Metolachlor. As a germination inhibitor used mainly for weed control of grasses, metolachlor is one of the most heavily used agricultural pesticides in the United States and Canada. etolachlor is among one of those herbicides most frequently detected in surface water (Jaynes et al., 1999) and the concentrations of metolachlor have been reported for the period 1979-1985 in the range of 0.3-4.4 μ g/L for various locations along the Mississippi River (Chester et al., 1989). Since metolachlor is non-volatile and has a long hydrolysis half-life (Chiron et al., 1995), photolysis is an important abiotic degradation pathway for metolachlor under natural aquatic environment (Kochany and Maguire, 1994; Mathew and Khan, 1996; Wilson and Mabury, 2000; Dimou et al., 2005).

Metolachlor can be degraded through either direct or indirect photolysis, involving a series of reactions such as hydroxylation, dehalogenation, oxoquinoline formation, and demethylation (Mathew and Khan, 1996). In Kochany and Maguire's study (1994), four dechlorinated photoproducts (Figure 5.5) (species I, II, III, and IV) were identified in lake water after 40 days of sunlight irradiation. Wilson and Mabury (2000) focused on the extent of monochloroacetic acid (MCA) formation under simulated solar irradiation (Figure 5.5) (compound V), and found that direct photolysis resulted in 5.2% conversion of metolachlor to MCA while indirect photolysis in river water resulted in 12.6% conversion. In a recent study (Dimou et al., 2005), different aqueous media were used under solar and simulated solar irradiation and nine photoproducts were identified, among which 4-(2-ethyl-6-methyl-ohenyl)-5-methyl-3 -morpholinone (Figure 5.5) (compound III) was found as the main product in natural waters. This study further evaluated the toxicity of photoproducts and found that metolachlor photolysis produced more toxic compounds, which conflicted with the results from another study (Lin et al., 1999).

5.5.3 Chelating Agents

The environmental fate of chelating agents has received considerable attention, mainly due to their influence on metal mobility and bioavailability and their persistence in the environment (Nowack, 2002). Fe(III) and Cu(II) complexes of aminopolycarboxylates such as EDTA, NTA, DTPA, and EDDS are rapidly photodegraded in natural water (Trott et al., 1972; Langford et al., 1973; Lockhart and Blakeley, 1975a, 1975b; Kari et al., 1995; Metsärinne et al., 2001) while most other complexes are only slightly photodegradable or resist to photodegradation. Two common chelating agents (NTA and EDTA) and their photodegradation pathways and products in natural waters will be discussed.



Figure 5.5 Products of metolachlor photodegradation in natural water

NTA Nitrilotriacetate (NTA) is the first chemical synthesis of aminopolycarboxylic acids (APCAs). NTA is easily biodegradable and the biodegradation process is typically complete, as indicted by the compound iminodiacetate (IDA) does not accumulate in nature (Anderson et al., 1985). IDA is formed intracellularly during the microbial breakdown of NTA. Besides biodegradation, photodegradation has been demonstrated as another important pathway in limiting the accumulation of NTA (Trott, 1972; Langford et al., 1975). Photodegradation of Fe(III)NTA is rapid with a half-life of 1.5 hr under sunlight irradiation (Stolzberg and Hume, 1975), whereas that for CuNTA is much slower and the half-life is more than 100 times higher. The photodegradation of Fe(III)NTA is initiated by the excitation of the metal complex, during which an electron transfer from ligand to metal, resulting in a reduced metal ion and the formation of a ligand radical. The ligand radical then undergoes sequential decarboxylation, producing CO₂, formaldehyde, and iminodiacetate (IDA) (Trott et al., 1972; Lanford et al., 1973):

$$2Fe(III)NTA \rightarrow Fe(II) + Fe(II)NTA + IDA + CH_2O + CO_2$$
 (Eq. 5. 37)

Oxygen from air reoxidizes Fe(II) and Fe(III) is replenished to continue the reaction. Fe(III)IDA is further photodegraded forming glycine. The extent of NTA photodegradation is strongly determined by its speciation. Fe(III)NTA and Cu(II)NTA

are readily photodegradable in sunlight while photodegradation for other metal complexes (such as Cd(II)NTA, Pb(II)NTA, Mg(II)NTA and Cr(III)NTA) are not likely to occur due to the poor overlap of their absorption spectrum with the solar emission spectrum (Stolzberg and Hume, 1975).

EDTA. Ethylenediaminetetraacetic acid (EDTA) is widely used to remove metal ions that interfere with industrial processes. As a recalcitrant compound, EDTA resists biological degradation in sewage treatment plants, resulting in significant release of EDTA into surface waters. In European rivers and lakes, EDTA concentrations of 10-60 μ g/L are regularly found (Frimmel et al., 1989). Transport and fate of EDTA in surface waters has been widely studied. Among various physical, chemical and biological reactions, photodegradation may be a dominant pathway for the removal of EDTA from surface waters (Frank and Rau, 1990).

Generally, direct photochemical transformation of EDTA (in the form of Na₂-EDTA) is not possible in sunlight since Na₂-EDTA do not absorb light within the natural UV radiation range (Metsärinne et al., 2001). However, EDTA in natural waters are predominately in the form of metal complexes. For example, EDTA has a tendency to complex dissolved Fe(III) and adsorb at the surface of Fe(III) (hvdr)oxide. forming Fe(III)-EDTA complexes (Chang et al., 1983). Kari et al. (1995) and Kari and Giger (1995) reported that Fe(III)-EDTA complex is the only EDTA species that undergo the direct photolysis in natural waters. All other EDTA-species (such as Ca-EDTA, Zn-EDTA, Cu-EDTA, Ni-EDTA and Mn-EDTA) present in the river water are stable in the presence of light (Kari and Giner, 1995) because of their low concentrations in surface waters and low quantum yields for their photochemical degradation. Excited chromophores present in natural waters may generate photooxidants (such as hydroxyl radicals and singlet oxygen) but the impact of indirect photolysis on EDTA photodegradation is generally minor due to the extremely low concentrations of these photooxidants in natural waters (Kari et al., 1995). The key parameters to evaluate the photodegradation of EDTA in natural waters are the fraction of EDTA species present as Fe(III)-EDTA and the direct photolysis rate of Fe(III)-EDTA under sunlight conditions (Kari et al., 1995).

Fe(III)-EDTA complexes are known to photodegrade with relatively high quantum yields (an order of 10^{-2}) (Lockhard and Blakeley, 1975; Kari et., 1995). Rapid photodegradation of Fe(III)EDTA results in a mean half-life of a few hours in river water during summer and several days in winter (Kari et al., 1995). In aerobic conditions, Fe(III)EDTA is degraded in a stepwise process under successive decarboxylation (Lockhart and Blakeley, 1975a) and the major products of photodegradation are CO₂, formaldehyde, N-carboxymethyl-N, N'-ethylenediglycine (EDDA-N,N'), iminodiacetic acid (IDMA), N-carboxymethyl-N-aminoethyleneglycine (EDDA-N,N), N-amino-ethyleneglycine (EDMA), and glycine (Lockhart and Blakeley, 1975b):

 $Fe(III)EDTA \rightarrow Fe(II)ED3A + CO_2 + HCOH$ $Fe(III)ED3A \rightarrow Fe(II)EDDA + CO_2 + HCOH$ (Eq. 5.38)

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$Fe(III)EDDA \rightarrow Fe(II)EDMA + CO_2 + HCOH$

The formed Fe(II)-complexes are rapidly oxidized to Fe(III)-complexes in the presence of oxygen. The final product EDMA is stable in the presence of Fe(III) and light (Lockhard and Blakeley, 1975b). The photoproducts of Fe(III)EDTA are readily biodegradable compared to the recalcitrant parent compound (Nowack and Baumann, 1998).

5.5.4 Pharmaceutical Compounds

Pharmaceuticals and personal care products (PPCPs) are an emerging class of aquatic contaminants that have been increasingly detected in natural waters globally (Halling-Sorensen et al., 1998; Ternes, 1998; Kolpin et al., 2002; Calamari et al., 2003). Potential concerns from the environmental presence of these compounds include abnormal physiological processes and reproductive impairment, increased incidences of cancer, the development of antibiotic-resistant bacteria, and the potential increased toxicity of chemical mixtures (Kolpin et al., 2002). Despite the fact that many PPCPs are produced and used in significant amounts and maybe pose an environmental threat, relatively little is known about their occurrence and fate in natural waters.

There are several indications that photochemical degradation may be one of the potentially significant removal mechanisms for PPCPs in aquatic environment. Many of PPCPs have functional groups such as aromatic rings, heteroatoms, phenol, nitro, and napthoxyl, which can either absorb solar radiation, or react with free radicals and other reactive oxygen species generated by photosensitizers (Boreen et al., 2003). Moreover, many PPCPs are not completely removed or degraded in biological process of wastewater treatment plants (Ternes, 1998; Buser et al., 1999), which implies that photodegradation may be more important than biodegradation in determining the fate of PPCPs in sunlit waters.

The importance of photodegradation of PPCPs in aquatic environment has been demonstrated by several lab or field studies. Table 5.6 summarizes the quantum yields and half-lives of direct photolysis for common PPCPs under sunlight or simulated sunlight. The reported photodegradation rates vary widely, with half-lives ranging from less than 1 hour to more than 100 days. Some PPCPs (such as diclofenace. naproxen, and several estrogens) are very susceptible to photodegradation, whereas some PPCPs (such as carbamazepine and clofibric acid) degrade much slower. Some PPCPs that are resistant to direct photolysis, such as cimetidine (H₂ blocker), have been shown to react with singlet oxygen (¹O₂) and hydroxyl radical (OH[•]) and undergo indirect photolysis in natural waters (Latch et al., 2003b). Such indirect photolysis reactions are expected to dominate the photochemical fate of some PPCPs but so far this area remains poorly studied (Boreen et al., 2003).

Several PPCPs and their photodegradation pathways and products in natural waters will be discussed. These compounds are commonly detected in aquatic environment and have been extensively studied in the laboratory or field.

Naproxen. Naproxen may be the most studied pharmaceutical compound in the area of environmental photochemistry (Moore and Chappuis, 1988; Bosca et al., 1990; Vargas et al., 1991; Condorelli et al., 1993; Jimenez et al., 1997; Albini and Fasani, 1998; Martinez and Scaiano, 1998; Bosca et al., 2001; Packer et al., 2003). Naproxen is very susceptible to photodegradation under sunlight and the half-life is estimated to be around 1 hour (Packer et al., 2003; Lin and Reinhard, 2005). The high photolability of naproxen is due to the fact that absorption spectrum of naproxen exhibits a significant overlap with the solar spectrum (Packer et al., 2003).

The photodegradation pathways of naproxen (Figure 5.6) have been proposed by several studies (Moore and Chappuis, 1988; Bosca et al., 1990; Jimenez et al., 1997). The first step is conversion of the carboxylate (RC(=O)O-) group to a carboxyl radical ($RC(=O)O^{\bullet}$) by photoionization. Decarboxylation then occurs, yielding carbon dioxide and a benzylic radical. The benzylic radical further abstracts a hydrogen atom from a suitable donor resulting in a product with an ethyl side chain, or reacts with molecular oxygen, eventually leading to an alcohol or ketone moiety in place of the carboxylate group. Overall, irradiation of naproxen leads to photodecarboxylation products with ethyl, 1-hydroxyethyl and acetyl side chains. These photoproducts, however, may be more toxic than the parent drug (DellaGreca et al., 2004).

Diclofenac. Diclofenac is an excellent example to illustrate the importance of photochemistry on the fate of some PPCPs in aquatic environment. Diclofenace resists the chemical and biological degradation under natural conditions but it photodegrades rapidly under sunlight (Buser et al., 1998). It is not surprising, since diclofenac has an absorbance maximum at 273 nm that tails well over 300 nm, which indicates significant amount of light absorbance in the solar spectrum. The decomposition quantum yield determined ranges from 0.038 to 0.22 while the half-lives ranged from less than 1 hour to several hours (Moore et al., 1990; Buser et al., 1998; Andreozzi et al., 2003; Packer et al., 2003). Photodegradation has been demonstrated as the dominant pathway for diclofenac elimination in a lake (Buser et al., 1998; Poiger et al., 2001).

The primary process of photodegradation of diclofenace (Figure 5.7, step 1) is the loss of HCl and yield 8-chlorocarbazole-1-acetic acid. This intermediate is then dechlorinated to carbazole-1-acetic acid in the presence of H-source (Figure 5.7, step 2) or form 8-hydroxycarbazole-1-acetic acid via photosubstitution in the absence of H-source (Figure 5.7, step 3). 8-hydroxycarbazole-1-acetic acid is not stable under natural conditions and may further photodegrade rapidly. These photoproducts were identified in the laboratory experiments but were not detected under the natural conditions in the lake (Buser et al., 1998), possibly due to the extremely low concentrations of these compounds (less than the current detection limits) in the lake (Poiger et al., 2001).

| Chemical | Quantum yields ϕ | Half- life | References |
|--|-----------------------|----------------------|---------------------------|
| Carbamazepine | 0.000048 | ~100 day | Andreozzi et al. (2003) |
| - | 0.00013 | 115 hr | Lam and Mabury (2005) |
| Ciprofloxacin | 0.001 | | Albini and Monti (2003) |
| Clofibric acid | 0.0055 | ~30 day | Andreozzi et al. (2003) |
| | 0.002 | 50 hr | Packer et al. (2003) |
| Diclofenac | 0.22 | | Moore et al. (1990) |
| | 0.13 | < 1hr | Buser et al. (1998) |
| | 0.038 | $\sim 6 \text{ hr}$ | Andreozzi et al. (2003) |
| | 0.094 | < 1hr | Packer et al. (2003) |
| Enoxacin | 0.13 | | Albini and Monti (2003) |
| Estriol | 0.0048 | 2.9 hr | Lin and Reinhard (2005) |
| Estrone [E1] | 0.0296 | 2.3 hr | Lin and Reinhard (2005) |
| 17β-estradiol [E2] | 0.0048 | 2.0 hr | Lin and Reinhard (2005) |
| 17α -ethinylestradiol[EE ₂] | 0.0048 | 2.3 hr | Lin and Reinhard (2005) |
| Furaltadone | - | 0.086-0.36 hr | Edhlund et al. (2006) |
| Furazolidone | - | 0.24-0.90 hr | Edhlund et al. (2006) |
| Ibuprofen | - | 14.8 hr | Lin and Reinhard (2005) |
| _ | - | 2.6 hr | Packer et al. (2003) |
| Levofloxacin | 0.05 | - | Lam and Mabury (2005) |
| Lomefloxacin | 0.55 | - | Albini and Monti (2003) |
| Naproxen | 0.012 | - | Moore and Chappuis (1988) |
| - | 0.036 | <1 hr | Packer et al. (2003) |
| | 0.026 | 1.4 hr | Lin and Reinhard (2005) |
| Nitrofurantoin | - | 0.44-1.7 hr | Edhlund et al. (2006) |
| Norfloxacin | 0.06 | - | Albini and Monti (2003) |
| Ofloxcin | 0.000078 | ~ 2 day | Andreozzi et al. (2003) |
| Propranolol | 0.002 | ~ 2 days | Andreozzi et al. (2003) |
| - | 0.0052 | 1.1 hr | Lin and Reinhard (2005) |
| Ranitidine | 0.0053 | < 1 h | Latch et al. (2003a) |
| Sulfamethoxazole | 0.004 | $\sim 10 \text{ hr}$ | Andreozzi et al. (2003) |
| | 0.02 | - | Lam and Mabury (2005) |
| Triclosan | 0.03 | - | Latch et al. (2003b) |

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Table 5.6 Quantum yields and half-lives of photodegradation for PPCPsunder sunlight or simulated sunlight



Figure 5.6 Products of naproxen photodegradation in natural water (adapted from Jimenez et al., 1997)



Figure 5.7 Products of diclofenac photodegradation in natural water (adapted from Poiger et al., 2001)

Carbamazepine. Carbamazepine serves as an example demonstrating that some PPCPs that commonly undergo slow photodegradation may photodegrade rapidly under a specific environmental condition. In the distilled water irradiated by sunlight, the photodegradation of carbamazepine is very slow, with a quantum yield of 4.8×10^{-5} and a half -life of 100 days (Andreozzi et al., 2003). However, in the

presence of chloride, photodegradation of carbamazepine was found to be substantially enhanced in estuarine waters (Chiron et al., 2006). The chlorideenhanced carbamazepine photodegradation may result from the interaction between Fe(III) colloids and chloride ions under sunlight irradiation, yielding Cl_2^{\bullet} :

$$= Fe^{III} - OH + Cl^{-} \xrightarrow{hv} Fe^{2+} + OH + Cl^{\bullet}$$
 (Eq. 5.39)

$$Cl^{\bullet} + Cl^{-} \Leftrightarrow Cl^{\bullet-}$$
 (Eq. 5.40)

Various intermediates of carbamazepine photodegradation have been detected under both direct and indirect photolysis conditions (Chiron et al., 2006). A major photoproduct of direct photolysis is acridine (Figure 5.8), which is toxic, mutagenic, carcinogenic and more harmful than parent compound. In the chloride-enhanced photodegradation process, various hydroxylated/oxidized intermediates as well as chloroderivatives are formed. The health and environmental impact of these photoproducts remain unknown.



Figure 5.8 Formation of acridine during photodegradation of carbamazepine (adapted from Chiron et al., 2006)

5.6 Factors Influencing Photolysis

5.6.1 Suspended Particles

In the environment, varying amounts of suspended particles are present in the water and the particles (sediments) may change the rate or mechanism of photolysis of a contaminant in several ways. Suspended particles may reduce the photolysis rate by either shielding the organic from the available light or by quenching the excited states of the organic molecules before they react to form products. It is also possible for suspended particles to enhance the rate of organic photolysis if sediment absorption of light produces excited state or free radicals that can then react with the organics. In this way it is possible for organic materials that do not absorb sunlight to be photolyzed indirectly.

This type of indirect photolysis does occur with semiconductors such as TiO_2 , which are common constituents of clays, sediments and soils. A question is that, whether the mechanism analogous to photosensitized semiconductor reactions is import in natural waters? Oliver et al. (1979) evaluated the role of suspended sediments and clays on the photolysis of pollutants in water and concluded that suspended particles do not appear to enhance the photodegradation of organic pollutants, even though suspended particles can contain TiO_2 and other semiconductor in the 5-10% range. In contrast, suspended particles were found to reduce the rates of photolysis by shielding the pollutant from the available light.

A more complicated issue is the photolytic transformation of sorbed compounds. Although the role of semiconductors may be insignificant in natural water, the indirect photolysis of sorbed compounds may be important. For example, the rate of photolytic transformation of a series of alkylated anilines was found to be significantly accelerated by algae (Zepp and Wolfe, 1987). The accelerating effect increased with increasing hydrophobicity of the compound, indicating that sorption of the compound was rate determining.

5.6.2 Dissolved Organic Matter

It is well known that dissolved organic matter (DOM) plays an important part in sunlight-induced photochemical processes in surface waters. DOM can act as inner filter, radical scavenger or precursor of reactive species:

Inner filter. DOM can absorb solar radiation in a broad range of wavelengths and thus reduce the available energy for the target compound in the solution.

Radical scavenger. DOM is one of the most important radical scavengers in photochemical reactions.

Precursor of reactive species. After being activated by solar UV photons, DOM can be promoted to a transient excited state (triplet state), in which they may react with oxygen forming reactive species (Haag and Hoigne, 1986), or react directly with other organic species, thus promoting their phototransformation (Zeep et al., 1985).

The overall effect of DOM on the phototransformation rate of an aquatic contaminant will therefore depend on a balance of the above three contributions. When DOM acts mainly as an inner filter, the addition of DOM will result in a decrease of photolysis rate. On the other hand, if DOM mainly acts as a precursor of reactive species, the presence of DOM will accelerate the photolysis process. In the hydroxyl radical (OH[•]) -mediated photochemical reactions, DOM will scavenge OH[•] and thus inhibit the photodegradation of contaminants.

Table 5.7 summarizes the effects of DOM on the photodegradation of some organic compounds. Generally, DOM reduces the photolysis rate for most of the compounds that photodegrade rapidly via the direct photolysis. It is not surprising, since DOM–induced indirect or sensitized photolysis plays insignificant role in their photodegradation and DOM effectively compete with the target compounds for the

solar radiation. The photodegradation of some compounds could be enhanced in natural waters through reactions with intermediates produced photochemically from chromophoric DOM. However, the degree of enhancing effects on photodegradation depends on the concentration of DOM in water. It has been found that the degradation rate of a target compound increased rapidly with the amount of DOM added but the rate reached a plateau at high levels of DOM (Doll and Frimmel, 2003; Miller and Chin, 2005). In this case, DOM may also act as a sink for reactive species produced from DOM-induced reactions and the enhancing effects compromised due to scavenging of these reactive species.

| Chemical | Concentration of ^a DOC/DOM (mg/L) | ^b Effect | Reference |
|--------------------------|---|---------------------|------------------------------|
| 12 PAH compounds | Unknown | 0 | Fasnacht and Blough (2002) |
| 3 nitrofuran antibiotics | 5.9 (DOC) | 0 | Edhlund et al. (2006) |
| 5 sulfa drugs | 5.9 (DOC) | + | Boreen et al. (2005) |
| Acetochlor | 2.3-7.4 (DOC) | - | Brezonik ans Brekken (1998) |
| Alachlor | 2-14 (DOC) | + | Miller and Chin (2005) |
| Atrazine | 5.3 (DOC) | - | Torrents et al. (1997) |
| | 10.2-12.8 (DOM) | - | Konstantinou et al. (2001) |
| Carbamazepine | 5 (DOM) | - | Andreozzi et al. (2003) |
| | 1-7 (DOC) | + | Doll and Frimmel (2003) |
| Carbofuran | 5-30 (DOC) | - | Bachman and Patterson (1999) |
| Cimetidine | 16 (DOC) | + | Latch et al. (2003) |
| Clofibric acid | 5 (DOM) | + | Andreozzi et al. (2003) |
| | 16 (DOC) | + | Packer et al. (2003) |
| Dehydroabietic acid | 25.5 (DOC) | + | Corin et al. (2000) |
| Diclofenac | 5 (DOM) | - | Andreozzi et al. (2003) |
| | 16 (DOC) | 0 | Packer et al. (2003) |
| Fipronil | 2.5-10 (DOM) | - | Walse et al. (2004) |
| Ibuprofen | Unknown | + | Lin and Reinhard (2005) |
| | 16 (DOC) | + | Packer et al. (2003) |
| Metolachlor | 4-24 (DOM) | - | Dimou et al. (2005) |
| | 0.5 (DOC) | - | Wilson and Mabury (2000) |
| Ofloxacin | 5 (DOM) | + | Andreozzi et al. (2003) |

 Table 5.7 Effects of DOM on photodegradation of some compounds

^a DOC: dissolved organic carbon; DOM: dissolved organic matter

^b o: no effect; +: enhance photolysis rate; -: reduce photolysis rate

The effects of DOM on nitrate-induced, OH[•] mediated degradation of aquatic contaminants have been extensively studied (Miller and Chin, 2005; Lam et al., 2003; Brezonik and Fulkerson-Brekken, 1998; Torrents, 1997). As mentioned before, nitrate is the primary source of OH[•], one of the principal intermediates in natural water photochemistry. DOM is a significant natural OH[•] scavenger and the importance of DOM as a OH[•] sink can be directly estimated from the dissolved organic carbon (DOC) concentration of a water (Brezonik and Brekken, 1998). Research by Lam et al. (2003) showed that the effects of DOM on the photodegradation of target organic compounds strongly depended on the concentration of nitrate in water. At low concentrations of nitrate, OH[•]-mediated degradation was unimportant and increasing