several kinds of carbonate and in the organic detritus it is found in dissolved fractions (dissolved organic matter, DOM) and particulate forms (particulate organic matter, POM). The ratio between DOM and POM for the organic forms has been found to be about 6 to 10:1 (BIRGE & JUDAY, 1926;1934; OHLE, 1972; SAUNDERS, 1972; OTSUKI & WETZEL, 1974; RAI & HILL, 1980).

With regard to the origin of carbon forms in aquatic environments, five main sources have usually been found: 1°.organic compounds from allochthonous origin; 2°.organic matter derived from decomposition of aquatic organisms; 3°.extracellular metabolites or photosynthesized products released by the phytoplankton; 4°. extracellular metabolites or photosynthesized products released by aquatic macrophytes of littoral zone; and 5°.fauna excreted. For the reservoirs, in particular, the sources of detrital organic matter may be put in three categories, two of which from the internal environment (autochthonous) and the other one from external media (allochthonous). As autochthonous sources one may mention the detritus derived from primary production processes (exsudates, aquatic macrophytes and phytoplankton debris) and the phytomass incorporated during the filling phase. Particulate and dissolved fractions of organic matter carried through the tributaries and runoff establishes the basis of the allochthonous sources.

For some lacustrine systems, the biomass production from aquatic plants may comprise up to half of the organic carbon inflow to the system and very little of this photosynthesized carbon remains in its reduced form for long. On the other hand, this carbon is an essential resource for the metabolic maintenance of the system (GODSHALK & WETZEL, 1978). In the reservoirs located in tropical regions, aquatic macrophytes generally find suitable climatic conditions to develop the whole year (MENEZES, 1984; CAMARGO & ESTEVES, 1995). The high potential for growth of these organisms can be illustrated by a culture of Salvinia sp kept under lab conditions and supplied with water from an eutrophic reservoir, which showed a biomass growth rate of the order of 9.7% per day (SAIA & BIANCHINI Jr., in press). This high growth potential combined with the high temperatures and favorable nutrients conditions prevailing in tropical reservoirs are responsible for the importance of aquatic macrophytes as detrital organic matter source in this type of environment.

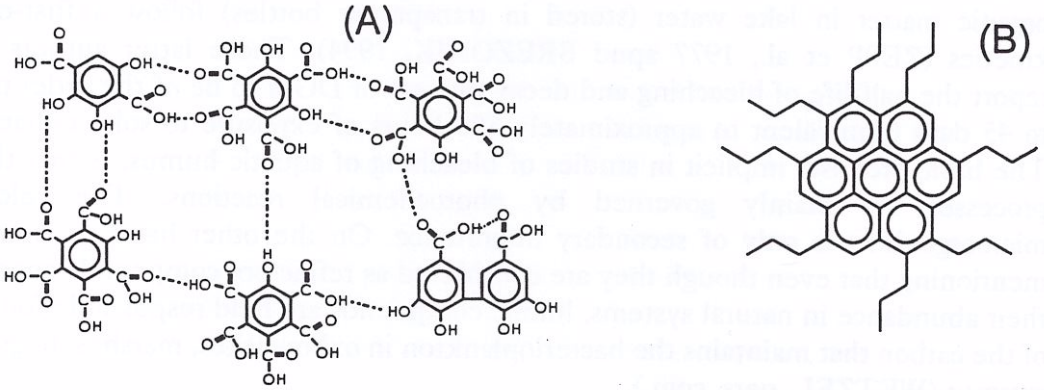
Previous experience in the construction of reservoirs in areas covered by plants has indicated that depending on the amount of phytomass present in the watershed, the plants drowned may be a significant source of detritus. The decay of this detritus could cause tremendous changes in the water quality, including favorable conditions for the quick development of anaerobiosis and eutrophication processes in the reservoir (BAXTER, 1977; TUNDISI, 1978; GARZON, 1984; PLOSKEY, 1985). This may jeopardize the long-term health of the aquatic ecosystem, and also the multipurpose uses for the water and the equipment related with the power generation units (PAIVA & SALLES, 1977). Owing to the particular origin of this detritus source, knowledge is lacking on some stages of decomposition of these resources, associated with the physical, chemical and biological processes involved.

The allochthonous organic compounds (such as: POM and DOM derived from the terrestrial ecosystems and the wetlands close to the reservoirs) are mainly constituted by dissolved material. In general these compounds have low content of nitrogen (C:N≈50:1) and could represent the main source of DOM to the aquatic ecosystems. Probably they have low nitrogen and carbon ratios owing to the high concentration of humic substances (SHAPIRO, 1957; SCHNITZER & KHAN, 1972). The organic compounds from autochthonous origin, in their turn, are basically produced by aquatic macrophytes and algae, being richer in nitrogen C:N≈12:1 - (WETZEL, 1983).

According to GOLTERMAN (1975), the dissolved organic matter may interact with the biota in five ways: 1°. by supplying energy or organic carbon for bacteria and algae; 2°. as an aiding agent for growth (e.g. vitamins); 3°. by having a toxic effect on larvae and algae; 4°.by forming organic complexes with trace elements which may (or not) be beneficial to the organisms; 5°.by absorbing light, and therefore affecting the photosynthetic processes.

Large quantities of these organic detrital compounds (particulate or dissolved) are assimilated directly by the microbes as a supply of organic carbon and energy. However, fractions that are not consumed together with those that are resynthesized suffer chemical condensations, leading to humic substances (BIANCHINI Jr. 1985). Hence, two classes of organic matter are found in the aquatic systems: one that possess well defined chemical nature (e.g. amino acids, carbohydrates, organic acids, cellulose, lignin, etc.) and the humus *(Figure 1)* which has a heterogeneous, polyfunctional nature with distinct degrees of polymerization (TOLEDO, 1973).

Owing to their importance for maintaining the metabolic routes (energetic and constitutive) of microorganisms, the non-humic compounds are generally present in low contents in aquatic systems. Because they are recalcitrant and produced from resynthesis, the humic compounds tend to accumulate and may remain in the environment for several years. They are characteristic of an intermediate stage of organic matter, between the processes of decomposition and mineralization. Since these processes are relatively slow, the humus plays an important role as these compounds possess chemical properties that make them interact with the biota or even with the environment itself. The complex nature of these compounds has led to a large variety of reports on their biochemical and physiological effects, such as: 1°.a favorable influence on the growth and productivity of phytoplankton, (SHAPIRO, 1957; PRAKASH & RASHID, 1968; AZEVEDO, 1982; BIANCHINI Jr. et al., 1982); 2°. formation of organic aggregates (SIEBURTH & JENSEN, 1968; 1969; SIEBURTH, 1969); 3°.attenuation of solar radiation on the water (KIRK, 1976; BIANCHINI Jr. et al., 1984) and 4°.making it possible for algae to survive in toxic environments (TOLEDO et al., 1980). Even though experimental evidence has been gathered about effects from organic matter and dissolved humic substances on the physiological and biochemical processes, the way by which these substances act has not been established (TOLEDO, 1973). However, the physiological activities have been attributed to several characteristics of humic acids which include: 1°.ability to chelate metallic ions (PRAKASH & RASHID, 1968); 2°.participation in catalytic reactions associated with the cell metabolism (KHRISTEVA apud KONONOVA, 1966); 3°.increase in the cell permeability (FLAIG apud KONONOVA, 1966).



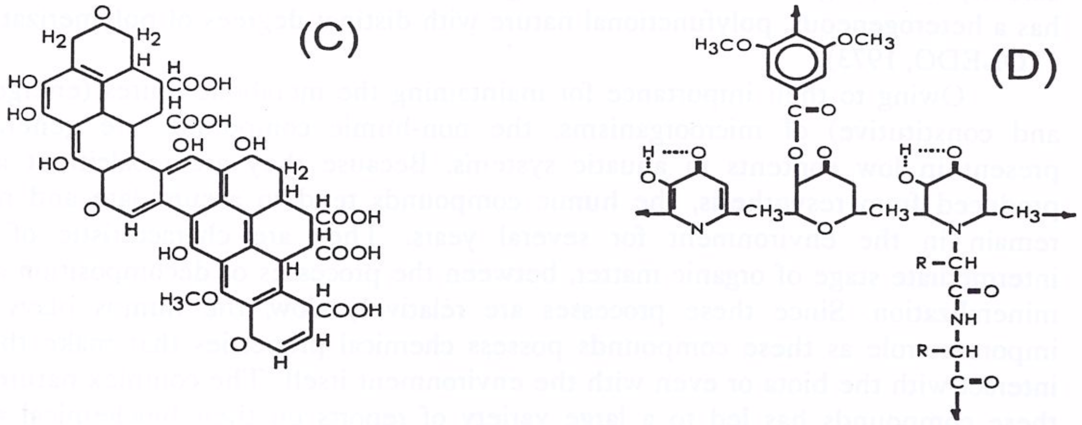


Figure 1 . (A) Fulvic acid according to SCHNITZER & KHAN (1972). (B, C e D) Humic acids proposed by KASATOKHIN et al. apud dos SANTOS (1978), FELBECK Jr. (1965) and FUCHS apud KONONOVA (1966), respectively.

In spite of various studies supporting effects and properties described above, the processes (and their origin) responsible for degradation of humic compounds in aquatic systems remain obscure to a large extent. In this context, there are a number of studies describing this degradation process using chemical methods for identifying the structure and composition of the humic compounds. Experiments describing biological aspects are scarce, however, and several aspects have not been addressed yet. The loss of color by the dissolved organic matter due to the sun light has been reported for decades. HUTCHINSON (1957), for instance, mentions studies dating from the end of XIX century in which a substantial loss of color was reported for water samples (incubated in bottles) on the surface of lakes. More recent studies have indicated that oxygen is essential for the bleaching reactions. Also, it has been shown that the loss of color as well as the degradation of dissolved organic matter in lake water (stored in transparent bottles) follow a first-order kinetics (ZEPP et al., 1977 apud BREZONIK, 1994). These latter authors also report the half-life of bleaching and decay process of DOM to be of the order of 35 to 45 days (equivalent to approximately 500 hours of exposure to solar radiation). The basic premise, implicit in studies of bleaching of aquatic humus, is that these processes are mainly governed by photochemical reactions. The role of microorganisms is only of secondary importance. On the other hand, it is worth mentioning that even though they are considered as refractory compounds owing to their abundance in natural systems, humic compounds are held responsible for 80% of the carbon that maintains the bacterioplankton in oxbow lakes, marshes, bogs and swamps (WETZEL, pers. com.).

Preliminary experiments on the aerobic mineralization of humic compounds originating from degradation of an aquatic macrophyte, (*Scirpus cubensis*), have suggested that a period of 60 days is sufficient for a substantial bleaching of humic substances, humic acids and fulvic acids (CUNHA & BIANCHINI Jr., 1994). Bleaching, in this case, is indicative of mineralization. However, the colorimetric method may not be adequate for monitoring the transformation of organic carbon in CO_2 (mineralization) because the biopolymer is extremely reactive. It so happens that the possibility exists of resynthesis of these compounds generating molecules with low contents of organic carbon, but more colored. In this case, the monitoring of color loss as indicative of mineralization may underestimate the rate and yield of the process. On the other hand, the aerobic mineralization of organic resources, including total humic compounds (BITAR & BIANCHINI Jr., in press), have been shown to proceed with high rate. Such a rate is higher than those obtained for the mineralization of various aquatic macrophytes that possess fragile structures such as *Lemnia* sp, *Cabomba* sp, *Salvinia* sp, among others. However, the amount of oxygen uptaken in the mineralization of humic compounds is the lowest among the substrates used, which points to the possibility of mineralization of only part of the humic compounds, the labile fraction. Another possibility is a distinct stoichiometry for the mineralization process of these substances.

3. *General Comments on the Decomposition Process*

In the aquatic ecosystems the cycling and transformation of carbon basically consists of three types of process: assimilation of inorganic carbon through photosynthesis and chemiosynthesis, aerobic decomposition and anaerobic decomposition (THURMAN, 1985). Essentially, the decomposition results in a change of state of a given resource, under the influence of biotic and abiotic factors characteristic of the environment. This simplified version of the process may be visualized in the diagram of *Fig. 2.* One may see that during the time period from t_1 to t_2 the state of the resource changes from R_1 to R_2. The "valve" symbol represents the influence of regulating factors (driving forces) and the arrow represents the process of chance or reaction rate (SWIFT et al., 1979).

The simplest way to identify a resource state change, derived from the decay processes, is to verify their decrease in mass. A more detailed analysis shows that this includes a loss of matter from the resource and a change in the chemical composition of the remainder. These alterations may be attributed to the effect of three distinct processes; those of leaching, catabolism and comminution (SWIFT et alli, 1979).

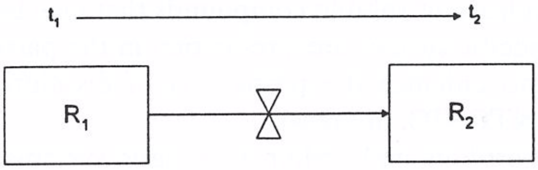


Figure 2 .Schematic diagram depicting the progress of the decomposition process from time t_1 to t_2, during which the resource is changed from state R_1 to R_2. The rate of change (represented by the arrow) is subjected to regulations (valve symbol) due to biotic and abiotic factors (adapted from SWIFT et al., 1979).

Leaching is the abiotic process whereby soluble matter is removed from the resource by the action of water. Thus, this process causes weight loss and changes in the original detritus chemical composition. In the ecosystem, this process may promote transference of soluble compounds to another site, where it may be acted upon by further decomposition processes (SWIFT et alli, 1979). Catabolism is the biochemical process responsible for transforming complex organic compounds into smaller and simpler organic or inorganic molecules. However, within a given time period, the catabolism process may be incomplete, thus creating intermediates or resynthesized compounds such as the humic compounds (TOLEDO, 1973; WETZEL, 1983; BIANCHINI Jr. et alli, 1984; THURMAN, 1985).

Through the comminution process, the particle size of the resource is reduced. This process is different from catabolism because of its physical nature. However, in many cases it is related with the feeding activity of the decomposers. Then, during digestion the fragmentation may be accompanied by catabolic changes and the remaining matter is excreted as smaller particles with a chemical composition that is different from the ingested food material (SWIFT et alli, 1979). Sometimes the resources may be fragmented with no organisms action, by the climatic changes and by the turbulence action of water and of the wind (LUSH & HYNES, 1973; SWIFT et alli, 1979).

In *Figure 3* (A) the changes described above are presented schematically. In a relatively short time period (from t_1 to t_2), of the order of days to months, the original resource is attacked by organisms that cause its fragmentation into chemically unaltered residues and/or cause size reduction thus catabolizing it into inorganic compounds, cell structures and humic compounds. Simultaneously, the processes of leaching remove the soluble fractions from the original substrate. The decomposition is usually observed in a longer time scale (*Figure 3B*), which may be of the order of years to decades, owing to the slow cycling of humic substances and other structural compounds from plants such as lignin and cellulose. By way of illustration, one may mention that trees and trunks were still found in the 1960's, over 110 years after the filling of the Marion Millpond (Wisconsin-USA) reservoir (BORN et. al., 1973).

In practice these three processes act simultaneously on the same organic resource, sometimes making it difficult to distinguish between them. They also have a global effect on the substrate. The catabolic activity may weaken the structures and make them more prone to fragmentation. The catabolic processes may also lead to the release of soluble compounds that may be removed. Because of the increase in the specific surface area, reduction in the particle size may favor the access of enzymes and enhance the probability of dissolution of the compounds (BIANCHINI Jr. & ANTONIO, in press).

The flow of nutrients and carbon in aquatic systems depends on its input and output temporal functions. In the ecosystems, these fluxes depend upon the pathways through which the uptake of elements and decay of organic resources processes take place. The rates with which nutrients and carbon are cycled and accumulated depend mainly on the balance between the immobilization and mineralization processes. By immobilization of a given element or carbon it is meant the incorporation or maintenance in the organic form. In aquatic systems this kind of process is usually conducted by phytoplanktonic and microorganisms communities, and also by the aquatic plants roots and chemical interactions involving the humic substances and the adsorption processes.

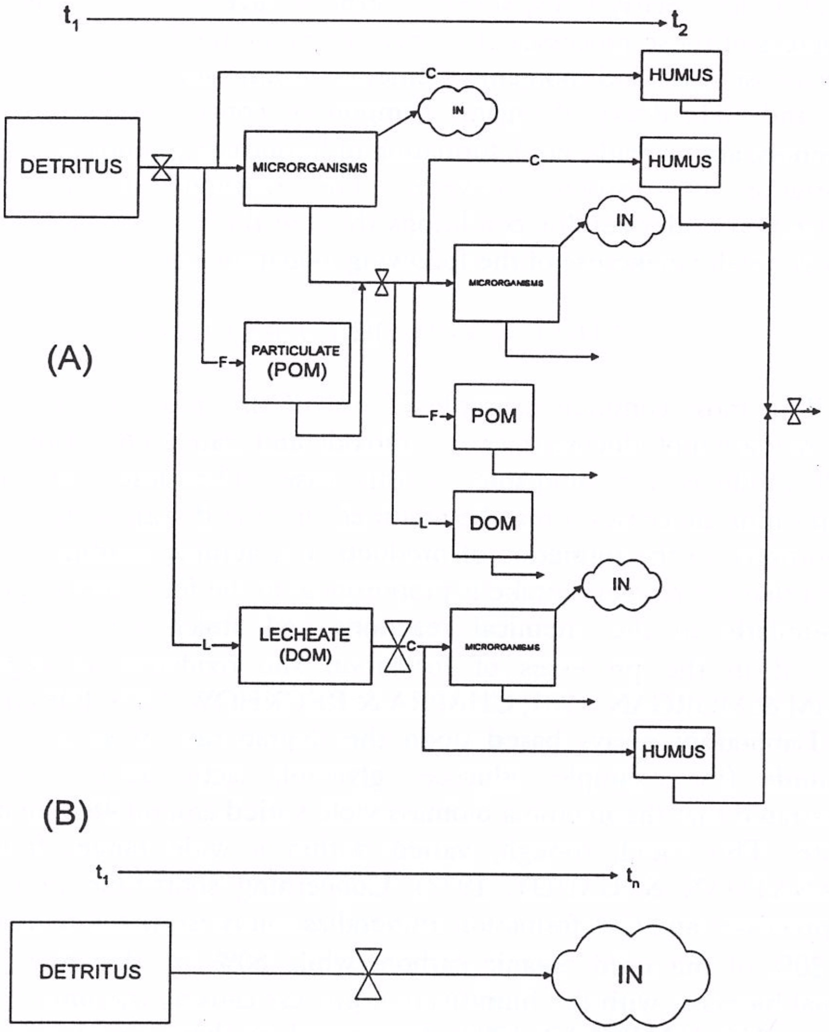


Figure 3.Subsystems of detritus decomposition: (A) decomposition of a resource within a short time period (t_1 to t_2). The three components, catabolism (C), fragmentation (F) and leaching (L) alter the chemical composition (e.g. mineralization generating the inorganic forms (IN) and resynthesis leading to the formation of microorganisms and humus) and the physical characteristics of the detritus (e.g. reducing the particle size of the chemically unaltered resource and removing soluble compounds to other sites). (B) Decomposition of a resource of a long time period (t_1 to t_n) resulting in a complete mineralization (adapted from SWIFT et al., 1979).

Mineralization occurs when the inorganic forms of a given element are released during the catabolism of a resource (e.g.: SO_4^{-2}, CO_2, NH_3, etc.). In this way; the availability of a specific nutrient element depends on the net mineralization, in which the result of the mineralization process exceeds the immobilization one (SWIFT et alli, 1979). These mechanisms together with leaching build up what we referred to as decomposition processes.

Owing to the importance of mineralization processes for biogeochemical cycles of aquatic ecosystems, several methods have been proposed for describing the progress of these processes. The most common methods include: monitoring of radioactive isotopes and inorganic elements; monitoring of evolution of gases such as CO_2 and CH_4; decay of organic compounds concentration (e.g. carbohydrates, polyphenols, amino acids, etc.); formation of humic compounds and depletion in the concentration of dissolved oxygen. The methods involving estimates of mineralization under aerobic conditions through the kinetics of decay of dissolved oxygen generally make use of the following oxidation reaction:

$$C_xH_{2y}O_z + [\ x+((y-z)/2)]\ O_2\ \text{Þ}\ x\ CO_2 + y\ H_2O$$

The most common example of use of this reaction stoichiometry is the aerobic oxidation of glucose to carbon dioxide and water. The oxidation is complete and all products are inorganic in this case. Therefore, for the kinetics of decomposition processes it may be assumed that the disappearance of the substrate is proportional to the formation of products. For aerobic conditions, it may also be assumed that the oxygen uptake is proportional to the formation of products such as CO_2, similarly to the chemical reactions and stoichiometric relations usually considered in the processes of formation and oxidation of organic resources (STUMM & MORGAN, 1981; CHAPRA & RECKHOW, 1983; JORGENSEN, 1986).

Laboratory essays based upon the degradation of several simple organic compounds (for example: glucose, glycerol, lactic acid, and others) have demonstrated that the microbia biomass yield varied around 48%, depending on the substrate. This yield, though, varied within a wide range, from 26 to 88% (RAMANATHAN & GAUDY, 1972). Concerning short-time periods of glucose decay processes and CO_2 formation, mineralization is estimated to be responsible for about 20% of the used organic carbon, while 60% are due to the formation of microbial biomass, with the humification process causing the immobilization of the remaining 20% (ANTONIO, 1992). Issues such as these are of major relevance on studies aimed at describing the budget of organic matter and dissolved oxygen in aquatic systems.

In addition to the variety of organisms involved in the decomposition process (Bacteria, Fungi, Actinomycetes, Protozoa, Nematodes, Oligochaetes, Arthropods, Mollusca and Crustacea), specific studies on terrestrial and aquatic ecosystems have shown that immobilization and mineralization basically depend on the following abiotic factors: 1°. temperature (SOROKIN & KADOTA, 1972; CARPENTER & ADAMS, 1979; EPA, 1985; DAVIS & CORNELL, 1991; BREZONIK, 1994;); 2°. nutrients contents in the environment and detritus (COULSON & BUTTERFIELD, 1978; ERÍQUES et alli, 1993; HOHMANN & NEELY, 1993; BITTAR & BIANCHINI Jr., 1994; LEMOS & BIANCHINI Jr., in press); 3°. kind of detritus and its amount of refractory compounds (MINDERMANN, 1968; RICE & TENORE, 1981); 4°. pH and salinity of the environment (CHAN, 1985; OGBURN et alli, 1988; KOK & VAN der VELDE, 1991); 5°.amount of dissolved oxygen (JEWELL, 1971; TWILLEY et alli, 1986; MOORE Jr. et alli, 1992; GALE et alli, 1992); 6°.particle size of the detritus (LUSH & HYNES, 1973; SWIFT et alli, 1979; BIANCHINI Jr. & ANTONIO, in prep.).

An increase in temperature generally induces an exponential increase in the rates of catabolic processes (ANTONIO, 1996). The enrichment of nutrients in the environment does not necessarily lead to an increase in catabolic activity (LEMOS, 1995). However, it is well accepted that metabolic rates vary with the concentration of nutrients according to the relation proposed by Michaelis-Menten (ANTONIO, 1996). The half-life time for the cycling of the detritus is basically determined by the contents and composition of the refractory compounds. The smaller the particle size the larger the specific surface area amenable to catabolic processes is (SWIFT et al., 1979). However, for very small particles it is possible that the humic compounds formation process is favored (BIANCHINI Jr. & ANTONIO, in press). The pH and salinity generally determine the occurrence of communities and interfere with the reaction rates mediated by enzymes.

Among all procedures employed for investigating mineralization processes, the method of monitoring the dissolved oxygen uptake is one of the most popular since DBO tests make use of this principle. However, in order to make the results comparable, for the DBO tests the experimental conditions such as preparation of samples, temperature and duration of experiments were fixed. The results may then reflect the effective amount of oxygen required for oxidizing the organic matter that is highly prone to degradation in a given sample. On the other hand, since the oxygen uptake rates may also be affected by several driving functions of the mineralization process, experiments similar to the DBO essays have been proposed for investigating the biotic and abiotic factors involved in the cycling process of organic matter of aquatic systems (ANTONIO, 1996; ANTONIO & BIANCHINI Jr., in press).

Fig. 4 highlights some differences between aerobic and anaerobic processes on the basis of the concepts involved in the degradation of organic resources. It is seen that the composition of released gases depends on the content of dissolved oxygen (DO). This reflects the relative predominance of microorganisms involved in each condition. The selection of microorganisms, in its turn, requires adoption of distinct metabolic pathways for the degradation of the detritus. With regard to the characteristics of the organic resources processing it has been observed that the aerobic process is important over a wide range of organic matter forms. This process generates the most stable final products and a larger amount of microorganisms cells. Under low concentrations of organic matter, the aerobic process is usually quick, efficient and relatively odorless. The anaerobic decomposition (fermentation) of organic matter comprises two stages. In the first, the complex organic compounds are converted into volatile acids of low molecular weight. In the second stage, these acids are converted into CH_4 and CO_2. The main products generated by the anaerobic decomposition are: CH_4, CO_2 and H_2O. Other products such as NH_3, H_2S and mercaptans have also been observed (DAVIS & CORNELL, 1991). Owing to these three compounds, this process has a strong odor. In general, the anaerobic oxidation process generates less microorganisms cells, that is, in comparison with the aerobic degradation, immobilization is less favored. Experiments of anaerobic degradation in which sediment samples were bathed have indicated the following composition for the formed gas mixtures: $CH_4 = 85.2\%$, $N_2 = 7.5\%$ and $CO_2 = 7.1\%$ (SOROKIN & KADOTA, 1972).

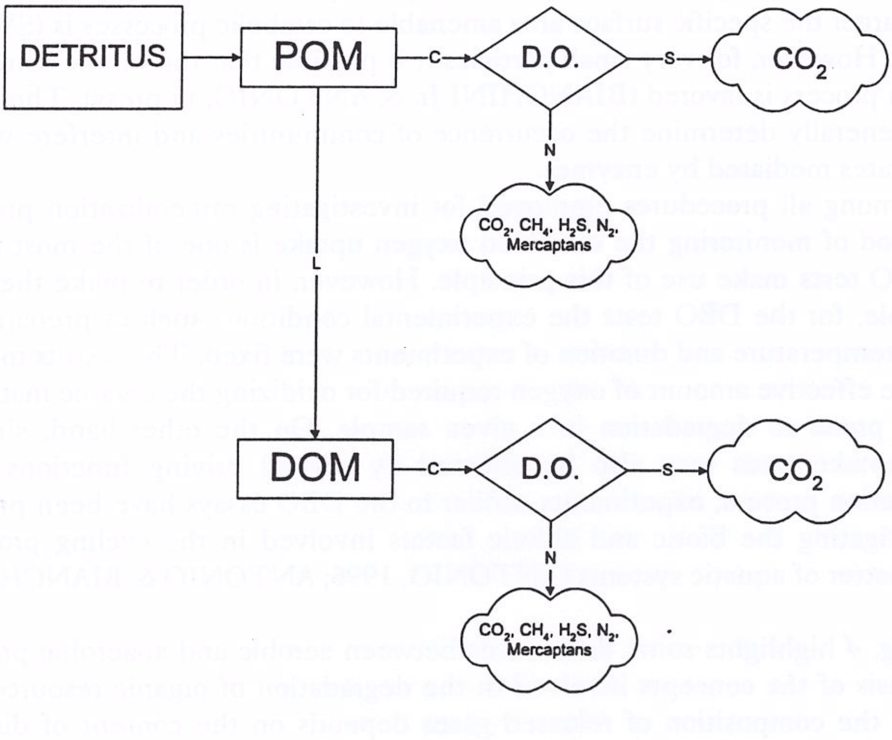


Figure 4. Schematic diagram for mineralization as function of the presence of oxygen.

Under anoxic and anaerobic conditions, the generation of N_2, CO_2 and H_2O is also possible owing to the denitrification process . The amount of energy available for this process is of the same order of magnitude of that generated in the aerobic oxidation process, and therefore there is a relatively high degree of immobilization. However, it is not as favored as in the aerobic decomposition (SCHLEGEL, 1975; DAVIS & CORNELL, 1991). Even though it is usually accepted that aerobic processes for organic matter oxidation are faster (WETZEL, 1983; ANTONIO & BIANCHINI Jr., in press), kinetic studies conducted in an oxbow lake (ANTONIO, 1996) have suggested that under low contents of dissolved oxygen the decay rates for aerobic and anaerobic processes may be approximately the same. This is due to the likely predominance of facultative anaerobic bacteria. Baths of water samples from an eutrophic reservoir (represa do Monjolinho, Sã o Carlos - SP) enriched with glucose have shown that the decay of this sugar under aerobic conditions has a half-life of approximately 97 days. This period of time is 10 times longer than that observed when the environment became anaerobic. It was also noted that the gas formation started after the establishment of anoxic conditions, more precisely after the concentration of dissolved oxygen had fallen below 0.2 mg/L (ANTONIO et. al. 1996; BIANCHINI et al., 1996).

Experiments on the aerobic mineralization of aquatic macrophyte species, branches of shrub sample and humic compounds have indicated that the mineralization kinetics of organic resources may reflect qualitative effects from the substrates, as suggested by a distinct stoichiometry for the various processes (BITAR & BIANCHINI Jr., in press). As for a quantitative analysis, aerobic mineralization essays carried out with glucose indicate that the increase in the mineralization rate may be also due to the increase in the initial concentration of the substrate, according to the model proposed by Michaelis-Menten. They also suggest that the change in the substrate concentration may interfere in the yield of the immobilization processes (BITAR & BIANCHINI Jr., 1994).

In the specific case of environmental studies for the construction of a hydroelectric power plant (HPP), the analysis of information from similar reservoirs may provide a general overview about the influence of submerse vegetation, thermal regime and hydrodynamic characteristics. However, such information is generally insufficient for an accurate characterization of the processing of detritus and its effect on the limnological characteristics of the reservoir. For the latter purpose, one usually employs degradation bioassays and mathematical modeling which consider biotic and abiotic factors of the environment under study. Following suggestions from environmental control boards and international funding agencies, in Brazil experiments on the degradation of phytomass for assessing damage to the environment in building hydroelectric power plants have been conducted since 1986. In such experiments the procedures adopted are similar to those proposed by GARZON (1984). More specifically, these essays are aimed at helping in assessing the impact to the environment when forming reservoirs and also estimating the areas to be deforested. In this context, the studies developed for ELETRONORTE and COPEL (CNEC/ELETRONORTE, 1987; MDK/CENCO/COPEL, 1988) are worth mentioning. In recent years, from 1993 to 1995, two other experiments on the phytomass degradation were conducted: one as an integral part of the study to assess impact to the environment for the HPP Porto Primavera (CESP) and another in the Environment Control Program of the HPP Tijuco Alto (CBA/VOTORANTIM).

These experiments have provided important information for assessing changes in the limnological characteristics caused by degradation of detritus, since they encompass quantitative as well as qualitative aspects of the detritus effects on the chemical characteristics of the water and on the other limnological variables. It is also worth stressing that the mathematical models usually make use of kinetics parameters available in the literature which may not be appropriate for the environment to be simulated. Therefore, in addition to shedding some more light on the processes involved, degradation essays may also provide the kinetics parameters that are closer to the local conditions. This is extremely important for improving the calibrating process in the use of mathematical models, thus decreasing the associated degree of uncertainty.

In mathematical terms, the overall effect from some of the variables mentioned is illustrated in Equation 1 since the decomposition rates obtained in field essays and lab experiments normally reflect effects from the various biotic and abiotic factors.

$$k_{(t)} = f([P]_{(t)}, [N]_{(t)}, [DO]_{(t)}, T(t), pH_{(t)}, PZ_{(t)}, \text{etc.}) \ldots\ldots\ldots\ldots \text{(Eq. 1)}$$

where:

$k_{(t)}$ =instantaneous decomposition rate of the detritus, as a function of the temporal variables
$[P]_{(t)}$ = phosphorus content at the instant "t";
$[N]_{(t)}$ = nitrogen content at the instant "t";
$[DO]_{(t)}$ = content of dissolved oxygen at the instant "t";
$T_{(t)}$ = temperature at the instant "t";
$pH_{(t)}$ =degree of acidity at the instant "t";
$PZ_{(t)}$ =particle size at the instant "t".

4. *Mathematical Modeling*

One of the greatest difficulties for an accurate description and mathematical simulation of decomposition processes in reservoirs lies in the diversity of the detritus sources. For the biomass drowned during filling of reservoirs, in particular, one has to take into account: the procedures adopted in the filling process, the heterogeneity of vegetation (forests, grasslands, annual and perennial cultures, marshes, bogs, etc.), the proportion of each type of vegetation, the diversity and relative contribution of vegetal structures (leaves, branches, barks and litter) and the chemical composition of each structure (e.g. lignin, cellulose, protoplasmic fractions, etc.), or groups of compounds (refractory and labile fractions). For detritus originating from autochthonous processes of primary production, the composition of the dominating species/communities (phytoplankton and aquatic macrophytes) and their life cycle should also be known. The temporal variations of water flow and the contents and composition of POM and DOM are required for estimating the load of detrital organic matter of allochthonous origin.

The degradation of this large set of organic compounds follows specific metabolic routes, producing different intermediate substances that interact in distinct ways with other compounds and with the biota. In this context, the trees and shrub contain more refractory material (cellulose, resins, waxes, lignin) per unity weight than the herbaceous vegetation, and therefore they require a longer time for decomposition (SYLVESTER & SEABLOOM, 1965; BALL et al., 1975).

In Table 1 the chemical composition of plant tissues is presented (GOLDSTEIN, 1981). It is seen that the vegetation biomass is basically formed by compounds that are difficult to degrade. The lignin is the most resistant to biochemical degradation. It may be broken by fungi mainly, and it has been considered as non-degradable in anaerobic processes (HOBSON, 1974). In the other end of the spectrum of compounds, the sugars, proteins and starches are quickly decomposed which make them the substances of immediate importance for changes in water quality. The green parts of vegetation not only have a large proportion of these substances but are also tender and more vulnerable to attack by bacteria owing to their large ratio between surface area and volume.

Table 1 . General composition of plant tissues (GOLDSTEIN, 1981).

COMPONENTS	(%)
CARBOHYDRATES	
Sugars and starches	1-5
Hemicelluloses	10-28
Celluloses	20-50
LIPIDS, WAXES AND TANNINS	1-8
LIGNIN	10-30
PROTEINS	
hydrosoluble and totals	10-15

One may consider that the decomposition processes are governed by consecutive, monomolecular reactions of first order of the type:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

where: A would represent, for instance, the content of glucose; R represents the intermediate compounds (such as humic substances and/or biomass from microorganisms) and S represents the final products. In the case of a complete aerobic mineralization of glucose S would be the carbon dioxide. It is possible to define the following rate equations for the three components:

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \ldots\ldots\ldots\ldots \text{(Eq. 2)}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \ldots\ldots\ldots\ldots \text{(Eq. 3)}$$

$$r_S = \frac{dC_S}{dt} = -k_2 C_R \ldots\ldots\ldots\ldots \text{(Eq. 4)}$$

where k_1 and k_2 refer to the decay coefficients of A and R, respectively.

In *Fig. 5* the general characteristics of the time evolution for the concentration of the three components are presented. It is observed that: 1°. [A] decreases exponentially; 2° . [R] increases up to a maximum value, then decreasing; 3°. [S] increases monotonically, with the maximum increase rate of [S] occurring when [R] is maximum.

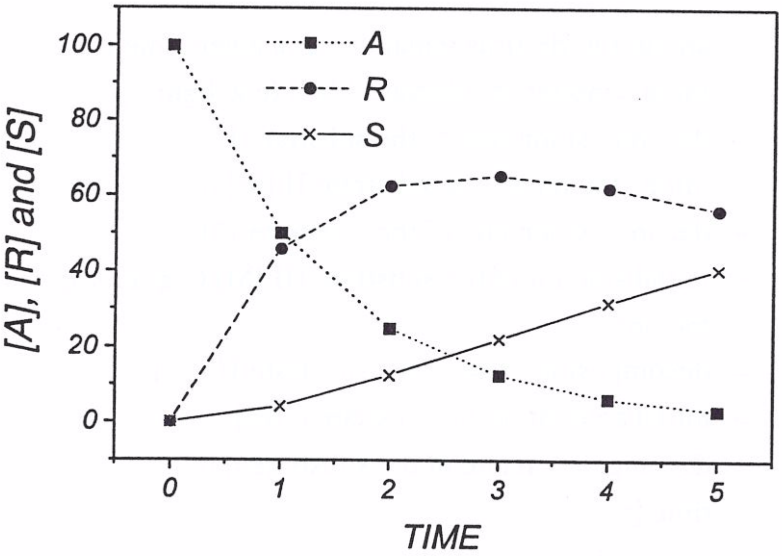


Figure 5 . Time evolution of concentrations for A, R and S according to the kinetics model proposed for the consecutive, monomolecular reactions of first order.

Exponential equations such as those of Eq. 2-4 have often been used for describing and simulating the decomposition and mineralization processes of several resources, for terrestrial as well as for aquatic ecosystems (OTSUKY & WETZEL, 1974; GODSHALK & WETZEL, 1977; 1978; CARPENTER & ADAMS, 1979; BIANCHINI Jr., 1982; 1985; BIANCHINI & TOLEDO, 1996). However, owing to the great diversity of organic compounds in a given resource, these equations may not be applicable to the substrate as a whole. In this context, MINDERMANN (1968) has shown that first-order kinetics is adequate for describing the decay of each structural element of the substrate (e.g. cellulose, lignin, protoplasmic fractions, etc.). Nevertheless, the global decomposition process cannot be represented by a single exponential function. It may rather be described as the sum of several exponential functions (Equation 5). Hence, because of the structural heterogeneity of the substrates, for each element of interest (carbon, nitrogen, phosphorus, etc.) and/or type of structure (leaves, branches, algae, aquatic macrophytes, etc.) the rate equations must be rewritten for representing the distinct mechanisms involved in the decomposition (catabolism, leaching and fragmentation) of each element and/or for each type of structure.

$$W_t = W_1 \exp[-k_1 t] + W_2 \exp[-k_2 t] + W_3 \exp[-k_3 t] + \ldots + W_n \exp[-k_n t] \quad \text{(Eq. 5)}$$

where:

W_t = amount of detritus remaining at a given time [M];
W_1 = initial amount of substrate I [M] (e.g. lignin);
k_1 = decomposition rate of the substrate I [t^{-1}];
W_2 = initial amount of the substrate II [M] (e.g.: cellulose);
k_2 = decomposition rate of the substrate II [t^{-1}];
W_3 = initial amount of the substrate III [M] (e.g. protoplasmic fraction);
k_3 = decomposition rate of the substrate III [t^{-1}];
W_n = initial amount of the substrate n [M];
k_n = decomposition rate of the substrate n [t^{-1}];
t = time [t];

By way of illustration, through Eq. 6 to 10 the processes of mineralization of a given detritus are described by taking into account the hypotheses presented in *Fig. 6.* According to these hypotheses the mineralization may occur through three distinct pathways. In the first, the labile compounds (such as the reduced carbohydrates, the polysaccharides and polyphenols) would be quickly oxidized, simultaneously with leaching (dissolution). The second pathway would encompass the consecutive processes of leaching and consumption (catabolism) of the dissolved fractions of organic matter (DOM). In the third pathway, the oxidation of the refractory particulate detritus (POM) would be responsible for the mass loss. This idealized kinetics model considers the detritus as a non-homogenous substrate from the structural point of view (chemical composition). From the parametrization of the kinetics model, and from the knowledge of the correlations among reaction rates and the abiotic factors (temperature, dissolved oxygen, nutrients, etc.) and the drive functions of the environment (such as time changes of detritus input and abiotic factors), it is possible to simulate the mineralization processes in a given aquatic system. It is worth stressing that the accuracy of the simulation results generally depends on the degree of certainty about the factors mentioned.

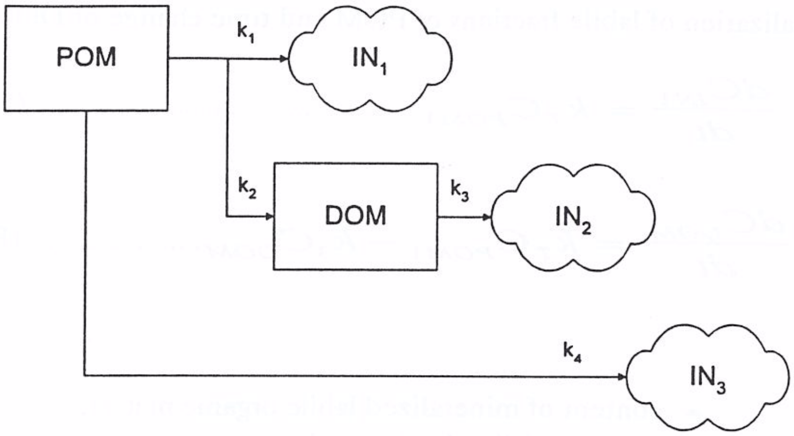


Figure 6 .Kinetics model for illustrating the mineralization processes. k's = reaction rates (day $^{-1}$*); IN = inorganic compounds originating from mineralization;* k_T *= global decay rate of POM due to oxidation processes in labile fractions and due to dissolution;* k_1 *= oxidation rate of labile fractions;* k_2 *= leaching rate;* k_3 *= oxidation rate of DOM;* k_4 *= oxidation rate of POM;* IN_1 *= content of organic matter that is easily oxidized and mineralized according to* k_T*;* IN_2 *= content of leached and mineralized organic matter (according to* k_T *and* k_3 *respectively) and* IN_3 *= content of particulate organic matter, mineralized according to* k_4*.*

I. Decay of POM: dissolution (formation of DOM) and oxidation of labile and refractory compounds from particulate fractions.

$$\frac{dC_{POM1}}{dt} = -k_T C_{POM1} - k_4 C_{POM2} \quad \text{..........................} \quad \text{(Eq. 6)}$$

where:

$PPOM_1$ = content of labile compounds and/or soluble detritus (≈ protoplasmic fractions and other soluble compounds);

POM_2 = content of refractory organic matter from particulate detritus (≈cellulose, lignin, etc.);

k_T = global decay rate of POM_1 (k_1+k_2), day^{-1}.

k_1 = mineralization rate for labile compounds, day^{-1};

k_2 = leaching rate of soluble compounds, day^{-1};

k_4 = mineralization rate of refractory compounds, day^{-1}.

5. Conclusions

From the discussion above one may conclude that: 1.the release of CO_2 and other gases from the cycling of detritus in aquatic ecosystems arise from the predominance of mineralization processes over immobilization (chemical and biological); 2.the rates and yield of these processes are affected by temporal changes in chemical, physical and biological factors of the environment; 3.depending on the amount and quality of detritus and on the conditioning factors, the decomposition process may be a relevant source of CO_2; and 4.the mathematical modeling of degradation processes and formation of CO_2 is feasible. The results will be most accurate when reliable data are obtained from field assessments and from experiments to input as parameters in the mathematical model.

6. Acknowledgments

The author thanks the Organizing Committee of the International Workshop on Greenhouse Gas Emissions from Hydroelectric Reservoirs for the opportunity of presenting this paper. He is also indebted to Dr. Osvaldo N. Oliveira Jr. (IFSC-USP) for his critical proofreading of the manuscript.

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