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## A review of environmental characteristics and effects of low-molecular weight organic acids in the surface ecosystem

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### ABSTRACT

Low molecular weight organic acids (LMWOAs) are prevalent on the earth's surface. They are vital intermediate products during metabolic pathways of organic matter and participate in the tricarboxylic acid cycle during life activities. Photochemical reactions are pivotal for LMWOAs' origination and play a large role in determining their diversity and their ultimate fate. Within the long time that organic matter is preserved in sediments, it can be decomposed and converted to release organic and inorganic pollutants as well as C, N, and P nutrients, which are of potential ecological risk in causing secondary pollution to lake water. The sediment pool is a comprehensive and complex compartment closely associated with overlying water by various biochemical processes, during which LMWOAs play critical roles to transport and transform elements. This article elucidates geochemical behaviors of LMWOAs in the surface environment in details, taking natural water, soil, and aerosol as examples, focusing on reviewing research developments on sources and characteristics, migration and mineralization of LMWOAs and relevant environmental effects. Simultaneously, this review article depicts the categories and contents of LMWOAs or their contribution to DOC in environmental media, and evaluates their importance during organic matter early diagenesis. Through concluding and discussing the conversion mechanisms and influencing factors, the next research orientations on LMWOAs in lake ecosystems are determined, mainly concerning relationships with hydrochemical parameters and microorganisms, and interactions with pollutants. This will enrich the knowledge on organic matter degradation and related environmental effects, and help reconstruct a theoretical framework for organic compound succession and influencing factors, providing basic data for lake eutrophication and ecological risk assessment, conducive to better control over water pollution and proper management of water quality.

## Introduction

Dissolved organic matter (DOM) mineralization consumes a large amount of oxygen and releases C, N, P, and S, thus seriously deteriorating water quality and promoting water eutrophication. Low molecular weight organic acids (LMWOAs), which could be produced and consumed in

this complicated ecological and physiological process, and are utilized as an index of water quality evolution (Stinley et al., 2004; Petra et al., 2004), are ubiquitous water soluble organic compounds that have been detected in a variety of environmental samples (Brinkmann et al., 2003; Gogou and Stephanou, 2004; Tedetti et al., 2006). LMWOAs regulate heavy metals and toxic organic compounds in terms of their ecological toxicology and environmental migration, through adsorption and chelation/complexation with them (Elkhatib et al., 2007; Gao et al., 2010). As important carriers of materials and energy in the biosphere,

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LMWOAs are of great significance during these processes, being consumed by microorganisms and converted to become part of the organisms to increase biomass. Conversely, they are also released from these organisms' own excretion and macromolecular organic matter's decomposition (Kleerebezem et al., 1999). Bottom sediments strongly influence the eutrophication and biodiversity of lakes, and preserve the historical records of environmental change. Simultaneously, sediment provides an important field for organic matter activities, such as the biogeochemical cycle of carbon, nitrogen, phosphorus and the fate of pollutants. Many organic compounds are produced and consumed with nutrient (N and P) regeneration during sediment particulate organic matter mineralization (Wu et al., 2008). During sediment diagenetic processes, the molecular composition of organic matter changes, and these changes follow some general patterns leading to the definition of diagenetic indicators, the amino acids whose relative abundance and composition have been used as the basis of evaluating diagenesis (Cowie, 1994). However, studies have suggested that LMWOAs function similarly to indicate sediment early diagenesis. Moreover, LMWOAs are useful to elucidate photochemical effects and corresponding biological effects in lake waters (Zagarese et al., 2001; Jonsson et al., 2007). Therefore, the components and characteristic dynamic features of LMWOAs, whether in lake water or in sediments, became the main emphasis of their discussion. Therefore, the influence of LMWOAs' biogeochemical processes on water environment chemistry, as well as their sources, characteristics and migration-transformation, and other environmental effects will also be expounded comprehensively in this paper.

## 1 Source, characteristics of LMWOAs and the influencing factors

Water-soluble organic compounds include complex constituents, and not only consist of dissociative macromolecules such as enzymes, aminosaccharides, polyphenols and humic acid, but also contain dissociative low molecular weight organic acids, amino acids and saccharides. Natural fresh waters contain a wide array of low molecular weight organic molecules together with more complex organic constituents such as humic substances and detritus (Drozd et al., 1997). The origin of LMWOAs is considered to be microbial decomposition of various plant materials, and some are even used as identifiers for certain genera of decomposers (Berdie et al., 1995).

Low molecular weight organic acids and related polar compounds are ubiquitous water-soluble compounds that have been detected in a variety of environmental samples, including aerosols, rainwaters, ice-cores, marine sediments, freshwaters, and soils as illustrated in **Table 1**.

LMWOAs also participate in many biological processes. They are important intermediates in the tricarboxylic acid and glyoxylate cycles, in catabolism and anabolism of amino acids. In anoxic marine sediments, LMWOAs act as important active intermediates between large biomolecules and the ultimate remineralization products  $\text{CH}_4$  and  $\text{CO}_2$  during their metabolic activities. Through HPLC detection, the carboxylic acids have been found to be mainly formate and acetate all year round, with the concentration rising from the interface to an asymptotic value of 150–200  $\mu\text{mol/L}$  at 30-cm depth. However, during summer pooling of fermentation products as described above, the identified portion of  $\Sigma\text{COOH}$  rose to 80%–90% and was composed mostly of acetate and propionate (Albert and Martens, 1997). This information can be useful to determine carboxylic acids and their role in the anaerobic carbon cycle. The organic acids from Lake Aydat, a small eutrophic lake located in the French Massif Central, have been analyzed to determine their possible sources and their fate during early diagenesis. Researchers found that the  $\text{H}^+$ -labile components, assumed to be mostly of bacterial origin, disappeared rapidly with depth. In contrast, notable  $\text{OH}^-$ -labile compounds, mostly derived from algae and terrestrial plants, survived in the deepest samples analyzed (Stefanova and Disnar, 2000).  $\text{C}_2$ – $\text{C}_5$  dicarboxylic acids and malic, glyoxylic, and pyruvic acids were determined using capillary electrophoresis. Oxalic acid dominated in these acids, with seasonal average concentrations of 107–412  $\text{ng/m}^3$ , malic and succinic acids were comparable mutually in different seasons within the concentration range from 20–60  $\text{ng/m}^3$ , glutaric acid was less at an average of 10  $\text{ng/m}^3$ , and the total organic acids in  $\text{PM}_{2.5}$  accounted for 3%–15% of the organic carbon. These organic acids in the atmosphere were mainly formed through secondary photo-reactions, as well as vehicular emissions and coal combustion (Huang et al., 2005). The organic acids which contribute to the acidity in rain have been discussed mainly in terms of their sources and transformation mechanisms. The formic and acetic acid in rainfall ranged from 1.5 to 30 and 1.5 to 20  $\text{mol/L}$ , organic acids originating from natural, anthropogenic sources and chemical transformation of organic matter in aerosol (Yu, 2000; Sigha-Nkamdjou et al., 2003; Kawamura et al., 2007). In addition, soil and ants' release and oceanic aerosol discharge all contributed to organic acids in the atmosphere (Khare et al., 1997; Kesselmeier and Bode, 1997; Li et al., 2000).

A homologous series of  $\alpha,\omega$ -dicarboxylic acids ( $\text{C}_2$ – $\text{C}_{10}$ ),  $\omega$ -oxocarboxylic acids ( $\text{C}_2$ – $\text{C}_9$ ), pyruvic acid, and  $\alpha$ -dicarbonyls ( $\text{C}_2$ – $\text{C}_3$ ) were measured in Greenland ice core samples using capillary gas chromatography and mass spectrometry. Concentration ranges of the total diacids,  $\omega$ -oxoacids, and  $\alpha$ -dicarbonyls were 3.1–32.5  $\text{ng/g}$ , 0.13–2.8  $\text{ng/g}$ , and 0.09–1.7  $\text{ng/g}$ , respectively. Relative abundances of diacid carbon contents in total organic carbon

**Table 1** Sources and Characteristics of LMWOAs from different environmental mediums

Environmental mediums	Organic acid	Contents and contribution to DOC	Sources	References
Soil	Acetic	1–100 mmol/L	Plant residue decomposition	van Hees et al., 1999, 2000, 2001, 2002, 2003, 2005; van Strobel et al., 2001; Li et al., 2003
	Citric	1%–32%	Biotic source	
	Fumaric			
	Lactic			
	Oxalic			
	Shikimic			
	Malic			
	Propionic			
Plant	Lactic	100 $\mu$ mol/L	Root exudation	Strobel, 2001; Sandnes et al., 2005; Wang et al., 2003
	Formic	1.45–3.71 g/g		
	Shikimic			
	Oxalic			
	Malonic			
	Butyric			
Aerosol	Oxalic	350–460 ng/m <sup>3</sup>	Photooxidation	Kerminen et al., 2000; Kawamura et al., 1996
	Malonic		coal combustion	
	Succinic		Oceanic release	
Rain/fogwater	Monocarb	0.33–79 $\mu$ mol/L	Automobile exhaust	Millet et al., 1997; Kawamura and Kaplan, 1984; Sempere and Kawamura, 1996
	Oxylic	0.9%–12.3%	Transformation of organic	
	Dicarboxylic		matter in aerosol	
	Malonic			
Porewaters/sediments	Acetic	157 nmol/g dw	Organic matter	Miller et al., 1979; Smith and Oremland, 1983; Albert et al., 1997; Routh et al., 2001
	Formic	78–688 $\mu$ mol/L	Anaerobic degradation	
	Propionic		Microbes mediation	
	Oxalic		Kerogen pyrolysis	
Sea water	Glyoxylic	58 $\mu$ g/L	Sulfate reducing bacteria photolysis	Albert et al., 1995; Tedetti et al., 2006; Kieber et al., 1989; Kieber et al., 1990
	4-Oxobutyric	0.9%–2.4%		
	Lactic			
	Acetic	11.5–19.3 $\mu$ mol/L		
Ice core	Formic	$\leq$ 10 ng/g	Long distance transport in atmosphere	Lee et al., 2002; Kawamura et al., 2012
	Acetic			
	Pyruvic			
	MSA			
Lake/bog water	Formimic	0.31%–6.4%	Photochemical degradation of organic matter	Brinkmann et al., 2003; Lindell et al., 1995; Wetzel et al., 1995
	Acetic	0.2–6.2 nmol/L		
	Pyruvic			
	Oxalic			
	Propionic			
	Succinic			
	Pyruvic			

(TOC: 0.7–5.7  $\mu$ g C/g) ranged from 0.04% to 1.3%. The good consistency between temporal trends of diacids and the reconstructed air temperature in the Northern Hemisphere can be used to explain past changes in the sea-to-air emissions of marine organic matter, which is subsequently subjected to photochemical oxidation in the atmosphere during long-range transport toward the Greenland ice sheet. Further, it was found that the historical trend of oxalic acid-C/TOC correlates with the reconstructed solar

irradiance since 1600, suggesting that oxalic acid was more efficiently produced in the past atmosphere by photochemical oxidation of biogenic species during enhanced solar radiation periods. Oxalic acid signals were also suggested to be modulated by the frequency of biomass burning inputs (Kawamura et al., 2012).

It has been proposed that oxalic and glyoxylic acid remain mostly in the aerosol particle phase upon droplet evaporation, and that formation of these secondary or-

ganic compounds in clouds depends on photochemical reactions of isoprene, alkenes and aromatics (Carlton et al., 2006). Alternatively, some research demonstrated that oxalic acid originated from the precursors ethene and acetylene (Warneck, 2003). In the cloud particle phase, glyoxylic and oxalic acid accounted for about 75% and 90% (Limbeck et al., 2003). It was proposed that in marine aerosols, a heterogeneous environment, many chromophoric species, including organic matter, aldehydes, ketones, organic fatty acids, polycyclic aromatic hydrocarbons, transition metals and their complexes, nitrate anions, and other organic molecules contribute to the observation of UV-Vis absorption, and DOM is possibly the main contributor of chromophores in aerosols. The most likely major photochemical products in marine aerosol particles are OH radicals, singlet oxygen, and hydrogen peroxide, all of which are transient and reactive species that could potentially have some effects on atmospheric processes in the local environment depending on formation of intermediate volatile organic carbon compounds or biologically available DOM and other inorganic carbon species (Zika and Clark, 2000).

In soil solution, the concentration of organic acids followed the series: propionate > citrate > oxalate, with mean organic acid concentration =  $8.7 \pm 2.3 \mu\text{mol/L}$ . However, citrate and oxalate concentrations typically ranged from 1–100  $\mu\text{mol/L}$  (Westergaard et al., 1998; van Hees et al., 2000); these compounds are believed to be of importance for rhizosphere processes such as mobilization of nutrients (e.g., Fe,  $\text{PO}_4^{3-}$ ) and protection against Al toxicity (Jones, 1998), moreover, they can increase the weathering rate of primary minerals (Lundström and Öhman, 1990) and take part in translocation of Fe and Al (Lundström et al., 2000). These organic acids also have been hypothesized to play a key role in long-term pedogenic processes such as podzolization (van Hees et al., 2000; van Hees and Lundström, 2000). Substrates such as LMWOAs can be expected to form an important source of labile C in the soil and have been shown to be decomposed rapidly by soil microorganisms (Qualls and Haines, 1992; Jones et al., 1996). The balance between production and degradation determines the soil solution concentration of LMWOAs and their efficiency in soil processes. Concentration-dependent biodegradation studies showed that mineralization kinetics conformed well to a single Michaelis-Menten equation with  $V_{\text{max}}$  following the series: oxalate > citrate > propionate (mean  $9.8 \pm 1.0 \text{ nmol/(g}\cdot\text{hr)}$ ). The  $V_{\text{max}}$  declined with soil depth, consistent with the general reduction in microbial activity down the soil profile, and organic acid mineralization constituted about 3%–15% of total soil respiration (van Hees et al., 2003).

It was pointed out that oxalic acid was usually the dominant diacid species ( $14 \pm 12 \text{ ng/m}^3$ ), followed by malonic ( $2.5 \pm 3.3 \text{ ng/m}^3$ ) and succinic acid ( $3.8 \pm 3.5 \text{ ng/m}^3$ ) (Kawamura et al., 1996). These dicarboxylic acids derived

mainly from anthropogenic and biogenic sources, followed by photochemical reactions. In  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  aerosols in Beijing, oxalic acid was also the most abundant carboxylic acid; total concentrations of carboxylic acids averaged 541 and 615  $\text{ng/m}^3$  respectively in these two aerosol particulates. It was suggested that traffic/dust/soil/vegetation emissions, coal/waste/biomass burning, cooking and secondary formation from anthropogenic or natural gas-phase precursors could be the major sources of these acids; meanwhile, contribution from primary sources was higher at rural sites than at urban sites and the contribution of biomass burning was estimated to be 30%–60% for formic and oxalic acids in aerosols (Wang et al., 2007).

In seawater samples, concentrations of homologous series of  $\text{C}_2$ – $\text{C}_9$  dicarboxylic acids as well as ketocarboxylic acids, including glyoxylic and 4-oxobutanoic acids in surface water and deep seawater samples, were 8–40 g/L with glyoxylic acid, being the dominant species, and total dicarboxylic acids and related water-soluble compounds accounted for 0.9%–2.4% DOC in seawater samples (Tedetti et al., 2006). In seawater, LMWOAs may be produced by phytoplankton photorespiration, e.g., excretion by algae and cyanobacteria during carbon assimilation (Steinberg and Bada, 1984; Teiser 1993), photochemical degradation of dissolved organic matter, e.g., from humic substance photooxidation (Kirk, 1994; Zuo and Jones, 1997; Pullin et al., 2004), and microbial degradation of long chain lipids (Kester and Foster, 1963). Other possible sources in seawater include diffusion from surface sediments (especially for oxalic acid), inputs of terrigenous material from rivers, and wet and dry deposition.

LMWOAs consist of microbial metabolites and plant secretions, in which a variety of functional groups are found. LMWOAs typically contain 1–6 carbon atoms and 1–3 carboxyl groups (such as oxalic, citric, malic, malonic, and succinic acid, etc.), and generally constitute only a minor part of the dissolved organic carbon (DOC) in surface earth with the proportion of less than 10% (Strobel, 2001; Xiao et al., 2009). The source of LMWOAs in lakes is illustrated in Fig. 1. And Fig. 1 summarizes the inputs and cycling of LMWOAs in the sunlit upper layer of the lake surface, the photic zone. Possible sources of LMWOAs in lakes include both river inputs and *in situ* production by phytoplankton and bacterioplankton, where simple monomers of degraded plant material may polymerize into more refractory macromolecules. DOM may be formed by the free radical cross-linking of unsaturated lipids released into lake water by algal/microbial action, especially after sunlight radiation in surface water. Upon absorption of sunlight, DOM undergoes a complex series of reactions which produce photodegraded or labile DOM as LMWOAs, which can be accessed by phytoplankton and bacteria for growth. Some portion of DOM is refractory (cannot be further degraded biologically), and is gradually lost to the deep lake. The photodegradation of DOM also

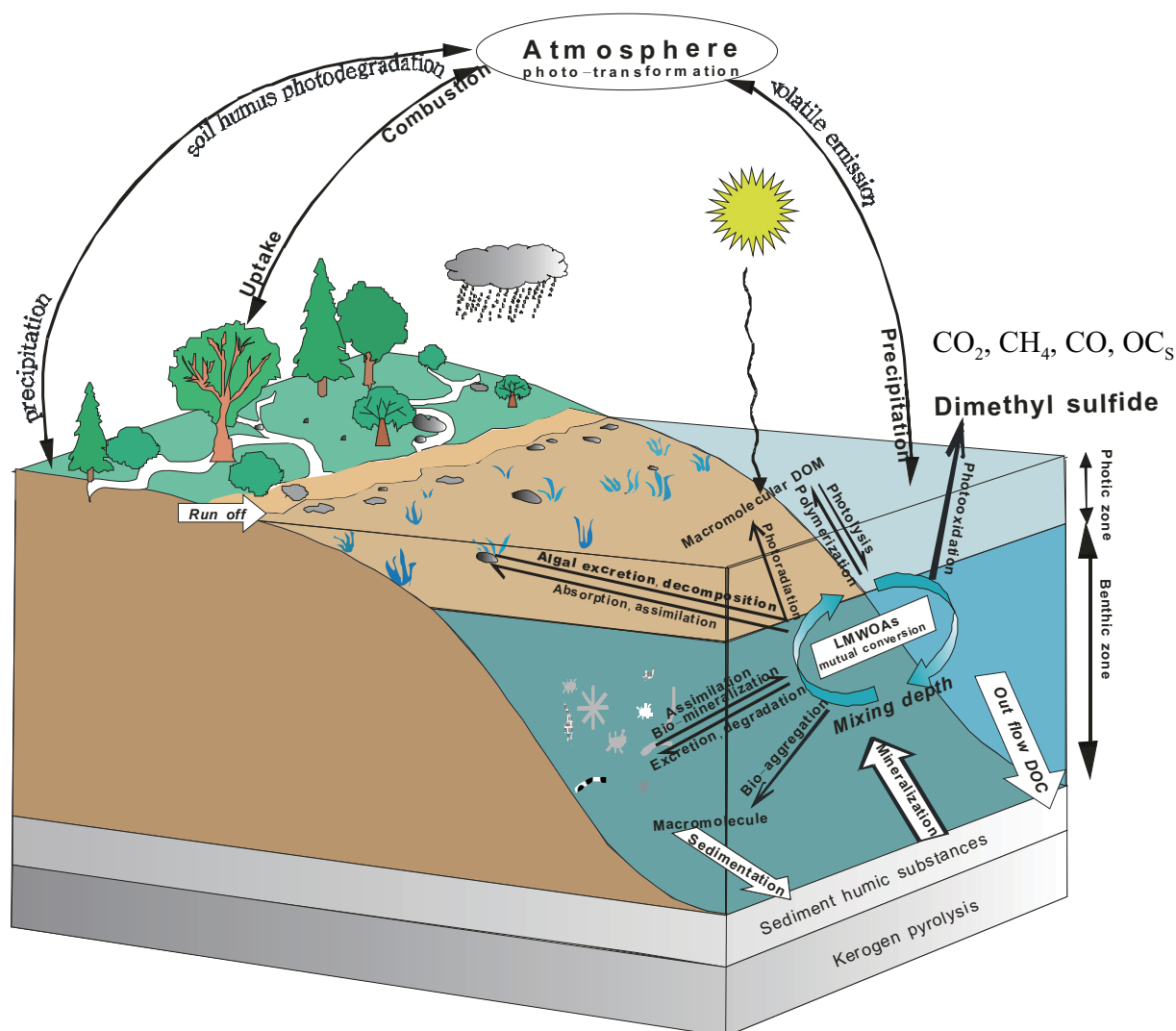


Fig. 1 Schematic diagram showing pathways of LMWOAs mediated by lakes (McKnight and Aiken, 1998).

produces volatile organic carbon compounds, sulfur gases and CO in sufficient quantities, which transfer to the lake boundary layer and participate in further reactions that impact the local atmosphere. Low molecular weight carbon compounds produced by the photodegradation of DOM stimulate the growth, reproduction and proliferation of bacteria. Photochemical and biological processes interact in the further degradation of DOM in the lake environment.

**Figure 1** also demonstrates the hydrological connections between possible sources of aquatic low molecular weight organic acids, e.g., the transport of LMWOAs in shallow groundwater to a stream with dissolved humic substances, which then flows into a lake where additional dissolved organic material enters the water column from sediments. In aquatic ecosystems, the largest pool of organic material in the water column is the dissolved organic material. The production, chemical properties and transformation of dissolved organic materials are intimately linked to the transfer of energy between and within aquatic ecosystems (Hessen et al., 1990). In fact, the

minor LMWOAs mediated during many biogeochemical processes in lakes as the intermediates of vital components and their functions should not be neglected. For example, photodegradation appears to be important in the cycling of biologically refractory DOC in lakes, in which LMWOAs serve as active transient intermediates. This role is likely to become more important in the future as depletion of atmospheric ozone increases the solar ultraviolet light flux.

Photochemical reactions are considered very important in LMWOAs' transformation. Malic, formic, acetic acid were considered mainly to originate from non-biodegradable macromolecular humic substances by photodegradation (Bertilsson and Tranvik, 1998). Formic, acetic, pyruvic, oxalic, malonic, and succinic acids were identified as important degradation products. Their contribution to DOC increased from 0.31% before to 6.4% after 24 hr irradiation and about 33% of the bioavailable photoproducts of DOM were comprised of these LMWOAs. However, not all photo-irradiation was found to be conducive to formation and accumulation of LMWOAs.

Generally, algae, an important source of LMWOAs, were investigated starting in the early part of this century concerning the interactions between LMWOAs and algae (Kisand and Tammert, 2000). Organic acids play a significant role in the development of diagenetic secondary porosity, in the transport of metals by ore-forming solutions, and as precursors to methane production in deeply buried sediments (Chapelle and Bradley, 1996). It is well established that organic acid production in aquatic surface sediments is microbially mediated, with acetogenic (acetate producing) bacteria being an important component of these microbial communities (Drake, 1994). Autotrophic acetogenic bacteria are able to grow using molecular hydrogen (H<sub>2</sub>) and carbon dioxide as sole substrates, producing acetate as a by-product:



In oceanic sedimentary porewaters, the formation of organic acids can occur biochemically, chemically, and thermally from complex precursors, including malonic, formic, acetic and propionic acid, which were observed to range from 0–3453 μmol/L, averaging from a few tens of to thousands of μmol/L (Haggerty and Fisher, 1995). In the Atlantic coastal plain sediment porewaters, formic, acetic and propionic acid were found to form during the mediation of acetogenesis, ranging from 50 μmol/L to 5 mmol/L, revealing that the acetogenic behavior of microbes during LMWOA production was the most important mechanism in low-temperature diagenetic sediments (Chapelle and Bradley, 1996).

## 2 Formation and conversion mechanisms of LMWOAs in different eco-environments

Degradation of organic matter in the sediment is an important part of geochemical cycling in lakes. However, this process is far from being fully understood. In aquatic systems, organic matter is produced in surface water by primary production of phytoplankton, and subsequently passed along the food chain. Matter from the surface fraction is transported to deeper water in the form of sinking dead organisms or fecal pellets of secondary producers. Bacteria degrade most of this sinking organic material in the water column, but the remaining parts reach the sediment, where degradation continues (Rullkötter, 2000). LMWOAs are involved in these degradation processes of organic materials.

Photochemistry in sunlit surface waters is dominated by colored dissolved organic material (CDOM), a predominantly humic substance that constitutes the most important dissolved light-absorbing material in natural waters. Many new studies demonstrated the importance of surface water photochemistry in ecological and biogeochemical cycles,

and CDOM lies at the center of the photochemical cycle and critically impacts the water environment (Blough and Zepp, 1995; Bertilsson and Tranvik 1998; Zika and Clark, 2000; Brinkmann et al. 2003). Biologically available/labile compounds form upon absorption of sunlight, and LMWOAs are typical such components. In one study, where DOM in bog lake water was converted into LMWOAs by simulated solar UV light and these organic acids were also utilized as substrates by bacterioplankton or oxidized into CO<sub>2</sub>, it was suggested that LMWOAs were most abundant where DOM was richest, and that the more hydrophilic moieties of the DOM were preferentially photodegraded while the more hydrophobic ones remained relatively unaffected or were even formed. Kinetic experiments indicated that degradation of LMWOAs occurred simultaneously during irradiation experiments, α-oxygen-substituted LMWOAs being more amenable to these processes. CDOM undergoes photochemical reactions, involving changes as diverse as homolytic and heterolytic cleavages, electron transfer (redox) and energy transfer reactions, which produce reactive species as excited triplet states, solvated electrons, organic cation radicals, OH and superoxide radical as well as organic carbon compounds. These species react in turn with each other, with trace metals such as iron, and with other substances in a complex series of secondary redox and photochemical reactions (Zika and Clark, 2000). In these reactions, dissolved iron was found to act as a reductant according to: Fe(II) + H<sub>2</sub>O<sub>2</sub> ⇒ Fe(III) + OH<sup>-</sup> + OH·, in which OH· actually played the part of oxidant to promote DOM photodegradation and LMWOAs photoformation. Copper played an antagonistic role in the irradiation experiments (Brinkmann et al., 2003). Photodecomposition may proceed either via direct photochemical reactions after absorption of photons by CDOM in Suwannee river or via indirect (sensitized) processes, involving DOM reactions with photochemically generated intermediates such as reactive oxygen species (ROS). If direct photochemical processes dominate, only the chromophoric portion of the DOM will be broken down by this mechanism, and the rates of photodecomposition and product formation will be proportional to the amount of light absorbed by the CDOM. If indirect photochemical processes are important, photo-decomposition of non-chromophoric material is also possible, due to energy transfers after absorption of sunlight by CDOM (Blough and Zepp, 1995). This indirect pathway could proceed with introduction of OH, and its photoformation was as follows: DOM + hν → DOM· + OH·. Bioassays indicated that OH· reactions with humic substances do not result in measurable formation of bioavailable carbon substrates other than the LMW acids, formic, acetic and malic, oxalic acid. They are also not likely to be a significant mechanism of photobleaching except in waters with very high OH· photoformation rates (Goldstone et al., 2002). Some reports also pointed out that the major sources of

$\text{OH}\cdot$  in natural waters are nitrate and nitrite photolysis,  $\text{NO}_3^- + h\nu + \text{H}_2\text{O} \rightarrow \text{NO}_2 + \text{OH}\cdot + \text{OH}^-$ , initiated by UV-B and UV-A (315–400 nm) respectively (Mack and Bolton, 1999), but the seasonal effects of solar radiation and  $\text{NO}_3^-$  on DOM bioavailability depended on its initial chemical composition (Tedetti et al., 2009). In addition to ultraviolet light, visible light also had important functions in speciation transformation and synthesis of LMWOAs. Chlorophyll-*a* and bacteriochlorophyll-*a* act as effective photosensitizers in photosynthesis reactions, and have their maximum absorption in the visible region. The synthesis of malic acid was induced from pyruvic acid and  $\text{HCO}_3^-$  enveloped in visible light with the combined system of a zinc chlorophyll derivative and malic enzyme in water media (Amao and Ishikawa, 2007). LMWOAs excreted by many algae were initially apt to hydrolyze with biological extracellular enzymes. These compounds became non-degradable due to the decrease of enzyme-cleavage sites through aggregation and condensation during photochemical reactions, thereby forming refractory macro-organic matter (Tranvik and Bertilsson, 2001).

Various processes occur in sediments after the deposition of organic material. In the course of degradation, intermediate products such as proteins, amino acids, sugars, fatty acids and other LMWOAs are released to the

environment (Jorgensen, 2000). These can serve either as substrate or as energy source for various organisms. Incorporation into bacterial biomass results in recycling of the molecules, which is often referred to as the ‘microbial loop’. Of course, the bacterial biomass becomes an important component of organic matter itself (Fenchel et al., 1998). Energy is released during the remineralization of organic matter, where organic molecules are oxidized, with  $\text{CO}_2$  being the final product. Similarly, organic nitrogen, phosphorus and sulfur are converted to their inorganic species. Different energy yields result in the subsequent depletion of these species during remineralization, causing zonation in the geochemical composition of the water column or sediment porewaters (Fig. 2). The availability of electron acceptors is determined by their initial concentrations in the bottom water, the rate of organic matter supply, and the degree of mixing in the water column. The final products are hence methane and carbon dioxide. The decreasing remineralization efficiency together with the depletion of easily degradable material causes the rate of degradation to decrease with sediment depth (Kristensen, 2000; Rullkotter, 2000). A refractory fraction of organic matter becomes ultimately buried in the sediment. Moreover, not all of the organic matter present in the sediment seems to be subject to remineralization, rather, an

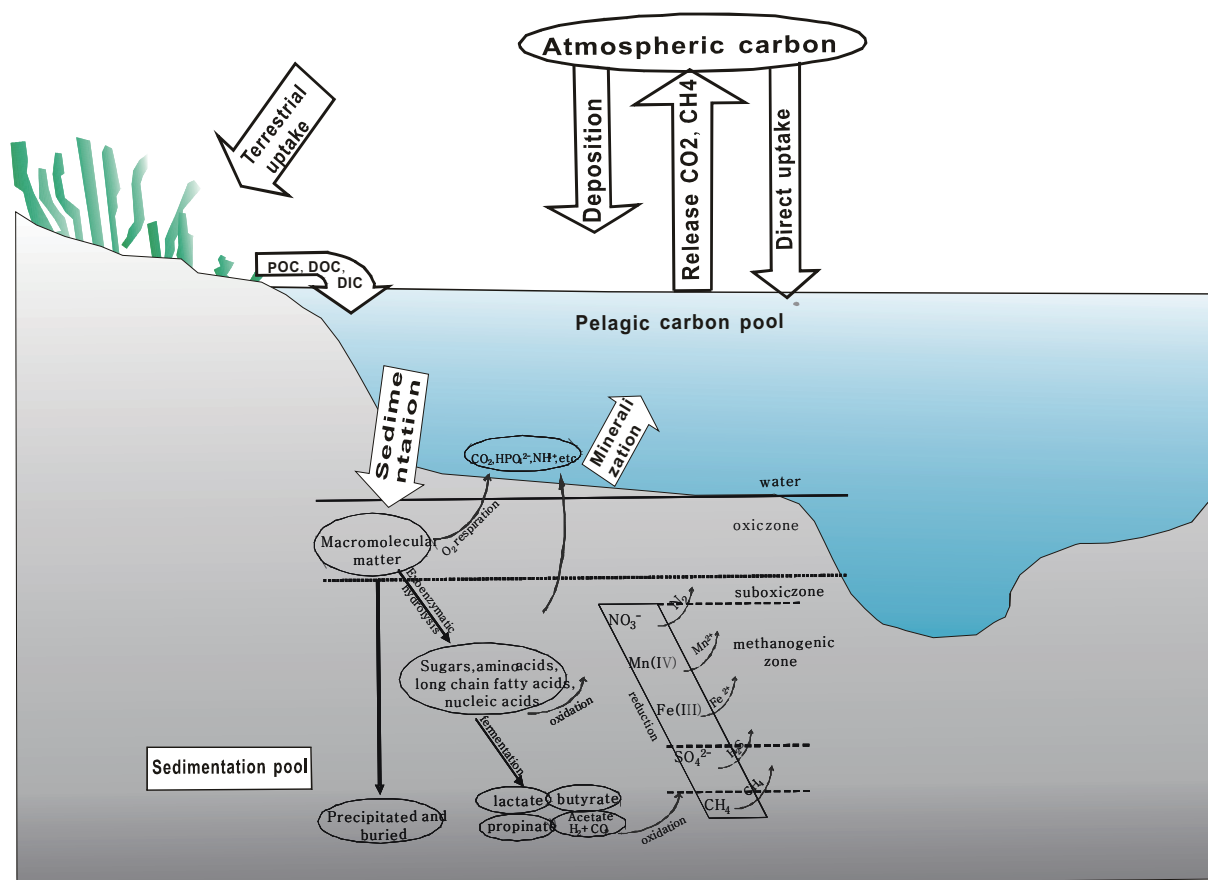
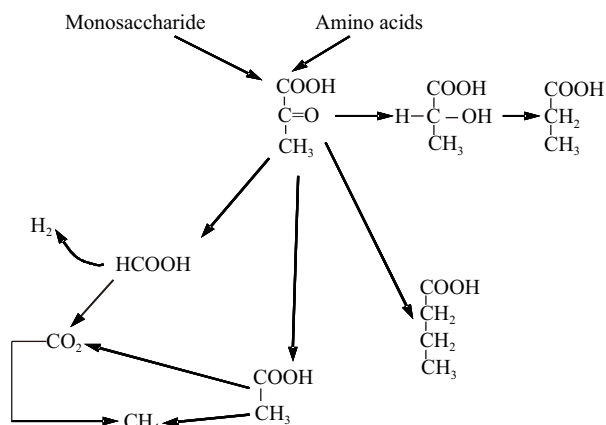


Fig. 2 Formation and transformation pathways of LMWOAs related to geochemical zonations in marine sediments. (From Jorgensen 2000).

increasing part of it becomes incorporated into so-called humic substances (Meckler et al., 2002). Whether in the degradation of organic matter to produce low molecular weight compounds or aggregation of these low molecular weight components, all LMWOAs participate. During the microbial degradation of organic matter, polymer compounds are hydrolyzed into monomers before microbial assimilation (as amino acids, monosaccharides and fatty acids). In the aerobic environment, aerobic bacteria could transform these monomeric substances into  $\text{CO}_2$  completely, but in the anaerobic environment, zymocytes generally convert the monomeric substances into low molecular weight fatty acids (Fenchel and Finlay, 1995). Under anaerobic conditions, organic acids are further mineralized into  $\text{CO}_2$  by denitrifying agents, sulfate reducers, metallic reducing agents and methanogenic bacteria (Thauer et al., 1989).

As shown in Fig. 3, dissolved organic matter, having chemical properties similar to soil humic substances, is degraded by fermentation microorganisms to produce the end products short chain organic acids and alcohol, which successively are decomposed by special organisms such as denitrifying and sulfate-reducing bacteria and methanogens (Stevenson, 1994). In paddy soil, glucose was found to be mainly anaerobically degraded to acetic acid and carbon dioxide, and 50%–80% of the consumed acetic acid originated from glucose degradation (Chidthaisong et al., 1999). During the aerobic microbiodegradation of PAEs (phthalic acid esters), the ester bond was first hydrolyzed to form MMP (monomethyl phthalate) and then PA (phthalic acid). Under the action of dioxygenase and bacteria, PA was degraded to catechin, which could be undergo ring-opening by symmetrical or asymmetrical pathways to form the corresponding organic acids. These organic acids were further transformed into pyruvic, succinic and oxaloacetic acid and then entered into the tricarboxylic acid cycle, and ultimately converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Chang and Zilstra, 1998; Eaton, 2001;

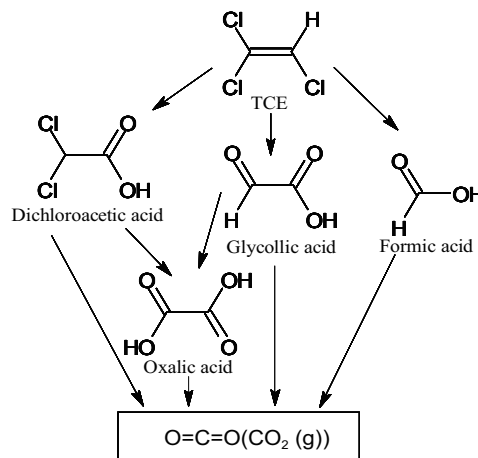


**Fig. 3** Main organic acids and methane produced from degradation of macromolecular organic matter in anaerobic systems (Stevenson and Cole, 1999).

Stinley et al., 2004). Trichloroethylene (TCE) was directly dechlorinated to form LMWOAs under aerobic conditions in pyrite suspension, as shown in Fig. 4.

The large algal excretions which were initially susceptible to hydrolysis by bio-exoenzymes, including abundant LMWOAs such bio-molecules, once they experienced photochemical processes, their enzymatic cleavage sites decreased through aggregation and condensation that they could not be degraded and formed refractory macromolecular organic matter (Tranvik and Bertilsson, 2001). Of the amount of organic matter imported annually, 40%–70% is photo-degraded and transformed into inorganic carbon to be preserved in sediment or released to the atmosphere (Gennings et al., 2001). Alternatively, humic substances are photodegraded into malonic, formic and acetic acid, which are assimilated as substrates by bacterioplankton or oxidized into  $\text{CO}_2$  (Bertilsson and Tranvik, 1998).

The photolysis of CDOM in aerosol produces low molecular weight organic compounds, presumably due to radical and fragmentation reactions arising from the net oxidative flow of electrons from CDOM to  $\text{O}_2$ , roughly expressed as:  ${}^3\text{HS} + {}^3\text{O}_2 \rightarrow {}^1\text{HS} + {}^1\text{O}_2$  (Zika and Clark, 2000). Aqueous-phase oxidation is a potentially important source of organic aerosol and could explain the atmospheric presence of oxalic acid. Methylglyoxal, a water-soluble product of isoprene, oxidizes further in the aqueous phase to pyruvic acid (Staudinger and Roberts, 1996). Aqueous-phase photochemical reactions of pyruvic acid and hydrogen peroxide demonstrated that photochemical oxidation of pyruvic acid yields glyoxylic, oxalic, acetic and formic acids (Carlton et al., 2006). In the proposed mechanism of Lim et al. (2005), isoprene is oxidized to glycolaldehyde, glyoxal and methylglyoxal in the gas phase and further oxidized by  $\text{OH}\cdot$  to form low volatility organic acids such as glyoxylic and oxalic acids. The model for formation of LMWOAs from CDOM and their transformation with reactive species from aerosol is exhibited in Fig. 5 as follows. Upon sunlight irradiation



**Fig. 4** Degradation pathway of trichloroethylene under aerobic conditions in pyrite suspension (Hara, 2012).



and photon absorption, CDOM could be directly homolytically and heterolytically cleaved to form volatile organic compounds, labile DOM and reactive species, or transfer the energy to non-CDOM and transform the stable triplet state  $^3\text{HS}$  into reactive singlet  $^1\text{HS}$  form. Eventually, these singlet substances are apt to undergo a series of complex photochemical reactions to form LMW compounds with the assistance of reactive species ( $e_{\text{aq}}^-$ ,  $^1\text{O}_2$ ,  $\text{O}_2^-$ ,  $\text{RO}_2^+$ ,  $\text{OH}$ , etc.). Hydroxyl radical reacts with pyruvic and acetic acid, but the subsequent formation of oxalic and glyoxylic acids does not begin until  $\text{OH}$  is formed. At the same time, glyoxylic acid production precedes oxalic acid production (Fig. 5).

In the investigation by Jorgensen (2000), it was also pointed that DOM was degraded into various organic acids that could be re-mineralized and eventually decomposed to  $\text{CO}_2$ , or alternatively they were able to be recycled as material and energy sources to enter into microbial loops. Degradation of organic matter in sediments is an important part of the geochemical cycle in lakes. The source, constituents and contents of LMWOAs, the role they play in DOM conversion and their eventual fate still remain to be resolved.

### 3 Environmental effects of LMWOAs

LMWOAs constitute an important part of microbe and plant secretions; their interfacial reactions with minerals interfere with migration and transformation and even bio-availability of metals and pollutants via different mechanisms (Koretsky, 2000; Errecalde and Campbell, 2000). Microbes and algae live for a long time, and the higher their activity, the faster the transportation and cycling of pollutants and nutrients in sediments, indicating that LMWOAs are more reactive. Nutritive elements and pollutants in sediments are always topics of discussion; they are incorporated with LMWOAs, and even substituted by LMWOAs. Their discharge into water or absorption by organisms could pose some potential ecological risks to lake systems. Thus, it is worthwhile to go into more detail on the relationship between the biogeochemical

characteristics of LMWOAs and lake eutrophication, as well as the dynamics of their combination with pollutants, both topics of great significance (An et al., 2011; Fujii et al., 2012).

#### 3.1 Hydrochemistry and the relationship with LMWOA behavior in lakes

The structure, diversity, stability, productivity and bio-substrate production of eco-systems are seriously affected by internal biogeochemical circulation in lakes, which has become a critical research field in the geosciences. Many physical and chemical processes were found to occur in sediments, where lake regional climate and environmental transition information were recorded (Song et al., 2006). Lake eutrophication has occurred and developed as an extreme phenomenon, caused by imbalances between biogeochemical flux and the water-food-web structure, and much chemical disturbance in lakes has resulted from human production activity spanning many years. In lake sediments, especially surface sediments, organic matter content has increased greatly. The physicochemical properties of aquatic ecosystems were adjusted by organic matter mineralization, e.g., oxygen was consumed and nutrients were released in anaerobic systems, influencing the accumulation and intermittent regeneration of P and  $\text{NH}_4^+$  at the sediment-water interface, and even the ebb and flow of life in the water, accelerating lake eutrophication. Mass propagation of phytoplankton with appropriate growing conditions in the surrounding water cause the pH and biochemical oxygen demand to rise, supersaturating dissolved oxygen; these all are signs and symptoms of lake eutrophication. LMWOAs are critical compounds intervening in these physical, chemical and biological processes, which could be used as a proxy for lake evolution.

LMWOAs produced in sediment porewaters were found to decrease pH in the local environment, when mixed with bicarbonates from groundwater from different defined hydrochemical ranges of fen-water (Siegel et al., 2006). Similar circumstances were also found in oceanic sedimentary porewaters, where the acid-base hydrochemistry was significantly impacted by LMWOAs, representing a pathway for transferring reduced-state carbon from sedimentary solids to solution (Haggerty and Fisher, 1995). The surrounding environment was acidified mainly by ionized  $\text{H}^+$  from LMWOAs (Bergelin et al., 2000). Conversely, the pH value in sediments disturbed the organic acids indirectly by influencing the microbial community activity.

The complicated components and structures of organic matter have been hypothesized to play key roles in a number of environmental processes that operate over a whole range of temporal and spatial scales at the eco-system level, particularly the LMW-constituents; they can interfere with polycyclic aromatic hydrocarbons, organochlorine

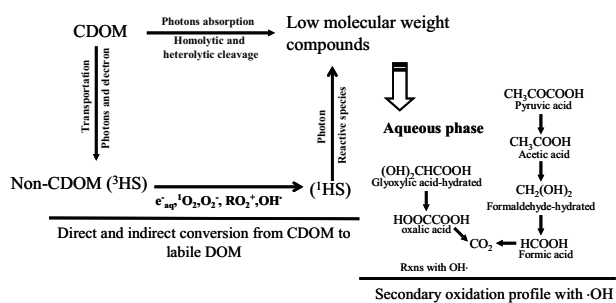


Fig. 5 Formation pathway of LMWOAs and their transformation with reactive species in aerosol (from Carlton et al., 2006).

pesticides, heavy metal distribution and migration, and their adsorption on soil and sediments (Jones et al., 2003). However, this influence is especially strong in water bottom and soil media. With respect to plant and microbial nutrition, LMWOAs have been predicted to play a big role in the solubilization and mobilization of poorly soluble nutrients such as Fe and P by activating and transforming the exchangeable and reducible phases (Fox, 1995; Jones, 1998; Jones et al., 2003; Vyas and Gulati, 2009; Ren et al., 2009). The P release was closely related to structural characteristics of LMWOAs, and it was postulated that the P released by LMWOAs resulted from three mechanisms, competition with phosphate for adsorption sites, changing the surface charge of adsorbents, and direct acidic dissolution, eliminating the adsorption sites for P, e.g., dissolving  $\text{CaCO}_3$ , oxides and hydrated oxides of  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  (Ma and Li, 1994).

LMWOAs only have transient existence, in that their concentration at any time reflects the dynamic balance status of synthesis and degradation of materials by microorganisms. These alterations of hydrochemical conditions caused by LMWOAs were concluded to be related to solar radiation, nutrients and water, allelopathy potential, and pH values (Einhellig, 1996). However, hydrochemical conditions also exerted some influence on LMWOAs. The Ca/Mg cation ratio in waters was found to cause changes in LMWOA accumulation and distribution (Magdziak et al., 2012). Furthermore, plants secreted different LMWOAs to promote P utilization under the stress of P deficiency, e.g., LMWOAs from plant excretion as citric and tartaric acid were 15%–23% and 10 times higher than in P non-deficiency (Ma and Li, 1994), and the P absorption and utilization mechanisms were provoked by the above 3 kinds of pathways. By forming soluble complexes with polyvalent cations from rocks and minerals, organic acids played an important role in dissolution, transport, and concentration of elements on the earth's surface (Jones et al., 2003). Although hydrochemical parameters in both Hongfeng and Dianchi Lakes, including electrical conductivity (EC), alkalinity (ALK), pH, and dissolved oxygen (DO), suggested that LMWOAs also originated from phytoplankton and bacterioplankton in addition to humic materials photolysis (Xiao et al., 2013), the question of how LMWOAs can be used to indicate lake evolution by monitoring hydrochemical components needs to be further investigated.

DOM is the most abundant form of organic matter in lakes, and its influence on physical, chemical and biological processes in the oceanic carbon cycle is widely recognized. Humic materials, a heterogeneous mixture of complex high molecular weight biopolymers, constitute a significant fraction of DOM. CDOM refers specifically to the fraction of DOM that absorbs light and hence imparts color to the water. Degradation of organic matter pulls down the water pH value, likewise, organic acids produced

during photo-degradation of organic matter have the same effect. In addition, this photochemical process also causes other hydrochemical alterations in water. Ultraviolet radiation is widely known as an energy source for chemical reactions in nature, providing a pathway for the degradation of organic compounds. Aquatic organic material is composed in part of light-absorbing polymers that are resistant to microbial assimilation and breakdown. However, this part of CDOM had further ecological significance as the main absorber of UV-A and UV-B radiation in natural waters to produce nutrients and carbon substrates for microorganisms, shielding aquatic organisms from sunlight's harmful effects (Williamson, 1995). The significant carbon flux from photomineralization of CDOM to dissolved inorganic carbon (DIC) may occupy an important position in the global carbon cycle, increase the penetration depth of sunlight into lake water and promote photo-oxidation of DOM (Miller and Zepp, 1995). Upon absorption of sunlight, CDOM undergoes a complex series of reactions that produce labile DOM (biologically available), and that these species or compounds in turn experience a series of reactions to affect the biota of the water environment and the atmospheric composition over the hydrosphere.

### 3.2 Interactions between LMWOAs and organisms

The tricarboxylic acid cycle is the predominant metabolic pathway in aerobic organisms. As illustrated in **Fig. 6**, this cycle is the metabolic nexus of three main forms of organic matter, saccharides, lipids and amino acids, which connects the metabolic steps of these nutrient substances. It is shown that the tricarboxylic acid cycle is the third step of the four-stage saccharide metabolism process that includes glycolysis, oxidative decarboxylation of pyruvate, the citric acid cycle, and the electron transport chain (respiratory chain). Before these rather large molecules can enter the TCA cycle they must be degraded into a two-carbon compound called acetyl coenzyme A, and once fed into the TCA cycle, acetyl CoA is converted into carbon dioxide and energy (**Fig. 6**). In this metabolic pathway, pyruvic acid, other LMW fatty acids and amino acids are the most critical precursors for synthesis of acetyl-CoA, which plays the role of primer to promote Krebs's cycle. In addition to providing the energy for life systems, the citric acid cycle supplies raw materials for bio-synthesis, and is therefore functional even in cells performing fermentation. Therefore, LMWOAs are not only indispensable participants in organic matter metabolism or Krebs's cycle, but also the elicitor of this cycle. LMWOAs play an important role in TCA, promoting vigorous life activities to go round and round.

Since burial of organic carbon in continental margin sediments provides a major sink for reduced organic carbon, the extent to which organic matter is ultimately buried in sediments is largely dependent on the activities of the heterotrophic microbial community (Arnosti and Holmer,

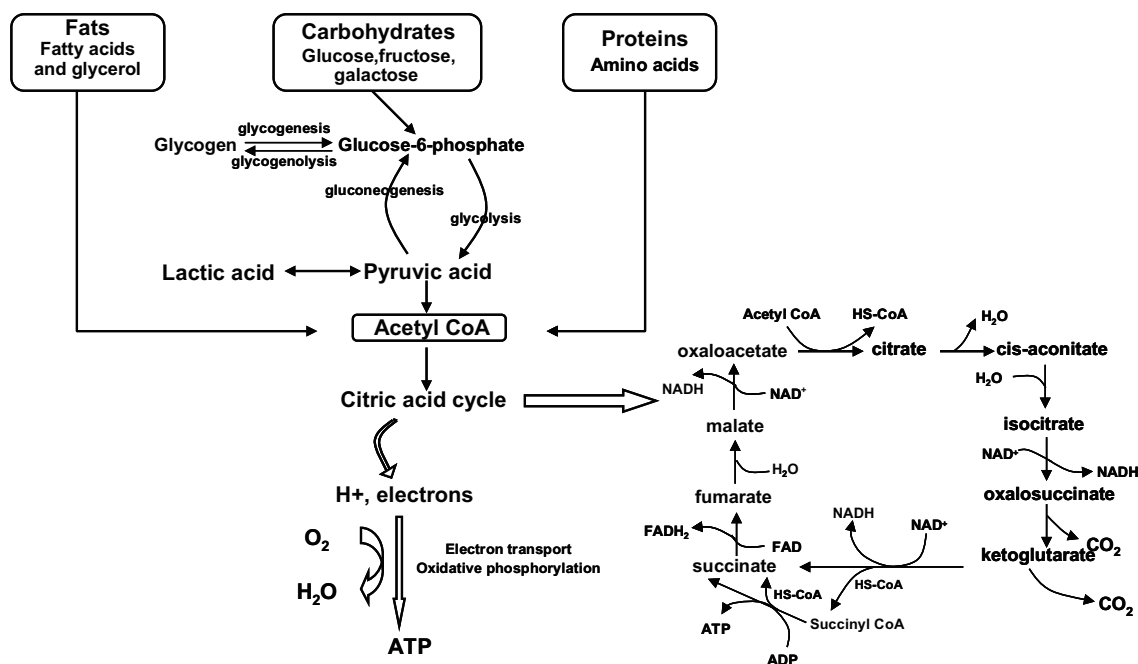


Fig. 6 Significance of dissolved organic matter glycolysis, LMWOAs production and cycle, and energy transport for life activities.

2003). Because oxygen penetration is generally limited to the upper millimeters or centimeters of continental margin sediments, the activities of anaerobic heterotrophic microbial communities are particularly important (Canfield et al., 1993). Via the microbial food chain, complex organic substrates are remineralized in a series of steps. High molecular weight dissolved organic carbon is enzymatically hydrolyzed to lower molecular weight substrates. These LMW substrates are transformed into fermentation products such as volatile fatty acids and amino acids, which are ultimately remineralized to CO<sub>2</sub> (Alperin et al., 1994; Jorgensen, 2000). These can be re-mineralized into CO<sub>2</sub> and serve either as substrate or as energy source for various organisms to support their activity. Microbes have been found to be important mediators in various source and transformation pathways of LMWOAs, however, different microbial communities performed different functions in producing and consuming LMWOAs. Taking methane-producing bacteria for example, PAEs were converted to acetate and H<sub>2</sub> by the microbial fermentation community first, and then acetate was successively transformed into methane and bicarbonate, and subsequently bicarbonate was deoxygenated to methane by *Hydrogenotrophic methanogenes* (Kleerebezem et al., 1999). Thus, different production and consumption of LMWOAs during this biogeochemical process facilitated various microbes and some kinds of organo-pollutant degradation. LMWOAs also reduced the oxidation-reduction potential in sediments to promote the anaerobic bacteria activity and accelerated microbe growth indirectly by dissolving and expelling Fe, Al, and Mn hydrated oxides (Zhao et al., 2002). Alterations would be particularly important when study-

ing LMWOAs participating in biological processes as substrates/exudates, which were adsorbed to surfaces and acted as electron donors/acceptors in redox processes. On the other hand, microbes could excrete and be decomposed to LMWOAs during their lifecycle (Bertilsson and Allard, 1996; Moran and Zepp, 1997; Bertilsson and Tranvik, 1998). In the model describing the temporal and spatial dynamics of LMWOAs, their microbial degradation was in quantitative terms the main process regulating solution concentrations. The amount of basal respiration that could be attributable to the microbial turnover of organic acids was on average 19% ± 22% of the basal CO<sub>2</sub> production across all sites and horizons for citrate and 7% ± 7% for oxalate (Kostaka et al., 2002). Generally, organic acids and organisms supplemented each other, but formic acid showed toxicity toward organisms and inhibited their growth (Hara, 2012). In addition, under suitable environmental conditions, organic acids may accumulate to poison plant growth (Kpombekou and Tabatabai, 2003). A large amount of LMWOAs such as phenolic and fatty acids inhibited the normal growth of plants and algae, acting as allelochemicals to change microflora, resulting in imbalance in the ratio of intercellular and extracellular enzymes and alteration of enzymatic configurations, and eventually inflicted adverse impacts on the physiological and ecological environment (Azmi et al., 2000).

In the whole lacustrine ecosystem, all kinds of organic acid behavior are intermediated by microbial activity to a great degree. Our previous research only made a preliminary assessment of this influencing mechanism using a molecular fluorescence method. Algae is an important provenance of organic matter in the lacustrine environ-

ment (Talbot and Livingstone, 1989; Henry and Anderson, 1992), as well as a critical source of organic acids, and the interactions between organic acids and algae have been discussed by researchers since the 1960s (Fogg, 1963; Maksimova and Pimenova, 1969; Juttner and Matuschek, 1978; Sakugaw et al., 1985; Kisand and Tammert, 2000). Degradation of organic matter by various microbes and exoenzymes not only influences the early diagenesis of lake sediments, but also the other organisms' distribution and activities in the deeper sedimentary environment. Overall, LMWOAs are accumulated and consumed along with various microbial respiration processes (Madsen and Ghiorse, 1993; Evans, 1998; Wellsbury and Parkes, 1995; van HEES et al., 2005). The production and consumption of acetic acid in deep sea sediments of the Atlantic Ocean were investigated (Jones et al., 1989), Liu and Suflita (1993) further confirmed the existence of acetic acid bacteria. The function of LMWOAs in microbial processes and their mineralization in soil and oceanic sediments increasingly attracted researchers' attention (Lundstrom, 1993; Fischer and Kuzyakov, 2010). Routh et al. (2001) investigated the dynamic processes of acetic and propionic acid, which were affected seriously by sulfate-reducing bacteria in the Texas Yegua aquifer sediment system (Routh et al., 2001). In order to discern bacterial categories and determine the activation mechanism of microorganisms, the conventional method is microscope counting and calculation of the dominant community. However, we can now use DNA extraction and PCR amplification to discern microbial communities and quantities. The interactions between microbes and LMWOAs as investigated by molecular biology techniques will be considered a major innovation in order to make accurate and swift judgments concerning the dominant species and quantities. Then, this strengthening of the research will help us elevate our understanding about the LMWOAs and organisms.

### 3.3 Influence of LMWOAs on heavy metals

LMWOAs represent important constituents of DOM that increase the bioavailability of heavy metals so that they are assimilated and transferred easily in the tissues of plants and microbes (Ahumada et al., 2001; Oburger et al., 2009). Variations in charge were found to impact Al adsorption and desorption on soils, which depended on the contents of iron oxides (Xu et al., 2005). Heavy metals are critical pollutants in soil, and their bioavailability and bio-toxicity are alleviated or enhanced by adsorption or desorption, in which the main mechanisms involve chelating or complexing with LMWOAs. Many researchers have reported on the effects of LMWOAs on adsorption of heavy metals on soils and minerals, moreover, LMWOAs serve dual functions for heavy metals attached to these two mediums. In different studies, the same LMWOAs imposed different effects on the same heavy metals; citrate and amino acids exhibited obvious inhibition of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  adsorption

on oxides and clay minerals in McBride (1989), whereas, these two LMWOAs promoted the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  on the surface of oxides and clay minerals in Elloit and Huang (1980). Similar to McBride (1989), it was also proposed that the adsorption of  $\text{Cd}^{2+}$  on  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  oxides, montmorillonite, and kaolinite was inhibited by citrate (Chubin and Steet, 1981). It is precisely because of such different mechanisms that LMWOAs acting on heavy metals and metal elements performed differently as well when integrated into microbial organisms. Citric acid enhanced the bio-adsorption of *Pseudomonas aeruginosa* for Cr and *Bacillus thuringiensis* for Cu, while it weakened that of *Citrobacter* for Pb, Cd, Zn (Puranik and Paknikar, 1999). Whether inhibition or promotion, the behavior was mainly dependent on the varieties and concentrations of LMWOAs and heavy metals, sediment type and surrounding conditions. The environmental conditions were altered by pH in significantly different ways, including charge on the sediment surface, the form of organic ligand, the fate of heavy metals in aqueous phase, and the dissolution of Fe, Al oxides and hydrated oxides by LMWOAs (Gao et al., 2003).

Cd in soils has attracted researchers' wide concern whether in agriculture or the environment because of its easy bio-assimilation and high toxicity. Cd pollution has increasingly occurred and threatened human health (Wang et al., 2013). LMWOAs were found to take part in the transfer of mineral elements, the uptake of metal and nutrient ions, and oxidation processes (Oburger et al., 2009), and could be utilized as the complexing agent in Cd and Pb mixtures (Dytrtová et al., 2009), and the structural configuration of the Cd-oxalate complex was confirmed by a combination of electrochemical techniques and mass spectrometry (Dytrtová et al., 2011). In research on the dynamics of Cd adsorption, it was shown that the concentration of tartrate influenced Cd strongly, with 0.3 and 0.7 mmol/L as the boundary concentrations to decide secondary and competitive adsorption. This indicated that the concentration of LMWOAs and soil properties such as clay content, charge character (constant charge and variable charge) and pH values were important factors influencing Cd adsorption (Hu et al., 2007). The speciation of heavy metals was strongly affected by LMWOAs, such that spiked acetate increased the quantity of Cu binding to SOM (Ahumada et al., 2001). Desorption processes of Cu from different soils were also investigated by Elkhatib et al. (2007), and it was suggested that desorption dynamics involving Cu complexation with LMWOAs fitted well to Elovich, Freundlich and parabolic equations, whereas the desorption capability of LMWOAs for Cu and rates conformed to the order citrate > malate > succinate. The desorption in sandy soil was more significant than in calcareous and clay soils.

Based on the above knowledge, LMWOAs excreted from microbes have been used to repair metal-polluted

environmental mediums. Citric acid excreted from *Pseudomonas aeruginosa* was used to bind to and expel heavy metals from soils to achieve the goal of ecological remediation (Thomas et al., 2000). Increasing the bioavailability for heavy metals in freshwater algae and vertebrates was achieved by absorbing LMWOA-ligands (van Ginneken et al., 1999; Errecalde and Campbell, 2000). Although LMWOAs influenced metals behaviors directly, some side effects were also brought about simultaneously. Their complexation with Cd reduced the respiration rate of soils (Renella et al., 2004). Cu, Cd and Zn combined with citric ligand were assimilated by organisms with the rates similar to free citric acid, whereas, distinct from free acid, these complexes and chelates could not be metabolized completely in cytoplasm (Brynhildsen and Allard, 1994). Therefore, the bioavailability of heavy metals might be modulated once LMWOAs participate in the process, likewise, the interaction mechanism between LMWOAs and organisms is also changed due to the presence of heavy metals. However, the direct bio-assimilation of LMWOAs was positive for organisms and that of complexes was potentially negative to the microbial loop. Heavy metal pollution is always a focus issue in environmental concerns, and the mechanism of their combination with LMWOAs has primarily been investigated to restrict pollution in soil. A new concept in this research is to use capillary zone electrophoresis to analyze the morphology of heavy metal complexes with LMWOAs and detect charge distribution on the soil coalition surface; this would be a new highlight in environmental effects research of LMWOAs in lake sediments and conducive to the acknowledge of heavy metals' potential ecological risk and the issues' resolution.

### 3.4 Dynamic mechanisms of interactions between organic acids and organo-pollutants

The normal growth of animals and plants is disturbed by various organo-pollutants entering into the environment that might interfere with or destroy the eco-balance (Halerc et al., 2006). In the experiments of White and Kottler (2002) and White et al. (2003), it was pointed out that 7 LMWOAs increased the amount of *p, p'*-DDE desorption from soils significantly, and the part desorbed with LMWOAs was higher by 19%–80% than that without LMWOAs. Luo et al. (2006) reported that oxalic acid greatly increased the desorption amount of *p, p'*-DDT from soils, and the increase fluctuated from 11%–54% for different soils. The soil structure was partly dissolved as an organic mineral combination when low molecular weight organic carbon was spiked, resulting in organic carbon and metallic ions being released, and an increase in the quantity of desorbed pollutants. A mechanism for organo-pollutants' release by LMWOAs was presented in Zhao et al. (2011); it was described as mineral and organic matter dissolution, complexation and chelation with pollutants to

release pollutants. Naphthalene can be dissolved by different LMWOAs, and it was also found that the solubility of naphthalene increased with the carbon chain length of LMWOAs, e.g., naphthalene was more susceptible to dissolution by butyric acid than by formic acid, and the standard migration free energy from water phase to water-acid phase for naphthalene was higher in formic acid than in propionic or butyric acid (Zhou et al., 2005). Phenanthrene and pyrene desorbed more and more with increasing LMWOAs in the follow-up surveys because these factors and DOM spiking decreased their allocation in the solid phase (Gao et al., 2010). It was found that LMWOAs are essential to improve the transferability of these materials, but the ecological risks were also promoted in soil by reducing the toxicity of pollutants to organisms utilizing phytoremediation of LMWOAs (Nwoko, 2010).

LMWOAs are actively involved in elements' adsorption, fixation, chemical oxidation and biodegradation on the earth's surface (van Hees et al., 2003, 2005), but few studies on LMWOAs in aquatic systems were carried out with respect to these aspects, especially in lakes (Bertilsson and Tranvik, 1998, 2000; Jonsson et al., 2007). Studies on LMWOAs in surface freshwater and sediments are currently relatively rare, especially in Chinese lakes whether in the aqueous phase or deposited sediment, instead being mainly focused on aerosol, rainwater, ice cores, and soils. LMWOAs are one of the chemical constituents of DOM, but their contributions and proportions in DOM are not concretely well known. Various HPLC technologies have been adopted to separate fatty acids in soil and waste extract solutions, but this kind of technology requires complicated DNPH derivation, ultra-filtration and cation exchange strategies (van Hees et al., 1999). Although a separation column mated with HPLC gave good selectivity, obvious peak tailing was still observed (Hue et al., 1986; Pohlman and McColl, 1988). CZE and GC are detection techniques for organic acids as well (Szmigielska et al., 1997; Zhou and Mopper, 1997), but the detection limit is not appropriate for micro-organic acid detection. The newest dynamic headspace-needle trap extraction method was used for separating formic and acetic acid, which were detected by GC, and this method had an improved detection limit, whereas, once the sample amount merely decreased slightly, the detection precision and stability fell (Lou et al., 2008; Lee et al., 2012). Based on the above detection limitations, ion chromatography is usually employed to identify the LMWOAs in lake overlying water such as in Hongfeng and Dianchi Lake, and to detect their concentrations and analyze their diurnal variations in summer and distribution profiles. The photochemical and biological behaviors and related environmental effects were investigated, and some valuable research achievements were also obtained, providing the theoretical foundation and justification for continuing investigation of LMWOAs. Studies on spatiotemporal variations of

LMWOAs in these two lakes showed that sunlight scattering on the lake surface was conducive to production and accumulation of LMWOAs, as well as physico-chemical and biological processes as terrestrial sources, thermal stratification, photochemical reactions and photo-aggregation, planktonic mineralization and assimilation, algal release all contributed to variation in LMWOAs distributions (Xiao et al., 2013). The six lakes Sihailongwan, Qinghai, Bosten, Erhai, Dianchi, and Changhai in southern and eastern China were preliminarily investigated, and the results suggested that total LMWOAs in sediment porewaters were as high as 91.96  $\mu\text{mol/L}$  and the ratios in DOC were higher than 10% (Xiao et al., 2009). It was also revealed that intense activity from microbes in surface sediments caused LMWOAs to experience cumulation-consumption-nonbioavailability stage in sediment profiles. The intricacy of microbial mediation in different lake environments led to significant differences in LMWOAs on the spatial scale. Low LMWOAs in surface water represented the strong reactive part of DOM. The research results in disparate lakes indicated discrepancies of LMWOA sources in sediment early diagenesis and microbial activities in vertical and lateral scales. There have been many studies on combinations of LMWOAs and organo-pollutants in soils, while the related progress of research in sediments is rarely discussed. In order to deepen our knowledge on the ecological risk of pollutants in sediments, it is necessary to investigate the dynamic processes of LMWOA behaviors. The next stage of research is mainly designed to detect the organo-pollutants by gas chromatography, discuss the effects of LMWOAs on these pollutants from physico-chemical conditions of sediments, concentrations of spiking substances and reaction time, and the transfer rates of pollutants from solid to aqueous phase. These aspects will be researched in a deep-going way.

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## 4 Discussion and conclusions

### 4.1 Insufficiency of LMWOAs research in the surface water environment and related investigation orientation

This coupling between photodegradation of CDOM and uptake of low molecular weight products by bacteria represents an important route for the loss of CDOM in lakes and an important component of the global carbon cycle. Likewise, organic matter degradation in sediments is an important remineralization of the geochemical cycle in lakes. However, the sources, constituents and concentrations of LMWOAs need to be investigated in depth, and the roles they play in the transformation of macromolecular organic matter and their eventual fate are relatively rarely known.

Seasonal and profile analysis should use hydrochemical data as the basis to improve the discussion and understanding of source, conversion and influencing factors (mainly referring to biotic factors), which would be significant for the elucidation of the evolution of lake water quality, even eutrophication. How do micro-organisms deal with organic acids in lakes and to what extent? These problems remain to be solved with new strategies. Sediment organic matter is the natural geological adsorbent for heavy metals and hydrophobic organo-pollutants (Xing, 2001), and a new scientific management framework and decision-making system should be created, containing eutrophic ecological models and eco-risk assessment methods and indexes. How organic acids, the crucial ingredients of DOM, react with pollutants is important both from the aspect of their biogeochemical dynamic cycles for investigating lake pollution and assessing eco-risks, conducive to scientific management of lake systems. Moreover, the interactions between organic acids and pollutants have been hotly debated recently, but the related research on sediments of lake ecosystems provides no more than a blank slate having vast and long-term research prospects in the future.

LMWOAs were found to be able to change the physico-chemical characteristics in microenvironments, such as pH values, oxidation reduction potential, nutrient speciation, integration of heavy metals and organo-pollutants through chelation and precipitation, alteration of the composition and activity of the microbial community and behavior of pollutants by excretion, decrease of the bioavailability of toxic pollutants, and prevention of the ecological hazards of ground-surface conditions, reducing ecological risks (Strobel, 2001; Marschner et al., 2004). Various environmental entities in the surface system contact and interact with each other, whereas LMWOAs are considered to be the bridge connecting all elements in this complicated habitat. Further understanding the biogeochemical characteristics and environmental effects in the surface environment will compensate for knowledge deficits on LMWOAs, help construct a theoretical framework for organic matter degradation and ecological effects, and provide basic data for ecological risk assessment, to establish the methodology for polluted water restoration and governance. Sources, transformation pathways of LMWOAs and the correlative environmental effects are summarized comprehensively in **Fig. 7**, which clearly manifests their relationships with bacterioplankton, and phytoplankton aquatic biota, and exhibits the positive and negative influence of each on LMWOAs, as well as organic and inorganic pollutants and atmospheric media impact. The figure charts the next tasks for LMWOAs in lakes, including analysis and judgment of sources by synthesis, to sketch the contours between them and water quality evolution by detection of nutrients, and development of a dynamic process model by monitoring the adsorption/desorption of pollutants from sediment.

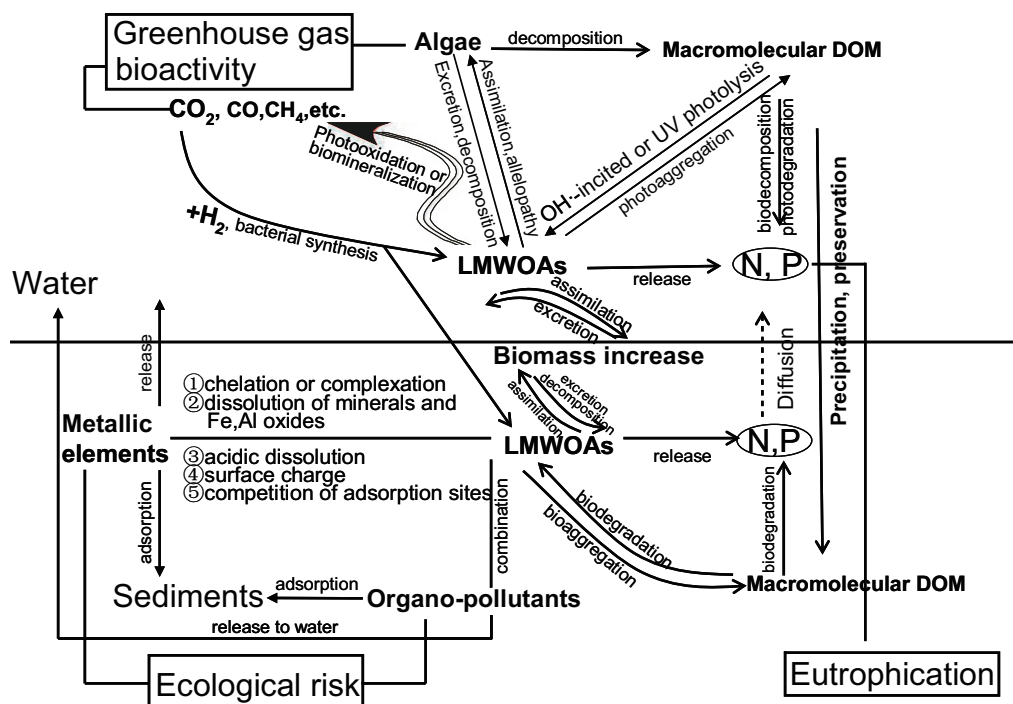


Fig. 7 Conceptual model of characteristic behaviors of LMWOAs and environmental effects in lake ecosystems.

In fact, all compartments of the earth's system are intimately connected with each other, and the critical stratagem for us is to grasp the biogeochemical characteristics of LMWOAs in lakes, and deeply investigate correlative environmental effects, analyze their main sources, fate and influencing factors on these vital and physiological processes, discuss LMWOAs' influence on hydrochemistry and bio-behavior in lake water, and elucidate the key roles from LMWOAs on pollutants' geochemical processes, providing a theoretical basis for lake environmental evolution progression and powerful evidence for lake ecological risk evaluation. Organic matter is retained within estuaries prior to its abouchement into coastal waters or lake waters, and during this retention period, terrestrial organic matter may be altered by biotic and abiotic processes, involving: microbial respiration, photooxidation and flocculation or scavenging with subsequent removal to estuary deposit. In addition to the direct input and transformation of terrigenous materials, high rates of primary production are typical of many rivers and estuaries, contributing to dissolved and particulate forms of organic matter. Since the mechanism of DOM formation is likely to affect its chemical composition and reactivity, DOM in river may very well behave differently from DOM produced in the surface lake water. Organic matter in river has been studied, whereas, as the critical intermediate life material of Krebs' cycle, LMWOAs in rivers have not been investigated (Countway et al., 2007; Mostofa et al., 2007). The biogeochemical behaviors of LMWOAs are connected in series in whole lake systems, and the characteristics and dynamic processes are significant for understanding

biogeochemical cycles of organic matter in lakes and its ecological effects, and also conducive to constructing an eco-model for organic matter's growth and decline, which would be helpful to rectify, repair and manage the lakes suffering from eutrophication. Consequently this will guarantee drinking water safety, national welfare and people's livelihood, and facilitate the sustainable development of human health and economic stability.

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#### REFERENCES

- Ahumada, I., Mendoza, J., Escudero, P., Ascar, L., 2001. Effect of acetate, citrate, and lactate incorporation on distribution of cadmium and copper chemical forms in soil. *Commun. Soil Sci. Plant. Anal.* 32(5-6), 771–785.
- Albert, D.B., Martens, C.S., 1997. Determination of low molecular weight organic acid concentrations in seawater and pore-water samples via HPLC. *Mar. Chem.* 56(1-2), 27–37.
- Albert, D.B., Taylor, C., Martens, C.S., 1995. Sulfate reduction rates and Low molecular weight fatty acids concentrations in the water column and surficial sediments of the Black Sea. *Deep-Sea Res. PT. I.* 42(7), 1239–1260.

- Alperin, M.J., Albert, D.B., Martens, C.S., 1994. Seasonal variations in production and consumption rates of dissolved organic carbon in an organic-rich coastal sediment. *Geochim. Cosmochim. Acta* 58(22), 4909–4930.
- Amao, Y., Ishikawa, M., 2007. Visible light and enzymatic induced synthesis of malic acid from pyruvic acid and  $\text{HCO}_3^-$  with the combination systems of zinc chlorophyll derivative and malic enzyme in water media. *Catal. Comm.* 8(3), 523–526.
- An, C.J., Huang, G.H., Wei, J., Yu, H., 2011. Effect of short-chain organic acids on the enhanced desorption of phenanthrene by rhamnolipid biosurfactant in soil-water environment. *Water Res.* 45(17), 5501–5510.
- Arnosti, C., Holmer, M., 2003. Carbon cycling in a continental margin sediment: contrasts between organic matter characteristics and remineralization rates and pathways. *Estuar. Coast. Shelf Sci.* 58(1), 197–208.
- Azmi, A.M., Abdullah, M.Z., Fujii, Y., 2000. Exploratory study on allelopathic effect of selected Malaysian rice varieties and rice field weed species. *J. Trop. Agric. Food Sci.* 28(1), 39–54.
- Berdie, L., Grimalt, J.O., Gjessing, E.T., 1995. Combined fatty acids and amino acids in the dissolved + colloidal fractions of the waters from a dystrophic lake. *Org. Geochem.* 23(4), 343–353.
- Bergelin, A., van Hees, P.A.W., Wahlberg, O., Lundström, U.S., 2000. The acid-base properties of high and low molecular weight organic acids in soil solutions of podzolic soils. *Geoderma* 94(2–4), 223–235.
- Bertilsson, S., Allard, B., 1996. Sequential photochemical and microbial degradation of refractory dissolved organic matter in a humic fresh water system. *Arch. Hydrobiol. Spec. Issues Adv. Limnol.* 48, 133–141.
- Bertilsson, S., Tranvik, L., 2000. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* 45(4), 753–762.
- Bertilsson, S., Tranvik, L.J., 1998. Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton. *Limnol. Oceanogr.* 43(5), 885–895.
- Blough, N.V., Zepp, R.G., 1995. Reactive oxygen species in natural waters. In: Foote, C.S., Valentine, J.S., (Eds.), *Active Oxygen in Chemistry*. Chapman and Hall, New York, pp. 280–333.
- Brinkmann, T., Horsch, P., Sartorius, D., Frimmel, F.H., 2003. Photoformation of low-molecular-weight organic acids from brown water dissolved organic matter. *Environ. Sci. Technol.* 37(18), 4190–4198.
- Brynhildsen, L., Allard, B., 1994. Influence of metal complexation on the metabolism of citrate by *Klebsiella oxytoca*. *BioMetals* 7(2), 163–169.
- Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. *Geochim. Cosmochim. Acta* 57(16), 3867–3883.
- Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., Seitzinger, S., 2006. Link between isoprene and secondary organic aerosol: pyruvic acid oxidation yields low volatility organic acids in clouds. *Geophys. Res. Lett.* 33(6), L06822. DOI:10.1029/2005GL025374
- Chang, H.K., Zilstra, G.J., 1998. Novel organization of the genes for phthalate degradation from burkholderia cepacia DBOL. *J. Bacteriol.* 180(24), 6529–6537.
- Chapelle, F.H., Bradley, P.M., 1996. Microbial acetogenesis as a source of organic acids in ancient Atlantic Coastal Plain sediments. *Geology* 24(10), 925–928.
- Chidthaisong, A., Rosenstock, B., Conrad, R., 1999. Measurement of monosaccharides and conversion of glucose to acetate in anoxic rice field soil. *Appl. Environ. Microbiol.* 65(6), 2350–2355.
- Chubin, K.G., Steet, J.J., 1981. Adsorption of Cd on soil constituents in the presence of complexity ligands. *J. Environ. Qual.* 10, 225–228.
- Countway, R.E., Canuel, E.A., Dickhut, R.M., 2007. Sources of particulate organic matter in surface waters of the York River, VA estuary. *Org. Geochem.* 38(3), 365–379.
- Cowie, G.L., Hedges, J.L., 1994. Biochemical indicators of diagenetic alteration in natural organic-matter mixtures. *Nature* 369(6478), 304–307.
- Drake, H.L., 1994. Introduction to acetogenesis. In: Drake, H.L., (Ed.), *Acetogenesis*. Chapman and Hall, New York, pp. 3–62.
- Drozd, J., Gonet, S.S., Senesi, N., Weber, J., 1997. The Role of Humic Substances in the Ecosystems and in Environmental Protection. In *Proceedings of the 8th Meeting of the International Humic Substances Society*, Wroclaw, pp. 1002.
- Dytrtová, J.J., Jakl, M., Šestáková, I., Zins, E.L., Schroder, D., Navrátil, T.A., 2011. New approach to study cadmium complexes with oxalic acid in soil solution. *Anal. Chim. Acta* 693(1–2), 100–105.
- Dytrtová, J.J., Šestáková, I., Jakl, M., Navrátil, T., 2009. Electrochemical detection of cadmium and lead complexes with low molecular weight organic acids. *Electroanalysis* 21(3–5), 573–579.
- Eaton, R.W., 2001. Plasmid-encoded phthalate catabolic pathway in *Arthrobacter keyseri* 12B. *J. Bacteriol.* 183(12), 3689–3703.
- Einhellig, F.A., 1996. Interactions involving allelopathy in cropping systems. *Agron. J.* 88(6), 886–893.
- Elkhatib, E.A., Mahdy, A.M., Saleh, M.E., Barakat, N.H., 2007. Kinetics of copper desorption from soils as affected by different organic ligands. *Int. J. Environ. Sci. Technol.* 4(3), 331–338.
- Elloitt, H.A., Huang, C.P., 1980. Adsorption of some Cu-amino acid complexes at solid-solution interface. *Environ. Sci. Technol.* 14(1), 87–93.
- Errecalde, O., Campbell, P.G.C., 2000. Cadmium and zinc bioavailability to *Selenastrum capricornutum* (Chlorophyceae): accidental metal uptake and toxicity in the presence of citrate. *J. Phycol.* 36(3), 473–483.
- Evans, Jr. A., 1998. Biodegradation of  $^{14}\text{C}$ -labeled low molecular weight organic acids using three biometer methods. *J. Chem. Explor.* 65(1), 17–25.
- Fenchel, T., Finlay, B.J., 1995. *Ecology and Evolution in Anoxic Worlds*. Oxford University Press, Oxford.
- Fenchel, T., King, G.M., Blackburn, T.H., 1998. Bacterial biogeochemistry. In: *The Ecophysiology of Mineral Cycling* (2nd ed.). Academic Press, San Diego.
- Fischer, H., Kuzyakov, Y., 2010. Sorption, microbial uptake and decomposition of acetate in soil: Transformations revealed by position-specific  $^{14}\text{C}$  labeling. *Soil Biol. Biochem.* 42(2), 186–192.
- Fogg, G.E., 1963. The role of algae in organic production in aquatic environments. *Eur. J. Phycol.* 2(4), 195–205.
- Fox, T.R., 1995. The influence of low-molecular-weight organic acids on properties and processes in forest soils. In: McFee, W.W., Kelly, J.M., (Eds.), *Carbon Forms and Functions in Forest Soils*. Soil Science Society of America, Inc, Madison, WI, pp. 43–62.
- Fujii, K., Aoki, M., Kitayama, K., 2012. Biodegradation of low molecular weight organic acids in rhizosphere soils from a tropical montane rain forest. *Soil Biol. Biochem.* 47, 142–148.



- Gao, Y.Z., He, J.Z., Ling, W.T., 2003. Effect of organic acids on cadmium desorption from soils. *Acta Pedol. Sin.* 40(5), 731–737.
- Gao, Y.Z., Ren, L.L., Ling, W.T., Kang, F.X., Zhu, X.Z., Sun, B.Q., 2010. Effects of low-molecular-weight organic acids on sorption-desorption of phenanthrene in soils. *Soil Sci. Soc. Am. J.* 74(1), 51–59.
- Gennings, C., Molot, L.A., Dillon, P.J., 2001. Enhanced photochemical loss of organic carbon in acidic waters. *Biogeochemistry* 52(3), 339–354.
- Gogou, A., Stephanou, E.G., 2004. Marine organic geochemistry of the eastern mediterranean: polar biomarkers in Cretan Sea surficial sediments. *Mar. Chem.* 85(1–2), 1–25.
- Goldstone, J.V., Pullin, M.J., Bertilsson, S., Voelker, B.M., 2002. Reactions of hydroxyl radical with humic substances: bleaching, mineralization, and production of bioavailable carbon substrates. *Environ. Sci. Technol.* 36(3), 364–372.
- Haggerty, J.A., Fisher, J.B., 1995. Short-chain organic acids in interstitial waters from western Pacific guyots. In: Haggerty, J.A., Premoli Silva, I., Rack, F., McNutt, M.K., (Eds.). *Proceedings-Ocean Drilling Programme Scientific Results. TX (Ocean Drilling Program), College Station, 144*, pp. 469–474.
- Halerc, L.A., Guardia, M.J., Harvey, E., Gaylor Michael O., Mainor T.M., 2006. Brominated flame retardant concentrations and trends in abiotic media. *Chemosphere* 64(2), 181–186.
- Hara, J., 2012. Chemical degradation of chlorinated organic pollutants for *in situ* remediation and evaluation of natural attenuation. In: *Organic Pollutants Ten Years After the Stockholm Convention-Environmental and Analytical Update. INTECH Open Access Publisher, 345–364*. ISBN: 978-953-307-917-2.
- Henry, A.L., Anderson, G.M., 1992. Alteration of organic matter in the Viburnum Trend. *Econ. Geol.* 87(2), 280–309.
- Hessen, D.O., Andersen, T., Lyche, A., 1990. Carbon metabolism in a humic lake: pool sizes and cycling through zooplankton. *Limnol. Oceanogr.* 35(1), 84–99.
- Hu, H.Q., Liu, H.L., He, J.Z., Huang, Q.Y., 2007. Effect of selected organic acids on cadmium sorption by variable and permanent-charge soils. *Pedosphere* 17(1), 117–123.
- Huang, X.F., Hu, M., He, L.Y., Tang, X.Y., 2005. Chemical characterization of water-soluble organic acids in PM<sub>2.5</sub> in Beijing, China. *Atmos. Environ.* 39(16), 2819–2827.
- Hue, N.V., Craddock, G.R., Adams, F., 1986. Effect of organic acids on aluminum toxicity in subsoils. *SoilSci. Soc. Am. J.* 50(1), 28–34.
- Jones, D.L., 1998. Organic acids in the rhizosphere—A critical review. *Plant Soil* 205(1), 25–44.
- Jones, D.L., Dennis, P.G., Owen, A.G., van Hees, P.A.W., 2003. Organic acid behaviour in soils—misconceptions and knowledge gaps. *Plant Soil* 248(1–2), 31–41.
- Jones, D.L., Prabowo, A.M., Kochian, L.V., 1996. Kinetics of malate transport and decomposition in acid soils and isolated bacterial populations: The effect of microorganisms on root exudation of malate under Al stress. *Plant Soil* 182(2), 239–247.
- Jones, R.E., Beeman, R.E., Sufita, J.M., 1989. Anaerobic metabolic processes in the deep terrestrial subsurface. *Geomicrobiol. J.* 7(1–2), 117–130.
- Jonsson, A., Strom, L., Aberg, J., 2007. Composition and variations in the occurrence of dissolved free simple organic compounds of an unproductive lake ecosystem in northern Sweden. *Biogeochemistry* 82(2), 153–163.
- Jorgensen, B. B., 2000. Bacteria and marine biogeochemistry. In: Schulz H.D., Zabel, M., (Eds.), *Marine Geochemistry*. Springer Verlag, Heidelberg, pp. 173–207.
- Juttner, F., Matuschek, T., 1978. The release of low molecular weight compounds by the phytoplankton in an Eutrophic lake. *Water Res.* 12(4), 251–255.
- Kawamura, K., Kaplan, I.R., 1984. Capillary gas chromatography determination of volatile organic acids in rain and fog samples. *Anal. Chem.* 56(9), 1616–1620.
- Kawamura, K., Kasukabe, H., Barrie, L., 1996. Source and reaction pathways of dicarboxylic acids, ketoacids, and dicarbonyls in Arctic aerosols: One year of observations. *Atmos. Environ.* 30(10–11), 1709–1722.
- Kawamura, K., Steinberg, S., Lai, N., Kaplan, I.R., 2007. Wet deposition of low molecular weight mono- and di-carboxylic acids, aldehydes and inorganic species in Los Angeles. *Atmos. Environ.* 35(23), 3917–3920.
- Kawamura, K., Yokoyama, K., Fujii, Y., Watanabe, O., 2012. A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and -dicarbonyls: A trend from little ice age to the present (1540–1989 A.D.). *J. Geophys. Res.* (1540–1989) 106(D1), 1331–1345.
- Kerminen, V.M., Virkkula, A., Hillamo, R., Wexler, A.S., Kulmala, M., 2000. Secondary organics and atmospheric cloud condensation nuclei production. *J. Geophys. Res.* 105(D7), 9255–9264.
- Kesselmeier, J., Bode, K., Hofmann, U., Muller, H., Schafer, L., Wolf, A. et al., 1997. Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms. *Atmos. Environ.* 31(6), 199–133.
- Kester, A.S., Foster, J.W., 1963. Diterminal oxidation of long-chain alkanes by bacteria. *J. Bacteriol.* 85, 859–869.
- Khare, P., Satsangi, S.G., Kumar, N., Maharaj, K.K., Srivastava, S.S., 1997. HCHO, HCOOH and CH<sub>3</sub>COOH in air and rain water at a rural tropical site in north central India. *Atmos. Environ.* 31(23), 3867–3875.
- Kieber, D.J., McDaniel, J.A., Mopper, K., 1989. Photochemical source of biological substrates in sea water: Implications for carbon cycling. *Nature* 341(6243), 637–639.
- Kieber, R.J., Zhou, X.L., Mopper, K., 1990. Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. *Limnol. Oceanogr.* 35(7), 1503–1515.
- Kirk, J.T.O., 1994. Optics of UV-B radiation in natural waters. *Arch. Hydrobiol. Beih.* 43, 1–16.
- Kisand, V., Tammert, H., 2000. Bacterioplankton strategies for leucine and glucose uptake after an cyanobacterial bloom in a eutrophic shallow lake. *Soil Biol. Biochem.* 32(13), 1965–1972.
- Kleerebezem, R., Hulshoff Pol, L.W., Lettinga, G., 1999. Anaerobic degradation of phthalate isomers by methanogenic consortia. *Appl. Environ. Microb.* 65(3), 1152–1160.
- Koretsky, C., 2000. The significance of surface complexation reactions in hydrological systems: a geochemist's perspective. *J. Hydrol.* 230(3–4), 127–171.
- Kostaka, J.E., Roychoudhury, A., Cappelen, P.V., 2002. Rates and controls of anaerobic microbial respiration across spatial and temporal gradients in saltmarsh sediments. *Biogeochemistry* 60(1), 49–76.
- Kpombekou, K.A., Tabatabai, M.A., 2003. Effect of low-molecular

- weight organic acids on phosphorus release and phytoavailability of phosphorus in phosphate rocks added to soils. *Agr. Ecosyst. Environ.* 100(2-3), 275–284.
- Kristensen, E., 2000. Organic matter diagenesis at the oxic/anoxic interface in coastal marine sediments, with emphasis on the role of burrowing animals. *Hydrobiologia* 426(1), 1–24.
- Lee, X.Q., Huang, D.K., Lou, D.W., Pawliszyn, J., 2012. Needle trap extraction for GC analysis of formic and acetic acids in aqueous solution. *J. Sep. Sci.* 35(13), 1675–1681.
- Lee, X.Q., Qin, D.H., Jiang, G.B., Zhou, H., 2002. Determination of light carboxylic acids in snow and ice from mountain glaciers. *Cold Reg. Sci. Technol.* 34(2), 127–134.
- Li, X.Q., Qin, D.H., Ren, J.W., Zhou, H., 2000. Organic acids: a review for their sources and measurements. *J. Glaciol. Geocryol.* 22(3), 270–277.
- Li, Y.H., Huang, B.X., Shan, X.Q., 2003. Determination of low molecular weight organic acids in soil, plants, and water by capillary zone electrophoresis. *Anal. Bioanal. Chem.* 375(6), 775–780.
- Lim, H.J., Carlton, A.G., Turpin, B.J., 2005. Isoprene forms secondary organic aerosol through cloud processing: Model simulations. *Environ. Sci. Technol.* 39(12), 4441–4446.
- Limbeck, A., Kulmala, M., Puxbaum, H., 2003. Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. *Geophys. Res. Lett.* 30(19), 1996. DOI: 10.1029/2003GL017738.
- Lindell, M.J., Graneli, W., Tranvik, L.J., 1995. Enhanced bacterial growth in response to photochemical transformation of dissolved organic matter. *Limnol. Oceanogr.* 40(1), 195–199.
- Liu, S., Suffita, J.M., 1993. H<sub>2</sub>CO<sub>2</sub>-dependent anaerobic O-demethylation activity in subsurface sediments and by an isolated bacterium. *Appl. Environ. Microb.* 59(5), 1325–1331.
- Lou, D.W., Lee, X.Q., Pawliszyn, J., 2008. Extraction of formic and acetic acids from aqueous solution by dynamic headspace-needle trap extraction. *J. Chromatogr. A* 1201(2), 228–234.
- Lundström, U., Öhman, L.O., 1990. Dissolution of feldspars in the presence of natural, organic solute. *J. Soil Sci.* 41(3), 359–369.
- Lundström, U.S., 1993. The role of organic acids in the soil solution chemistry of podzolized soil. *J. Soil Sci.* 44(1), 121–133.
- Lundström, U.S., van Breemen, N., Bain, D.C., van Hees, P.A.W., Giesler, R., Gustafsson, J.P. et al., 2000. Advances in understanding the podzolization process resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries. *Geoderma* 94(2-4), 335–353.
- Luo, L., Zhang, S.Z., Shan, X.Q., Zhu, Y.G., 2006. Oxalate and root exudates enhance the desorption of *p, p'*-ddt from soils. *Chemosphere* 63(8), 1273–1279.
- Ma, J., Li, C.J., 1994. The secretion of low-molecular weight organic acids by plants under stress of P deficiency and their activation on insoluble phosphorus in soil. *Agriculture Science and Technology Press of China, Beijing*.
- Mack, J., Bolton, J.R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: A review. *J. Photoch. Photobio. A* 128(1-3), 1–13.
- Macknight, D.M., Aiken, G.R., 1998. Sources and age of aquatic humus. In: Hessen, D.O., Trannvik, L.J., (Eds.). *Aquatic humic substances: Ecology and Biogeochemistry*. Springer-Verlag, Berlin Heidelberg, pp. 9–39.
- Madsen, E.L., Ghiorse, W.C., 1993. Groundwater water microbiology: Subsurface ecosystem processes. In: Ford, T.E., (Ed.), *Aquatic microbiology an Ecological Approach*. Blackwell Scientific Publications, London, pp.167–213.
- Magdziak, Z., Mleczek, M., Kaczmerek, Z., Golinski, P., 2012. Influence of Ca/Mg ratio and Cd<sup>2+</sup> and Pb<sup>2+</sup> elements on low molecular weight organic acid secretion by *Salix viminalis* L. roots into the rhizosphere. *Trees* 27(3), 663–673.
- Maksimova, I.V., Pimenova, M.V., 1969. Accumulation of organic acids by green unicellular algae. *Mikrobiologiya* 38(1), 77–86.
- Marschner, P., Crowley, D., Yang, C.H., 2004. Development of specific rhizosphere bacterial communities in relation to plant species, nutrition and soil type. *Plant Soil* 261(1-2), 199–208.
- McBride, M.B., 1989. Reactions controlling heavy metal solubility in soils. *Adv. Soil Sci.* 10, 1–56.
- Meckler, A.N., 2002. Assessment of organic matter degradation in lake sediments. PhD Thesis. Department of Hydrology, University of Bayreuth, ETH Zurich, Swiss.
- Miller, D., Brown, C.M., Pearson, T.H., Stanley, S.O., 1979. Some biologically important low molecular weight organic acids in the sediments of Loch Eil. *Mar. Biol.* 50(4), 375–383.
- Miller, W.L., Zepp, R.G.J., 1995. Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* 22(4), 417–420.
- Millet, M., Wortham, H., Sanusi, A., Mirabel, P., 1997. Low molecular weight organic acids in fogwater in an urban area: Strasbourg (France). *Sci.TotalEnviron.* 206(1), 57–65.
- Moran, A., Hodson, R.E., 1990. Bacterial production on humic and non-humic components of dissolved organic carbon. *Limnol. Oceanogr.* 35(8), 1744–1756.
- Moran, M.A., Zepp, R.G., 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* 42(6), 1307–1316.
- Mostofa, K.M.G., Yoshioka, T., Konohira, E., Eiichiro, T., 2007. Dynamics and characteristics of fluorescent dissolved organic matter in the groundwater, river and lake water. *Water Air Soil Pollut.* 184(1-4), 157–176.
- Nwoko, C.O., 2010. Trends in phytoremediation of toxic elemental and organic pollutants. *Afr. J. Biotechnol.* 9(37), 6010–6016.
- Oburger, E., Kirk, G.J.D., Wenzel, W.W., Puschenreiter, M., Jones, D.L., 2009. Interactive effects of organic acids in the rhizosphere. *SoilBiol.Biochem.* 41(3), 449–457.
- Petra, M., David, C., Ching, H.Y., 2004. Development of specific rhizosphere bacterial communities in relation to plant species, nutrition and soil type. *Plant Soil* 261(1-2), 199–208.
- Pohlman, A.A., McColl, J.G., 1988. Soluble organics from forest litter and their role in metal dissolution. *Soil Sci. Soc. Am. J.* 52(1), 265–271.
- Pullin, M.J., Bertilsson, S., Goldstone, J.V., Voelker, B.M., 2004. Photo-induced changes in dissolved organic matter bioavailability: formation of low molecular weight organic acids and other substrates by sunlight and hydroxyl radical. *Limnol. Oceanogr.* 49(6), 2011–2022.
- Puranik, P.R., Paknikar, K.M., 1999. Biosorption of lead, cadmium, and zinc by *Citrobacter* strain MCM B-181: Characterization studies. *Biotechnol. Prog.* 15(2), 228–237.
- Qualls, R.G., Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and stream water. *Soil Sci. Soc. Am. J.* 56(2), 578–586.

- Ren, W.X., Li, P.J., Geng, Y., Li, X.J., 2009. Biological leaching of heavy metals from a contaminated soil by *Aspergillus niger*. *J. Hazard. Mater.* 167(1-3), 164–169.
- Renella, G., Landi, L., Nannipieri, P., 2004. Degradation of low molecular weight organic acids complexed with heavy metals in soil. *Geoderma* 122(2-4), 311–315.
- Routh, J., Grossman, E.L., Ulrich, G.A., Suflita, J.M., 2001. Volatile organic acids and microbial processes in the Yegua formation, east-central Texas. *Appl. Geochem.* 16(2), 183–195.
- Rullkotter, J., 2000. Organic matter: the driving force for early diagenesis. In: Schulz, H.D., Zable, M., (Eds.), *Marine Geochemistry*. Springer Verlag, Heidelberg, pp. 129–172.
- Sakugaw, H., Handa, N., Ohta, K., 1985. Isolation and characterization of low molecular weight carbohydrates dissolved in seawater. *Mar. Chem.* 17(4), 341–362.
- Sandnes, A., Eldhuset, T.D., Wollebak, G., 2005. Organic acids in root exudates and soil solution of Norway spruce and silver birch. *Soil Biol. Biochem.* 37(2), 259–269.
- Sempere, R., Kawamura K., 1996. Low molecular weight DIC carboxylic acids and related polar compounds in the remote marine rain samples collected from western pacific. *Atmos. Environ.* 30(10-11), 1609–1619.
- Siegel, D.A., Glaser, P.H., So, J., Janecky, D.R., 2006. The dynamic balance between organic acids and circumneutral groundwater in a large boreal peat basin. *J. Hydrol.* 320(3-4), 421–431.
- Sigha-Nkamdjou, L., Galy-Lacaux, I., Pont, V., Richard, S., Sighomnou, D., Lacaux, J. P., 2003. Rainwater chemistry and wet deposition over the equatorial forested ecosystem of Zoétélé (Cameroon). *J. Atmos. Chem.* 46(2), 173–198.
- Smith, R.L., Oremland, R.S., 1983. Anaerobic oxalate degradation: widespread natural occurrence in aquatic sediments. *Appl. Environ. Microb.* 46, 106–113.
- Song, J.M., Li, X.G., Shao, J.B., 2006. Biogeochemical characteristics of nitrogen and phosphorus in the South Yellow Sea sediments. *Oceanologia Et Limlogia. Sini.* 37(4), 370–376.
- Staudinger, J., Roberts P.V., 1996. A critical review of Henry's law constants for environmental applications. *Crit. Rev. Env. Sci. Tec.* 26(3), 205–297.
- Stefanova, M., Disnar, J.R., 2000. Composition and early diagenesis of fatty acids in lacustrine sediments, Lake Aydat (France). *Org. Geochem.* 31(1), 41–55.
- Steinberg, S.M., Bada, J.L., 1984. Oxalic, glyoxylic and pyruvic acids in eastern Pacific Ocean waters. *J. Mar. Res.* 42(3), 697–708.
- Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition, Reactions* (2nd ed.). Wiley and Sons, New York, pp. 288.
- Stevenson, F.J., Cole, M.A., 1999. *Cycles of Soil: Carbon, Nitrogen, Phosphorus, Micronutrients* (2nd ed.). John Wiley and Sons, Inc., New York, pp. 496.
- Stinley, R.L., Brezna, B., Khan, A.A., Cerniglia, C.E., 2004. Novel organization of genes in a phthalate degradation operon of *Mycobacterium vanbaalenii* PYR-1. *Microbiology* 150(P11), 2749–3761.
- Strobel, B.W., 2001. Influence of vegetation on low-molecularweight carboxylic acids in soil solution—A review. *Geoderma* 99(3-4), 169–198.
- Szmigielska, A.M., van Rees, K.C.J., Cieslinski, G., Huang, P.M., 1997. Comparison of liquid and gas. chromatography for analysis of low molecular weight organic acids in rhizosphere soil. *Commun. Soil Sci. Plan.* 28(1-2), 99–111.
- Talbot, M.R., Livingstone, D.A., 1989. Hydrogen index and carbon isotopes and lacustrine organic matter as lake level indicators. *Palaeogeogr Palaeoclimatol. Palaeoecol.* 70(1-3), 121–137.
- Tedetti, M., Joux, F., Charriere, B., Mopper, K., Sempere, R., 2009. Contrasting effects of solar radiation and nitrates on the bioavailability of dissolved organic matter to marine bacteria. *J. Photochem. Photobiol. A Chem.* 201(2-3), 243–247.
- Tedetti, M., Kawamura, K., Charriere, B., Chevalier, N., Sempere, R., 2006. Determination of low molecular weight carboxylic acids and ketocarboxylic acids in seawater samples. *Anal. Chem.* 78(17), 6012–6018.
- Teiser, M.L.O., 1993. Extracellular low molecular weight organic compounds produced by *Synechococcus* sp. and their roles in the food web of alkaline hot spring microbial mat communities. Ph.D Thesis, University of Oregon, Eugene, pp.197.
- Thauer, R.K., Mollerzinkhan, D., Spormann, A.M., 1989. Biochemistry of acetate catabolism in anaerobic chemotrophic bacteria. *Annu. Rev. Microbiol.* 43(1), 43–67.
- Thomas, R.A.P., Beswick, A.J., Basnakova, G., Moller, R., Mac-askie, L.E., 2000. Growth of naturally occurring microbial isolates in metal-citrate medium and bioremediation of metal-citrate wastes. *J. Chem. Technol. Biot.* 75(3), 187–195.
- Tranvik, L. J., Bertilsson, S., 2001. Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. *Ecol. Lett.* 4(5), 458–463.
- van Ginneken, L., Chowdhury, M.J., Blust, R., 1999. Bioavailability of cadmium and zinc to the common carp, *CYPRINUS carpio*, in complexing environments: a test for the validity of the free ion activity model. *Environ. Toxicol. Chem.* 18(10), 2295–2304.
- van Hees, P.A.W., Dahlen, J., Lundstrom, U.S., Boren, H., Allard, B., 1999. Determination of low molecular weight organic acids in soil solution by HPLC. *Talanta.* 48(1), 173–179.
- van HEES, P.A.W., Jones, D.L., Finlay, R., Godbold, D.L., Lundstrom, U.S., 2005. The carbon we don't see-the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review. *Soil Biol. Biochem.* 37(1), 1–13.
- van Hees, P.A.W., Lundstrm, U.S., 2000. Equilibrium models of aluminium and iron complexation with different organic acids in soil solution. *Geoderma* 94(2-4), 201–221.
- van Hees, P.A.W., Lundstrm, U.S., Giesler, R., 2000. Low molecular weight organic acids and their Al complexes in soil solution-Composition, distribution and seasonal variation in three podzolized soils. *Geoderma* 94(2-4), 173–200.
- Van Hees, P.A.W., Vinogradoff, S.I., Adwards, A.C., Godbold, D.L., Jones, D.L., 2003. Low molecular weight organic acid adsorption in forest soils: effects on soil solution concentration and biodegradation rates. *Soil Biol. Biochem.* 35(8), 1015–1026.
- Vyas, P., Gulati, A., 2009. Organic acid production in vitro and plant growth promotion in maize under controlled environment by phosphate-solubilizing fluorescent *Pseudomonas*. *BMC Microbiol.* 9(1), 174.
- Wang, J.G., Lv, J.L., Fu, Y.L., 2013. Effects of organic acids on Cd adsorption and desorption by two anthropic soils. *Front. Environ. Sci. Eng.* 7(1), 19–30.
- Wang, Y., Zhuang, G.S., Chen, S., An, Z.S., Zheng, A.H., 2007. Characteristics and sources of formic, acetic and oxalic acids in PM<sub>2.5</sub> and PM<sub>10</sub> aerosols in Beijing, China. *Atmos. Res.* 84, 169–181.

- Warneck, P., 2003. In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere. *Atmos. Environ.* 37(17), 2423–2427.
- Wellsbury, P., Parkes, R.J., 1995. Acetate bioavailability and turnover in an estuary sediment. *FEMS Microbiol. Ecol.* 17(2), 85–94.
- Westergaard, B., Hansen, H.C.B., Borggaard, O.K., 1998. Determination of anions in soil solutions by capillary zone electrophoresis. *Analyst* 123(4), 721–724.
- Wetzel, R.G., Hatcher, P.G., Bianchi, T.S., 1995. Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. *Limnol. Oceanogr.* 40(8), 1369–1380.
- White, J.C., Kottler, B.D., 2002. Citrate-mediated increase in the uptake of weathered *p*, *p'*-DDE residues by plants. *Environ. Toxicol. Chem.* 21(3), 550–556.
- White, J.C., Mattina, M.I., Lee, W.Y., 2003. Role of organic acids in enhancing the desorption and uptake of weathered *p*, *p'*-DDE by *Curcubita pepo*. *Environ. Pollut.* 124(1), 71–80.
- Williamson, C.E., 1995. What role does UV-B radiation play in freshwater ecosystems? *Limnol. Oceanogr.* 40(2), 386–392.
- Wu, F.C., Wang, L.Y., Li, W., Zhang, R.Y., Fu, P.Q., Liao, H.Q. et al., 2008. Natural organic matter and its significance in terrestrial surface environment. *J. Lake Sci.* 20(1), 1–12.
- Xiao, M., Wu, F.C., Liao, H.Q., et al., 2009. Vertical profiles of low molecular weight organic acids in sediment porewaters of six Chinese lakes. *J. Hydrol.* 365(1–2), 37–45.
- Xiao, M., Wu, F.C., Wang, L.Y., Li X.Q., Huang R.S., 2013. Investigation of low-molecular-weight organic acids and their spatiotemporal variation characteristics in Hongfeng Lake, China. *J. Environ. Sci.* 25(2), 237–245.
- Xing, B., 2001. Sorption of naphthalene and phenanthrene by soil humic acids. *Environ. Pollut.* 111(2), 303–309.
- Xu, R.K., Jiang, J., 2005. Effect mechanisms of low-molecular-weight organic acids on aluminum adsorption by variable charge soils. *Ecol. Environ.* 14(2), 253–256.
- Yu, S.C., 2000. Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): A review. *Atmos. Res.* 53(4), 185–217.
- Zagarese, H.E., Diaz, M., Pedrozo, F., Ferraro, M., Cravero, W., Tartarotti, B., 2001. Photodegradation of natural organic matter exposed to fluctuating levels of solar radiation. *J. Photochem. Photobiol. B.* 61(1–2), 35–45.
- Zhao, X., Quan, X., Zhao, H.M., Chen, S., Chen, J.W., Zhao, Y.Z., 2002. The effects of organic matter and hydrous metal oxides on the anaerobic degradation of  $\gamma$ -666, *p,p'*-DDT in Liaohe river sediments. *Environ. Sci.* 23(3), 115–118.
- Zhao, Z.H., Xia, L.L., Wang, F., Jiang, X., 2011. Effects of low-molecular-weight-organic-acids on the release kinetic of organochlorine pesticides from red soil. In: Stoytcheva Dr. M., (Ed.), *Pesticides in the Modern World—Risks and Benefits*. InTech, ISBN: 978-953-307-458-0.
- Zhou, B.X., Li, J.H., Zhou, X.F., Shi, L.J., Cai, W.M., 2005. Effect of dissolved organic acids on the solubility and properties of transfer of naphthalene. *Environ. Chem.* 24(6), 678–681.
- Zhou, X., Mopper, K., 1997. Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange. *Mar. Chem.* 56(3–4), 201–213.
- Zika, C.D., Clark, R.G., 2000. Marine organic photochemistry: from the sea surface to marine aerosols. In: Wangersky, P.J., (Ed.), *Marine Chemistry*. Springer-Verlag, Berlin Heidelberg, pp. 1–32.
- Zuo, Y.G., Jones, R.D., 1997. Photochemistry of natural dissolved organic matter in lake and wetland waters—Production of carbon monoxide. *Water Res.* 31(4), 850–858.