BIODEGRADATION OF MICROPOLLUTANTS IN ERGENE RIVER DURING A DRY SEASON

by

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To memory of my dear father...

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ABSTRACT

BIODEGRADATION OF MICROPOLLUTANTS IN ERGENE RIVER DURING A DRY SEASON

In recent years, there have been an increase in consumption and production of micropollutants, such as surfactants, flame retardants, pharmaceuticals, personal care products, gasoline additives and their degradation products, biocides, pesticides and their degradation products and various endocrine disrupting compounds, which have resulted in their accumulation in influent and treated both groundwaters and surface waters. Yet, their removal efficiency in biological systems is highly unsteady, and it is still unclear how operational and environmental parameters change. Today, Ergene River is one of the most important examples of this phenomena in Turkey. Thus, determining source of micropollutants in Ergene River and their fates is required. In this study, 29 sampling points were determined and about 100 mL of filtered samples were transferred into 250 mL amber glass Erlenmeyer Flasks. Each flask was spiked with acetaminophen at 10 µg/L as a biodegradable reference substrate. Acetaminophen is known as an easily biodegradable compound; therefore, its degradation shows a control of biological activity. Also, same procedure was applied for autoclaved sample as a control flask. All flasks were incubated at room temperature between 20-25^{o}C and agitated at 100 rpm. Micropollutants were monitored for 30 days in the samples taken aseptically from each flask using AB SCIEX QTrap 4500 LC-MS^{n} system. Forty-seven micropollutants such as; oxybenzone, N-benzyldimethylamine, nonylphenol diethoxylate were biodegraded at least in one sampling point and their half-lives and biodegradation rate constants were calculated. On the other hand, 17 micropollutants such as hexa(methoxymethyl)melamine, quinoxyfen were not degraded at none of the sampling points.

ÖZET

ERGENE NEHRİ'NDEKİ MİKROKİRLETİCİLERİN KURAK DÖNEMDE BİYOLOJİK OLARAK BOZUNMASI

Son yıllarda yüzey aktif maddeleri, alev geciktiricileri, farmasötikler, kişisel bakım ürünleri, benzin katkı maddeleri ve bunların bozunma ürünleri, biyositler, böcek ilaçları ve bunların bozunma ürünleri ve çeşitli endokrin bozucu bileşikler gibi mikro kirletici maddelerin tüketiminde ve üretiminde artış olmuştur. Bu artışla giriş sularında mikrokirleticiler birikmekte ve yer altı ve yer üstü sularını tehdit etmektedirler. Ayrıca, bu kirleticilerin biyolojik sistemlerde arıtma verimi değişkendir ve operasyonel veya çevresel parametrelerin nasıl değişeceği belirsizdir. Bugün Ergene Nehri, Türkiye'deki bu fenomenin en önemli örneklerinden biridir. Bu nedenle, Ergene Nehrinde bulunan mikrokirleticilerin kaynağının ve akıbetinin belirlenmesi gerekir. Bu çalışmada Ergene Nehri üzerinde 29 örnekleme noktası belirlenmiş ve yaklaşık 100 mL nehir suyu filtre edilerek 250 mL amber cam Erlenmeyer Şişelerine aktarılmıştır. Acetaminophen biyolojik olarak kolayca parçalanabilen bir kimyasaldır. Bu nedenle biyolojik aktivitenin kontrolü için her şişeye 10 µg/L acetaminophen eklenmiştir. Otoklavlanan ve aynı prosedürler uygulanan örnek, kontrol örneği olarak kullanılmışır. Bütün şişeler 20-25^{o}C arası oda sıcaklığında ve 100 rpm'de çalkalanarak inkübe edilmiştir. Her şişeden aseptik olarak alınan numuneler, AB SCIEX QTrap 4500 LC-MSn sistemi kullanılarak 30 gün boyunca izlenmiştir. Kırk-yedi mikrokirletici; oxybenzone, N-benzyldimetilamine, nonylphenol diethoxylate gibi, en az bir örnekleme noktasında biyolojik olarak parçalanmıştır. Bu kimyasalların yarı ömürleri ve biyolojik parçalanma oranı sabiti hesaplanmıştır. Öte yandan, hexa(methoxymethyl)melamine, quinoxyfen gibi 17 mikrokirletici örnekleme noktalarının hiçbirisinde bozunmadan kalmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

Abbreviation	Explanation
C	Concentration of the Chemical
C_0	Initial Concentration
CE	Collusion Energy
CEC	Contaminants of Emerging Concern
COD	Chemical Oxygen Demand
D	Day
DEET	N,N-Diethyl-m-toluamide
DHBP	2,4-Dihydroxybenzophenone
DOC	Dissolved Organic Carbon
DP	Declustering Potential
K_S	Half Saturation Coefficient
logP	Octanol-Water Partition Coefficient
MRM	Multi Reaction Monitoring
OECD	The Organisation for Economic Co-operation and Development
OIZ	Organized Industrial Zone
PAH	Polyaromatic Hydrocarbons
PCB	Polychlorinated biphenyls
pH	Power of Hydrogen
PS	Priority Substance
Q1	Parent Ion
Q3	Fragment Ion
RBT	Ready Biodegradability Tests
RT	Retention Time
S_0	Substrate Concentration
SRT	Sludge Retention Time
TOC	Total Organic Carbon
UHPLC	Ultra-high Performance Liquid Chromatography
UV	Ultraviolet
µmax	Maximum Growth Rate
WWTP	Wastewater Treatment Plant

1. INTRODUCTION

The term “micropollutants” has been used to refer organic or inorganic chemicals present in water at concentrations ranging from a few nanograms to several micrograms per liter. Even though they are found at low concentrations, they have direct or indirect negative impact on biochemical processes in nature and on human heath substantially because of their toxic and bioaccumulative properties (Luo et al., 2014). Micropollutants consist of fundamentally two types substances which occur synthetically or naturally. Active pharmaceutical and cosmetics ingredients, detergents, compounds used for material protection and gardening, food additives are among the former whereas the hormones are among the latter (Federal Office for the Environment Bern, 2012). Among those micropollutants, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), phenols, metals, dioxin and furan, alkali phenols, flame retardants, phthalates etc. have high level of toxicity, high environmental durability and hydrophobicity. Due to their resistance against photolytic, chemical and biological degradation and, thus, extremely long decay time in nature, they are classified as ‘priority substances (PS)’ by USA and EU states and some of them are classified as ‘contaminants of emerging concern (CEC)’. There are about 1050 chemicals classified as PS and CEC and they are frequently detected in environment and exert risk for both human health and environment (Gasperi et al., 2008; Sanchez-Avilla et al., 2009; Chen et al., 2014 Birkigt et al., 2015).

CECs can be classified according to their origin which are domestic, industrial and agricultural. Currently, the most frequently monitored CECs are algal toxins, biocides, disinfection by-products, drugs of abuse, flame retardants, industrial compounds, organic and inorganic nanomaterials, personal care products including, UV filters, fragrances, insect repellents, etc., pharmaceuticals used in both human and veterinary medicine, plant production products, plasticizers, surfactants, trace metals and their compounds (Mandaric et al., 2015).

Pharmaceuticals are an important group of CECs due to their frequent detection in water bodies as well as their further estrogenic risk and other adverse effects on both fauna and flora (Lambert et al., 2016; Diamond et al., 2015). Pollution caused by this group of chemicals can be originated from the wastewaters of industries, houses or agricultural farms. More than 3000 different substances are used as active pharmaceutical ingredient in painkillers, antibiotics, lipid regulators, antidiabetics and other important drugs (Liu et al., 2015). Antibiotics, biocides and pesticides are other important CEC groups because of their potential contribution to the development of bacterial resistance after reaching the environment. Antibiotics such as clarithromycin, penicillin, chloramphenicol, sulfamethoxazole

and erythromycin are one of the most important pharmaceutical group that are used to combat human and animal infections (Hirsch et al., 1999). Today, consumption and contamination of waterbodies by antibiotics increase day by day. Even in drinking waters in Europe, people are exposed low level of antibiotics. Thus, monitoring and assessment of their potential risk have a crucial role (Carvalho et al., 2016). Also, they decrease biodegradation of plant materials which is the primary food chain activity in the environment (Zhang et al., 2015). Pesticides and biocides are generally used for agriculture and bituminous roof sealing membranes or grass and weed control. During rain events, they penetrate into the ground or find their ways to surface water via runoff (Weston et al., 2015; Tang et al., 2015). Biocides such as diuron, chlorothalonil and dichlofluanid are frequently used in aquacultures and they tend to accumulate in fish and shellfish. In addition, they may develop antibiotic resistance genes in some microorganisms such as bacteria (Guardiola et al., 2012). Algal toxins, as another important micropollutant group, have high toxicity in seafoods even at very low concentrations which further affects public health and economy adversely (Gago-Martinez et al., 2003). Plasticizers like phthalates which are used in food packaging, cosmetics and contraction materials are also pollutants of concern. Phthalates have endocrine disrupting activity and cause several human health problems (Huang et al., 2012). Colon et al. (2000) reported there is a relationship between high level of blood phthalates and abnormal reproductive problems in Puerto Rico. Flame retardants are compounds such as polybrominateddiphenyl ether, hexabromocyclododecane and tetrabromobisphenyl A, that are added to commercial products to reduce their flammability. Although there is restriction of usage of these chemicals, extensive use of these chemicals in manufactories causes surface water contamination. They also accumulate in sea mammals and terrestrial animals (Fayiga et al., 2017). Surfactants are widely used in detergents, cleaners, personal care products and plastics. They classified as anionic, non-ionic, cationic and amphoteric. Most of these chemicals are directly discharged to WWTPs after usage. Concentration of these chemicals in raw wastewater reaches to more than 40 mg/L, because of high consumption of surfactants in both household and industrial applications (Berna et al., 2007, Matthijs et al., 1999). Synthetic chelating agents such as tetra acetic acid, 1,3-propylenediamine tetra-acetic acid and diethyl triamine penta-acetic acid are used for binding and masking metal ions in industrial materials. They can easily reach to the receiving water bodies because their physicochemical properties prevent efficient removal from contaminated water (Knepper., 2003).

Point sources are defined as any single identifiable source of pollution from which pollutants are discharged by industrial and municipal sectors (Jining et al., 2002). Nonpoint sources such as residential areas, agricultural runoffs, aquaculture treatments also cause the pollution in water bodies.

Non-point source contamination is generally harder to control than point source contamination (Gang et al., 2016).

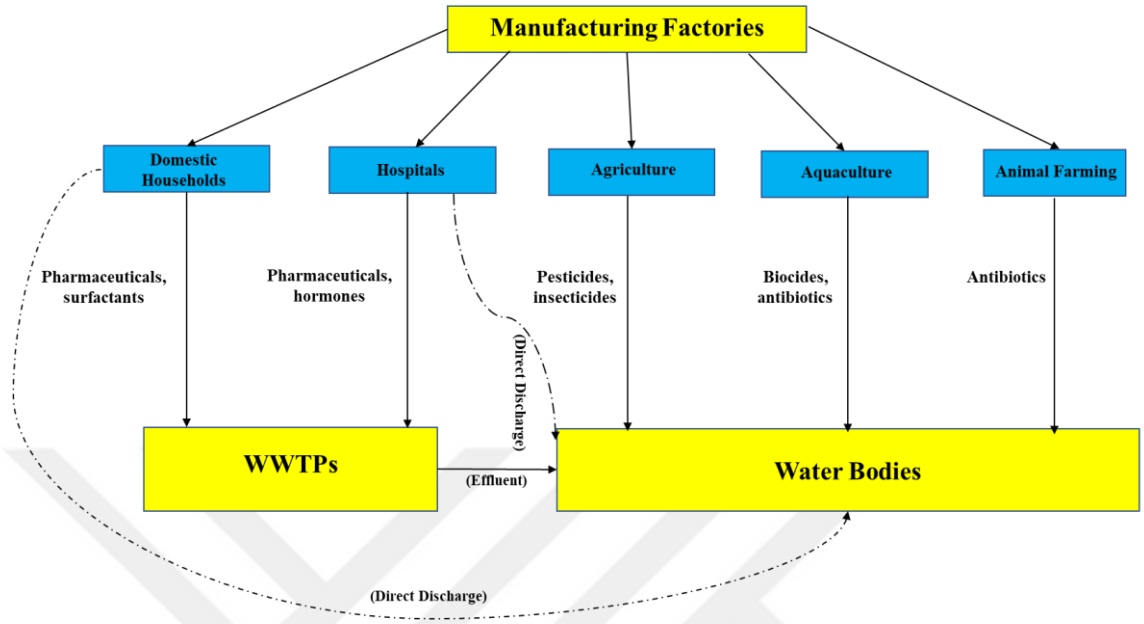


Figure 1.1. Emerging contaminants in the aquatic environment (Yang et al., 2014).

Chemicals transported by wastewater flows to treatment plants and/or receiving bodies contaminate water sources. Contaminated water sources threaten aquatic environment, ecosystem and human health in general. Wastewater from industries includes various chemicals depending on facility activities, facility location, raw materials used (paint, chemical compounds etc.) and chemical processes applied. In Figure 1.1, how pollutants reach WWTPs and surface waters is summarized. Contaminants from manufacturing factories directly reach WWTPs. For instance, pharmaceuticals find their way to surface waters via discharges of wastewaters of manufacturing factories, after using pharmaceuticals for aquaculture and livestock treatments, effluents from home and hospital to WWTPs.

Generally, WWTPs are not specifically designed to remove micropollutants. Thus, many of these micropollutants can pass through wastewater treatment processes. In addition, in most of the WWTPs, micropollutant monitoring and precautions for micropollutant removal have not been well constituted (Bolong et al., 2009). As a result, many of these compounds may reach in the aquatic environment where they pose a risk to both living organisms and water resources. Micropollutants in aquatic environment cause many harmful effects including short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms (Fent et al., 2006; Pruden et al., 2006).

Microbial biotransformation and mineralization are two main mechanisms controlling the fate of micropollutants in the environment and in most of cases, a toxic pollutant can be converted to a non-toxic compound or mineralized to inorganic molecules such as carbon dioxide and ammonium (Fent et al., 2006). In the water environment, many micropollutants are found together. Different strains of microorganisms or a group of microorganisms are involved in the biotransformation of those micropollutants which may reduce the toxicity of those chemicals. As the first phase of the biodegradation process is the uptake of micropollutants by cell and its affinity to the bacterial enzymes, bioavailability which is determined by the molecular structure of the chemical is an important factor for biodegradation, (Siegrist et al., 2005). The complexity of a chemical and its functional groups are two main features affecting biodegradability of a compound. In general, the easily degraded compounds are generally linear compounds with short side chains, unsaturated aliphatic compounds and compounds possessing electron donating functional groups. On the other hand, the persistent micropollutants are comprised of compounds with long, highly branched side chains, saturated or polycyclic compounds and compounds possessing sulphate, halogen, or electron withdrawing functional groups (Jones et al., 2005; Tadkaew et al., 2011). Given the fact that many micropollutants with different molecular structures are present together in the water environment, biodegradability of those pollutants should be tested together with a native microbial community present in that environment.

The Organization for Economic Co-operation and Development (OECD) offers several protocols for testing the biodegradability of a chemical substance. Those protocols are divided into three: (1) Ready biodegradability (Test no: 301A-F and 310) (OECD 1992), (2) Inherent biodegradability (Test no: 302A-C) (OECD 1981) and (3) Simulation biodegradability tests (Test no: 314A-E) (OECD 2008). In Ready biodegradability Tests (RBT), the test substance serves as the sole carbon and energy source. Relatively low concentration of biomass is used to avoid excessive adsorption of the test substance as well as to limit release of carbon due to endogenous decay. The test substance is not measured during the course of the experiment, but non-specific parameters such as dissolved organic carbon (DOC), oxygen uptake and carbon dioxide are measured to verify biodegradation. Complete removal of DOC is indicative of ultimate biodegradation. However, concentration of the test substance should be high enough to be measured by the mentioned non-specific methods. As a result, the initial concentration of a test substance in the screening test is generally kept at a very high level i.e. 2-100 mg/L and does not represent the actual concentrations in a wastewater. As an alternative to RBTs, “simulation tests” are performed. In simulation tests, the initial concentration of the test substance ranges between 1 µg/L and 100 µg/L which is low enough to ensure that the biodegradation kinetics obtained in the test reflect those expected in the environment being simulated as well as

higher than the limit of detection of the instrument used for the measurement of the chemical or the by-products. Biodegradation is measured either by radiolabeling techniques or using specific instrumental methods. Shortcomings of screening tests (ready biodegradability) like low biomass density, high initial test substance concentration and indirect measurement of biodegradation by non-specific parameters like DOC are eliminated in simulation tests (Kowalczyk et al., 2015).

On the other hand, biodegradation of a single chemical is tested in simulation tests which makes it a low-throughput testing method. Relatively recently, two high-throughput methods have been developed for testing biodegradability of chemical substances. One offer assessing compound biodegradation at 1-2 mg C/L by measuring microbial community growth over time with direct cell counting with flow cytometry (Czechowska et al., 2013). The other uses microwell plates for testing biodegradation of multiple compounds individually at 10 mg C/L. However, the latter method is applicable only for compounds containing aromatic groups since it uses a coloring agent which reacts with the aromatic ring (Matin et al., 2017).

Wastewater and surface water are complex matrices which contain many micropollutants at very low concentrations. The biodegradability tests are limited to mimic the real conditions in the environment since the initial concentrations of chemicals are too high and they are performed for only one chemical at a time.

The dry season is a yearly period of low rain activities. During a dry season, river water density increases and some of the branches may dried because of the low rain and high evaporation. Also, abundance of microbial communities shows variations according to the season (Chen et al., 2013). Qi et al. (2014) was monitored concentrations of a broad range of micropollutants in the Yangtze River for 14 months. They reported that concentration of many micropollutants changed seasonally.

The objective of this research is to assess biological fate of micropollutants existing in Ergene River during a dry season. Biodegradability as well as the biodegradation rate of micropollutants identified in the river water was measured following OECD Guideline for Testing of Chemical Protocol #309 “Aerobic Mineralization in Surface Water – Simulation Biodegradation Test” with a powerful liquid chromatography mass spectrometry with scheduled multiple reaction monitoring. The end-point of this research is the identification of pseudo first-order degradation rate constant and half-life of each micropollutant detected in the river water.

2. LITERATURE REVIEW

2.1. Occurrence of Micropollutants in Rivers

Chemical contamination of both groundwater and surface water becomes a worldwide concern because it is one of the major threats to aquatic biodiversity and human health. Rapid increase of pollution in water systems and their long-term effects cannot be estimated. (Vörösmarty et al., 2010, Schwarzenbach et al., 2006). Water quality monitoring studies have been performed focusing on different substances in various regions of the world by using different types of strategies (Sousa et al., 2018). Monitoring devices are selected according to the polarity, volatility or stability of the samples. Generally, liquid or gas chromatography is used for determination of micropollutants. Mass spectrometry methods allows for low concentration detections. It ensures precisely the identification and quantification of micropollutants (Farre et al.,2012).

Sousa et al. (2018) reviewed the studies on the occurrence of PSs an CECs in surface waters, reported in Europe and other countries which are also detected in our samples. Table 2.1 shows maximum detected concentration of compounds and detection locations.

Table 2.1. Maximum detected concentrations and detected locations of micropollutants.

Compound	Max. Concentration (ng L^{-1})	Location
Acetaminophen	9,606.0	Spain
Acetamiprid	380.0	Australia
Aclonifen	0.0	
Alachlor	271.0	Greece
Atrazine	15,000.0	Hungary
Azithromycin	16,663.0	Spain
Carbendazim	697.0	Spain
Carbofuran	>20,000	Canada
Chlorpyrifos	1,011.0	Greece
Ciprofloxacin	13,576.0	Turkey
Clarithromycin	2,403.0	Spain
Di(2- ethylhexyl)phthalate (DEHP)	1,520.0	China
Dichlorvos	250.0	India
Dimethoate	35,440.0	Canada
Diuron	5,008.0	Spain
Erythromycin	2,806.0	Spain
Nonylphenol	1,389.0	China
Norfloxacin	572.0	China
Ofloxacin	990.0	China
PAHs	59,600.0	Iran
Quinoxyfen	0.0	
Simazine	1,820.0	Taiwan
Sulfamethoxazole	1,500.0	Spain
Terbuthylazine	34,000.0	Spain
Terbutryn	1,000.0	Hungary

Soussa et al. (2018) also reported that most frequently studied PSs in the world are atrazine, simazine, chlorpyrifos, terbutryn, diuron and alaclor, respectively. Priority substances which are PAHs, atrazine, di(2-ethyl)phthalate, alaclor, nonyphenol, diuron, terbutryn, simazine and chlorpyrifos were monitored at least once and their concentrations were higher than 0.5 µg/L for the targeted period of time. Although some PSs found at low concentrations in some locations, they should not be underestimated due to their toxicity posing harmful environmental risks even at low concentrations. CECs were also monitored at great number of experiments and their concentrations were measured lower than PSs. Acetaminophen, ciprofloxacin, carbofuran, sulfamethoxazole and ofloxacin were also reported as the most frequently detected polar emerging contaminants.

2.2. Biodegradation of Micropollutants

Biodegradation is accepted as the most important mechanism that determines the fate of micropollutants in the environment. Thus, estimation of biodegradability of micropollutant plays a crucial role on estimation of pollutant behavior in the environment and to evaluate its risk on ecology and human health (Zgajnar et al., 1999). The rate of biodegradation may be affected by different factors including genetic changes, growth of specific degrader microorganisms and depression of enzymes (Shimp et al., 1987). Moreover, any changes in environmental conditions such as light, temperature, salinity, pH and chemicals may influence the rate of biodegradation. Bioavailability is another key factor for biodegradation of chemicals since dissolved chemicals are more likely to be degraded by aquatic microorganisms (Wilkinson et al., 2017).

Many of the hydrophilic organic compounds can be degraded by microorganisms considering environmental conditions such as temperature, pH and presence of capable microbial communities (Mandaric et al., 2015). Sometimes, micropollutant concentrations are relatively low in the wastewater and surface water, therefore, biotransformation of those pollutants requires the presence of additional growth factors (Tran et al., 2013). Biodegradation of micropollutants can be achieved by metabolic or co-metabolic reactions. During the metabolic reactions, microorganisms utilize both organic micropollutants and other organic compounds as growth substrates. These substrates are used to produce energy and carbon source that are used for cell growth and reproduction. If the micropollutant concentration is low, other substances should be present as other growth substrates for sustainable growth of cells (Benner et al., 2013). During co-metabolic reactions, micropollutants are biologically transformed by side reactions of the enzymes (di-oxygenase, hydrolases etc.) or cofactors produced by the microorganism (Fisher et al., 2014). Co-metabolism mostly brings generation of transformation products which may be used as a growth substrate for other

microorganisms (Benner et al., 2013; Tran et al., 2013). For example, Ting et al. (2011) reported that biodegradation rate of butylxanthenes in wastewater highly increased by adding starch, sucrose and glucose in wastewater. Furthermore, when the trace amount of peptone was added as a nitrogen source, similar results were obtained. In complex matrix systems, both metabolism and co-metabolism reactions occur simultaneously because of the diversity of microbial community (Fischer et al, 2014). Thus, biodegradation and biotransformation of micropollutants are considered as a whole and measured by biological removal of parent compound.

Xenobiotics can be defined as chemicals that are not produced by any organisms and environment naturally. Group of polycyclic aromatic hydrocarbons, halogenated aliphatic as well as aromatic hydrocarbons, nitroaromatic compounds, azo compounds, *s*-triazines, organic sulfonic acids, and synthetic polymers are classified as xenobiotics and they are used in drugs, pesticides, cosmetics, flavorings, fragrances and food additives. (Patterson et al., 2010) Persistent xenobiotics and their end products can accumulate in the environment body organs and tissues (Zhu et al., 2017) They can become part of the soil humus or enter the food chain leading to biomagnification. For example; tetrachloroethene and trichloroethene can be biodegraded to vinyl chloride which is carcinogen, in anoxic conditions. In natural environments, the products of bioconversion processes may be further biotransformed or biodegraded by other microorganisms, can lead to complete degradation of xenobiotics (Gibson et al, 1984). Figure 2.1 summarizes the possible fate of xenobiotic compounds.

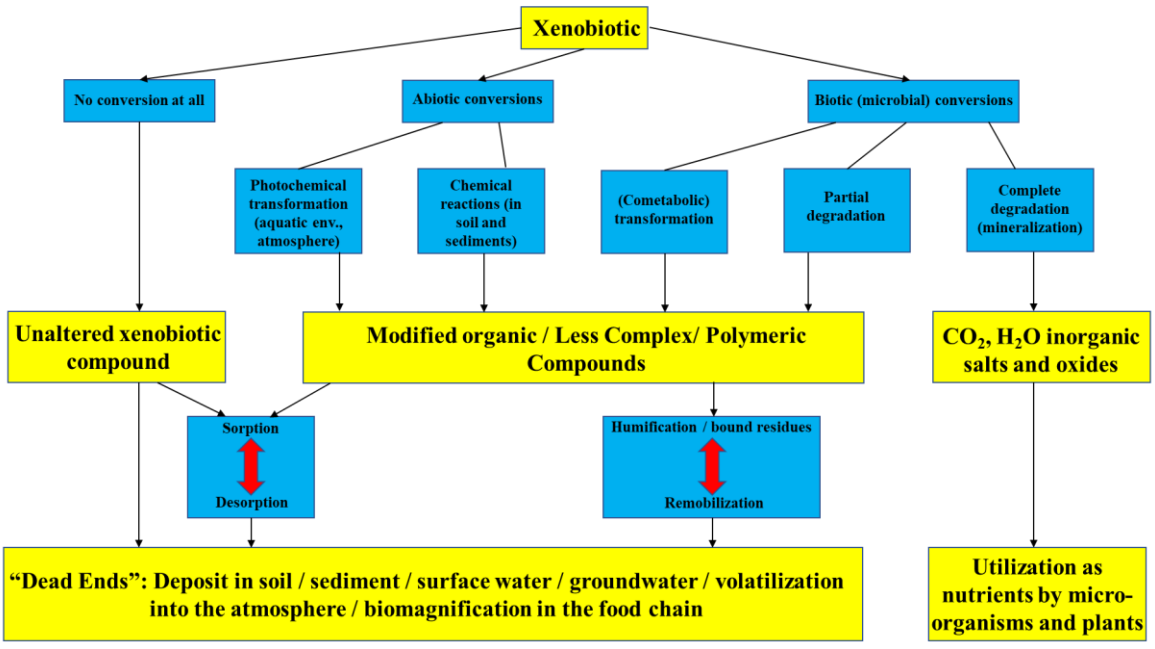


Figure 2.1. Possible environmental fate of a xenobiotic compound (Fetzner, 2001).

The structure of xenobiotic molecules is characterized by unphysiological substituents and stable chemical bonds, which can interrupt or prevent biodegradation. Moreover, concentration of xenobiotics can affect biodegradation. At high concentrations, many of them are toxic to microorganisms. Similarly, in low concentrations, xenobiotics cannot be biodegraded since catabolic enzymes may not be produced. The minimum threshold concentration depends mainly on the kinetic parameters of growth and metabolism, but also on the thermodynamics of the reaction. As a matter of fact, substrate affinity constant is the most important parameter for biodegradation of xenobiotics at very low concentrations. Under aerobic conditions, minimal substrate concentration might be in range between 0.1 and 1.0 mg/L. However, the ideal concentration in environmental systems are frequently less than 1 μg/L. The biodegradation rate of xenobiotics in the environment can range from days and weeks to years and decades. For example, malathion which is used as an insecticide, is completely degraded approximately in one week and 2,4-dichlorophenoxyacetic acid is degraded within four to six weeks. However, DDT which is extensively used from the 1930s to 1970s as an insecticide, have an average half-life of 4.5 years in field soils and 700 days in anoxic soils. Also, resistant metabolites of DDT have been detected not only in soil, but also, water bodies and tissue of organisms (Fetzner., 2001)

Bertelkamp et al. (2014) examined 14 organic micropollutants including ibuprofen, ketoprofen, gemfibrozil, acetaminophen, trimethoprim, caffeine, propranolol, metoprolol, atrazin, carbamazepine, phenytoin, sulfamethoxazole, hydrochlorothiazide and lincomycin relations with biodegradation rate and physico-chemical properties (charge, hydrophobicity and molecular weight) for six months. Biodegradation rates ranged from 1.4-16.3 days, while half-lives range from 0.0-0.5 days. Acetaminophen, ibuprofen, ketoprofen, gemfibrozil, trimethoprim, caffeine, propranolol and metoprolol were found to be biodegradable, while atrazine, carbamazepine, hydrochlorothiazide, lincomycin, phenytoin and sulfamethoxazole showed more persistent behavior. However, atrazine, carbamazepine, hydrochlorothiazide, lincomycin, phenytoin and sulfamethoxazole are not or very poorly biodegraded. Yamamoto et al. (2009) also studied the biotransformation and sorption potential of pharmaceutical compounds (acetaminophen, atenolol, carbamazepine, ibuprofen, ifenprodil, indomethacin, mefenamic acid, and propranolol) in aquatic environment. Almost all of the compounds were relatively persistent to biodegradation. Three of them namely, propranolol, indomethacin, and ifenprodil, were easily photodegraded while the other five were not photodegraded. Kunkel et al. (2008), worked on six commonly founded micropollutants in the aquatic environment. They found that half-lives of diclofenac, bezafibrate, ibuprofen, naproxen were in the range between 2.5 and 18.6 days and of gemfibrozil were 10.5 days.

Complete biodegradation of a chemical can be determined by measuring dissolved organic carbon, biochemical oxygen demand or formation of carbon dioxide. The advantage of this method is that it requires simple techniques. For dissolved organic carbon measurement method, it is difficult to distinguish whether the degradation is biotic or abiotic. However, determination of biochemical oxygen demand or formation of carbon dioxide proves biotic biodegradation. Their disadvantage is, on the other hand, transformation of test materials into biomass is ignored. This test gives accurate results for water soluble chemicals. Chemical specific analytical methods such as high-pressure liquid chromatography, gas chromatography are classified as substance specific analytical methods which require primary degradation of testing chemicals. These processes measure concentration decrease in a chemical and even at low concentrations, gives accurate data. However, they require more complex techniques (Pagga et al., 1997).

Biodegradation kinetics are generally measured by consumption of a chemical versus time in batch experiments and fitting the data with Monod substrate utilization model. Both scientific capacity of accurately determination of the kinetics from the available data and impact of the test technique on physiological condition of the microorganism are two essential qualities of biokinetic determination methods. When using Monod model, it is obvious that non-linear parameter fitting methods is mathematically superior to linear transformation methods such as Linewear-Burke method to estimate the kinetic coefficients. Also, Monod model ought to be utilized which gives a greatest specific substrate degradation rate (k) instead of the maximum growth rate (μmax) in the Monod equation. For Monod models, the recommended range of substrate concentration (S_o), cell concentration, and half-saturation coefficient (K_s) should be 1-20 mg/L, greater than 106 cells per mL and less than 1 mg/L, respectively. More frequent sampling and presence of measured concentration increase the reliability of experimental data (Holmberg, 1982; Ritchie et al., 1996). Additionally, physiological condition of the microorganism is affected by the biokinetic estimation methods which effects the biokinetics of the cultures (Bielefeldt et al., 1999). Ellis et al. (1996) reported that dissolved oxygen respirometry method on batch experiments can accurately determine extant kinetics. They used a fourth order Runga-Kutta fit to collect data at low concentrations. Another method to measure K_s is measuring of the beginning substrate exhaustion rates at a scope of initial substrate concentrations. The pitfall of this method is that incorrect measured S_o data can lead to unreliable results (Bielefeldt et al., 1999).

2.3. Study Area

Ergene basin which is the subject of this study, is one of the 23 basins within the boundaries of Turkey. Ergene basin is part of the Thrace region, located in Marmara region. Total area of basin is 12.438 km^2. Due to increase of industrialization in this region, population is increasing accordingly. Tekirdağ, Kırklareli and Edirne are located in this region and total of 1768000 people live in there (TurkStat, 2017). As can be seen on Table 2.2, although, population of Tekirdağ is higher than the others, all three cities show similar trend in population increase. Also, there are lots of organized industrial zones (OIZs). In Table 2.3, the size of 18 OIZs and their locations can also be seen.

Table 2.2. Population distribution of Ergene Basin over years (TurkStat, 2017).

Province / Year	2012	2013	2014	2015	2016	2017
Edirne	399708	398582	400280	402537	401701	406855
Kırklareli	341218	340559	343723	346973	351684	356050
Tekirdağ	852321	874475	906732	937910	972875	1005463
TOTAL	1593247	1613616	1650735	1687420	1726260	1768368

Table 2.3. Organized industrial zones locations and their sizes.

Organized Industrial Zones	Province	District	Total area (ha)
Edirne OIZ	Edirne	Merkez	589.0
Uzunköprü OIZ	Edirne	Uzunköprü	71.0
Çerkezköy OIZ	Tekirdağ	Çerkezköy	1234.0
Çorlu Leather OIZ	Tekirdağ	Çorlu	130.0
Hayrabolu OIZ	Tekirdağ	Hayrabolu	100.0
Malkara OIZ	Tekirdağ	Malkara	105.0
Veliköy OIZ	Tekirdağ	Çerkezköy	32.0
Ergene-1 OIZ	Tekirdağ	Çorlu	474.0
Ergene-2 OIZ	Tekirdağ	Çorlu	702.0
Çorlu-1 OIZ	Tekirdağ	Çorlu	340.0
Velimeşe OIZ	Tekirdağ	Çorlu	924.0
Muratlı OIZ	Tekirdağ	Muratlı	312.0
Kapaklı OIZ	Tekirdağ	Çerkezköy	210.0
Karaağaç OIZ	Tekirdağ	Çerkezköy	143.0
Yalıboyu OIZ	Tekirdağ	Çerkezköy	33.0
Kırklareli OIZ	Kırklareli	Merkez	850.0
Büyükkarıştıran OIZ	Kırklareli	Lüleburgaz	596.0
Evrensekiz OIZ	Kırklareli	Lüleburgaz	35.0

Ergene Basin has important agricultural areas especially for rice and sunflower plantation. More than 50% of rice and sunflover in Turkey are produced in this region. In addition to this, sugar beet, corn, oat, barley, tomatoes and other vegetables is produced in there (Ministry of Environment and Urbanization, 2016).

Ergene River, which is a 289 km long river, is the only running surface water in the area. It is born in Strandzha Mountain and joins to Maritsa River, then flows into the Aegean Sea from Gulf of Saros. Today, Ergene River is the most pollutant river in Turkey. Water quality in Ergene river is

classified as 4 which means “Highly Polluted”. Ergene River water contains micropollutants including algal toxins, gasoline additives, industrial chemicals, personal care products, pharmaceuticals, flame retardants, metals, pesticides, surfactants some of which are classified as priority pollutants. Pollution in river originated from not only industrial zones but also, domestic and agricultural activities contribute to pollution in river. Generally, in this region drinking water and irrigation water are supplied from groundwater. However, due to the drastic decrease in the water tables, water reuse and usage of surface water for irrigation and industrial activities are alternatives. In addition, the Ergene river water quality is posing a health threat to the surrounding community. As a result, Ministry of Forestry and Water Works is taking actions to improve the water quality of Ergene River and targeted to bring it class 2 by the year 2020 by installing wastewater treatment plants for both municipalities and industries and improving water quality monitoring. Thus, determining biological fate of micropollutants existing in Ergene River is so important for recovery of water quality in Ergene River.

3. MATERIALS AND METHODS

3.1. High-throughput Biodegradation Experiment

3.1.1. Source of Inoculum

About 100 mL of sample taken from the biological treatment unit of Luleburgaz Wastewater Treatment Plant was diluted with 900 mL secondary effluent which was taken from the same treatment plant in 2-L glass bottle. The reactor was operated fed-batch with 7-days solids retention time and fed with 0.250 g glucose and 0.250 g tryptone three times a week. In each time, secondary effluent was used to replace the liquid taken out of the reactor to maintain the SRT. The reactor was aerated continuously while agitated on a magnetic stirrer. The content in the reactor served as the inoculum for the biodegradability test described below.

3.1.2. Chemicals and Reagents

In this study, we tested biodegradability of 32 organic chemicals that have been listed either as CECs by NORMAN Network or “priority substances” in Water Framework Directive of European Commission. Those chemicals included: (1) antibiotics such as amoxicillin, azithromycin, ciprofloxacin, erythromycin, norfloxacin, ofloxacin, sulfamethoxazole; (2) industrial chemicals such as diphenylamine, hexadecyl benzyl dimethyl ammonium, drometrizole, 8-hydroxyquinoline; (3) pharmaceuticals and personal care products such as paracetamol, N,N-Diethyl-m-toluamide, galaxolide, gamma-methyl ionone, tonalide and (4) agricultural chemicals including prochloraz, linuton, alachlor, atrazine, isoproturon, simazine, triazophos, chlorfenvinphos, chlorpyrifos, dichlorvos, pyriproxifen, quinoxyfen, aclonifen, terbutryn, piperonylbutoxide. The water-octanol partitioning coefficient (logP) of these chemicals ranges between -1.03 and 6.23. These chemicals were purchased from Sigma Aldrich Chemical Company at their highest purity. The stock solutions of these chemicals were prepared in methanol at 1000 ppm and stored at -20 °C until used. Methanol and water used in sample preparation as well as in chromatography were obtained from Merck Chemicals at MS grade.

3.1.3. Experimental Set-up

Biodegradation experiments were performed according to the modified OECD Test No 314B: Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater. Experiment was performed in 250-mL amber Erlenmeyer Flasks with screw caps. About 5 mL of sample taken from the reactor described above was diluted with 45 mL of salt medium composed of 85 mg/L KH_2PO_4, 217.5 mg/L K_2HPO_4, 334.0 mg/L $Na_2HPO_4.2H_2O$, 5.0 mg/L NH_4Cl, 36.4 mg/L $CaCl_2.2H_2O$, 22.5 mg/L $MgSO_4.7H_2O$ and 0.25 mg/L $FeCl_2.6H_2O$. Then, a mixture of test substances was added in to the flask. The initial concentration of each substance in the flask was 10 µg/L. A flask without inoculum was served as a control. All flasks were agitated at 100 rpm and incubated at 22°C for 28 days. Samples taken from the flask at specified time intervals were mixed with an equal volume of methanol, centrifuged at 10,000 rpm and filtered through regenerated cellulose filter having 0.22 µm pore size. Chemicals were measured using liquid chromatography with mass spectrometry as described below.

3.2. Microcosm Experiment

3.2.1. Sampling Points

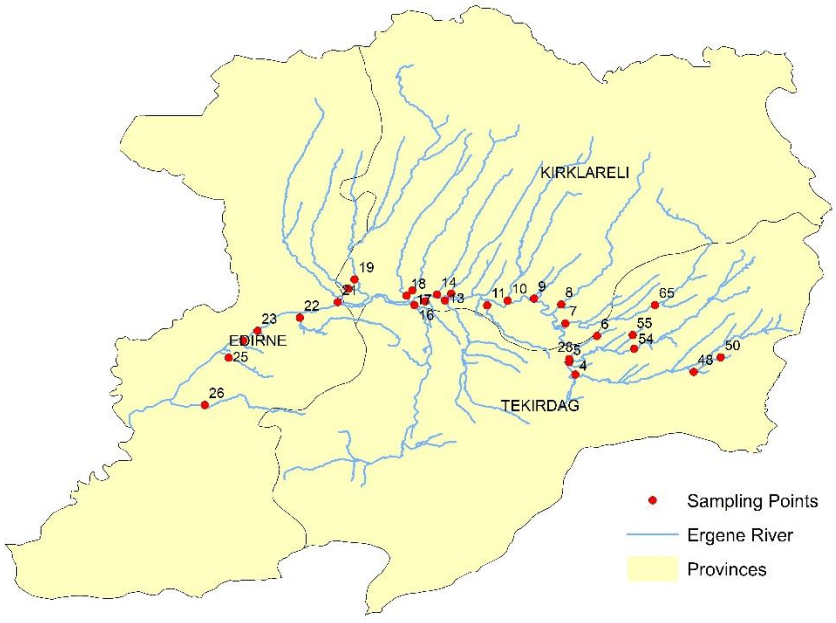


Figure 3.1. Map showing the all 29 sampling sites on Ergene River.

75 sampling points have been determined at the beginning of the project. 29 out of 75 sampling points were selected for biotransformation test in this project which are located on map as can be seen

in Figure 3.1. Among these 29 sampling points, discharging points are intentionally added to record the source of the micropollutants. From these sampling points selected, it is also aimed to observe dilution rate of micropollutants along the river. All points on map are located intentionally to cover all of the micropollutant sources such as agricultural areas, livestock farming, textile industrial areas, food factories, oil industry, painting industry and domestic direct discharges along with their exact coordinates.

Detailed sampling point coordinates and their all suspected source of micropollutants in Ergene river are given in Table 3.1. The samples were taken at the same day and stored in amber coated bottles at +4°C.

Table 3.1. Sampling point coordinates and its suspected source of micropollutants.

Sampling point	*Coordinate*	*Suspected source of micropollutant*
4	41°09'39"N 27°29'46"E	Urban waste water direct discharge, poultry farming, printing industry, textiles
5	41°11'36"N 27°28'33"E	Urban waste water direct discharge, vegetable oil industry, textile dye
6	41°15'44"N 27°32'52"E	Food industry, aluminum industry, dye industry, packaging industry, textiles
7	41°17'31"N 27°28'12"E	Milk and milk products industry, agriculture and livestock breeding
8	20°29'68"N 27°27'22"E	Food industry, breweries, paper mills, chemical factories, textiles
9	21°24'02"N 27°23'12"E	Urban waste water direct discharge, oil industry, flour mill
10	41°21'03"N 27°19'10"E	Urban waste water direct discharge, mixed agricultural area
11	41°20'16"N 27°16'05"E	Food industry, oil industry, non-irrigated agricultural area, organic agricultural enterprises
12	41°22'01"N 27°10'36"E	Non-irrigated agricultural area, food industry
13	41°22'05"N 27°09'37"E	Urban waste water direct discharge, non-irrigated agricultural area, milk and milk products industry
14	41°22'15"N 27°08'36"E	Urban waste water direct discharge, industrial waste water discharge, sugar refinery
15	41°20'56"N 27°06'32"E	Urban waste water direct discharge, oil industry,
16	41°20'23"N 27°04'54"E	Rice fields
17	41°22'38"N 27°04'33"E	Urban waste water direct discharge, oil industry, pharmaceutical industry, packaging industry
18	41°21'48"N 27°03'41"E	Rice fields

19	41°24'19"N 26°55'43"E	Mixed agricultural area
20	41°22'53"N 26°54'47"E	Rice fields
21	41°20'51"N 26°53'09"E	Mixed agricultural area
22	41°18'27"N 20°47'21"E	Rice fields, non-irrigated agricultural area
23	41°16'26"N 26°40'52"E	Rice fields, oil industry, meat packing industry
24	41°14'57"N 26°38'41"E	Rice fields, oil industry
25	41°12'18"N 26°36'28"E	Rice fields
26	41°05'05"N 26°32'48"E	Rice fields
28	41°12'06"N 27°28'39"E	Oil industry, textiles (denim), printing industry, fishery industry, textile dye
48	41°10'09"N 27°47'40"E	Chemical factories, flour mill, textiles
50	41°12'23"N 27°51'48"E	Urban waste water direct discharge, packaging industry, plastic factories
54	41°13'43"N 27°38'34"E	Milk and milk products industry, textiles
55	41°15'47"N 27°38'21"E	Paper mills, plastic factories, aluminum industry, dye industry, textiles
65	41°20'24"N 27°41'43"E	Beverage factories, textiles

3.2.2. Microcosm Biotransformation Experiment Set-up

The experiments were performed based on the OECD Guideline 309 “Aerobic Mineralization in Surface Water – Simulation Biodegradation Test”. This simulation test was a laboratory shake flask batch test to determine rates of aerobic biodegradation of organic substances in samples of natural surface water. The principal objective of the simulation test was to determine the mineralization potential of the test substance in surface water as well as the mineralization rate.

About 100 mL of sample was taken from each sampling point and transferred into 250 mL amber glass Erlenmeyer Flasks (Figure 3.2). Each flask was spiked with 10 µg/L acetaminophen as a biodegradable reference substrate. Acetaminophen is known to get degraded within 5 days in an active surface water microbial community, therefore its degradation served as a control of biological activity. Also, a flask which consisted of pure water and same concentration of reference substance was used as a control to detect any contamination.

After all flasks were prepared, they were incubated at room temperature between 20-25℃ and agitated at 100 rpm for 30 days. 1 mL of sample was taken from reactor at specified time intervals and mixed with 1 mL of methanol in a centrifuge tube. This mixture centrifuged at 10,000 rpm and filtered through regenerated cellulose filter having 0.22 µm pore size. These steps were performed for all reactors and micropollutants in each reactor were analyzed using liquid chromatography with tandem mass spectrometry during the incubation period.

Figure 3.2. Ergene river water samples.

3.3. Analytical Methods

An AB SCIEX QTrap 4500 shown in Figure 3.3 linear ion trap tandem mass analyzer system coupled with Eksigent Ekspert UltraLC 110 ultra-high performance liquid chromatography (UHPLC) unit was used in quantification of the chemicals used in this study.

Figure 3.3. Liquid chromatography and mass spectrometer.

UHPLC was equipped with Phenomenex Kinetex C18 2.6µ column (50 x 3 mm). Mobile phases included water (A) and methanol (B) buffered with 0.1% formic acid. A gradient elution was performed for separation of the analytes (Table 3.2). The flow rate was constant at 0.5 mL/min and the column was kept at 40℃. Overall run time was 14 minutes. All analytes were detected within 8 minutes. Scheduled Multiple Reaction Monitoring (MRM) was performed for detection and

quantification of the chemicals. Optimized MRM parameters were scanned at the determined retention times of the chemicals (parent compounds) during the gradient elution and can be found in Appendix A.

Table 3.2. Details of gradient elution applied for the separation of chemicals in UHPLC.

TIME	**A (%)**	**B (%)**
0:00:01	0	100
0:01:30	0	100
0:02:00	50	50
0:04:00	50	50
0:08:00	100	0
0:14:00	100	0

4. RESULTS AND DISCUSSION

4.1. High-throughput Screening of Biodegradation of Multiple Contaminants

Biodegradation test lasted 28 days. At the end of the incubation, only 7 out of 32 chemicals tested were degraded above 60 percent (Figure 4.1). Those chemicals were acetaminophen, benzyl dimethyl hexadecyl ammonium, diphenylamine, g-methylionene, pyriproxyfen, sulfamethoxazole and tonalide. The biodegradation extent of those chemicals was above 60% at the end of the incubation. Biodegradation rate (Equation 4.1) and the corresponding half-life ($t_{1/2}$) (Equation 4.2) of the chemicals were calculated by fitting first order degradation kinetics equation to the experimental data obtained for 28 days. The rate constant of a reaction under constant conditions is proportional to the concentration of the reactants. In first-order reactions, the reaction rate depends on the concentration of only one of the reactants. Thus, in complex systems, to calculate of each chemicals degradation rate constant, first order decay rate is used.

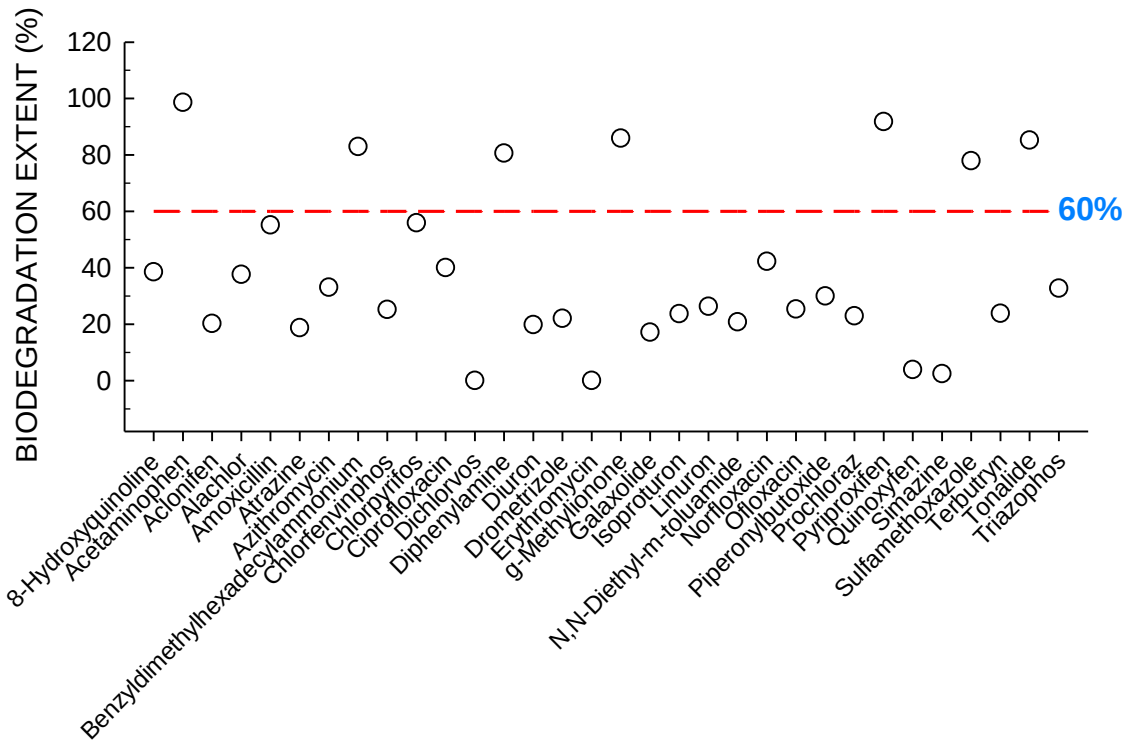


Figure 4.1. Biodegradation extent of chemicals.

$$\frac{C}{C_0} = e^{-kt} \tag{4.1}$$

$$t_{1/2} = \frac{ln2}{k} \tag{4.2}$$

where C is the concentration of the chemical (µg/L) at time t (d), C_0 is the initial concentration, k is the biodegradation rate constant (d^{-1}), $t_{1/2}$ is the half-life of a chemical (d).

Acetaminophen, which is an active ingredient of analgesic drugs, was completely degraded within 5 days (Figure 4.2.A). Its degradation rate and corresponding half-life were 1.24 d^{-1} and 0.56 d^{-1} (Table 4.1). Several microorganisms that can degrade acetaminophen have been isolated (De Gusseme et al., 2011, Hu et al., 2013). The main mechanism of the degradation is deacetylation which converts acetaminophen to p-aminophenol (Wu et al., 2012). P-aminophenol is more toxic than the parent compound.

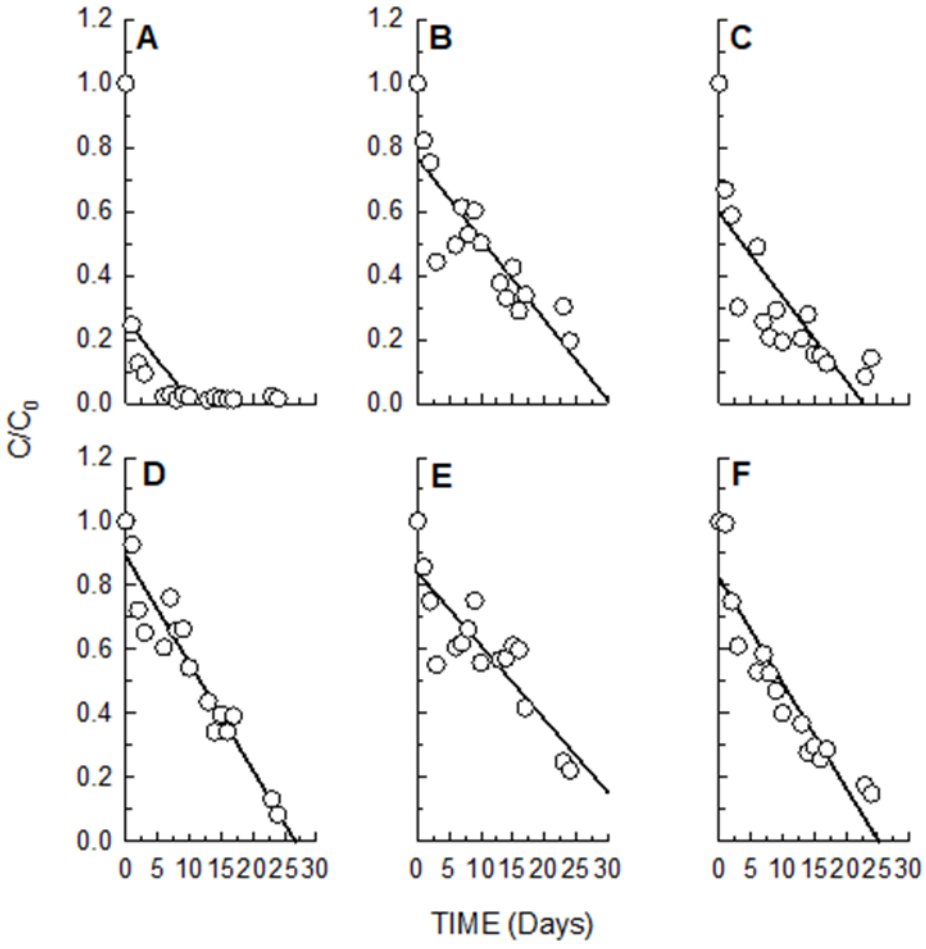


Figure 4.2. Biodegradation profile of (A) Acetaminophen; (B) Diphenylamine; (C) g-methylionene; (D) Pyriproxyfen; (E) Sulfamethoxazole and (F) Tonalide.

Diphenylamine is mainly used in the production of dyes, pesticides, pharmaceuticals, and photographic chemicals and as stabilizer for explosives. In addition, it is formed as a reaction byproduct during aniline production (Shin and Spain 2009). About 80% of dipenylamine amended into the test flasks were utilized within 28 days (Figure 4.2.B). Half-life of diphenylamine was 12 days which suggests that this chemical is not readily biodegradable (Table 4.1). On the contrary, half-life of diphenylamine was reported as 0.54 days in experiments performed with cultures of *Pseudomonas cepacia, Pseudomonas putida, Pseudomonas resinovorans* and mixed activated sludge (Christodoulatos et al., 1997). Diphenylamine biotransformation starts with integration of two hydroxyl groups to one benzyl group by an action of a novel dioxygenase enzyme. Reaction results in formation of aniline and catechol which are further mineralized to carbon dioxide and ammonium. Relatively, recently *Burkholderia* sp. strain JS667 and *Ralstonia* sp. JS668 which can utilize diphenylamine as both carbon and nitrogen source were isolated (Shin and Spain 2009).

g-Methylionene, which is a fragrance, was degraded rapidly. Over 80% of g-methylionene was utilized within 5 days (Figure 4.2.C). The half-life of this chemical was 5.6 days (Table 2.2). Yamazaki et al. (1988) showed that g-methylionene was degraded by cis/trans hydroxylation by *Aspergillus niger* (Yamazaki et al., 1988).

Pyriproxyfen, which is a pyridine-based pesticide, was completely degraded within 28 days (Figure 4.2.D). Its half-life was calculated as 11 days (Table 4.1). Similarly, Fathulla (1993) reported a half-life of 23 days for pyriproxyfen (Fathulla 1993). During the biodegradation of pyriproxyfen, two major by-products i.e. 4-(4'-hydroxyphenoxy)phenyl-2-(2-pyridyloxy)-propyl ether and 2-(2-pyridyloxy) propionic acid were identified (Fathulla 1993).

Sulfamethoxazole is one of the most frequently detected antibiotic in wastewater and surface water. Biodegradation of sulfamethoxazole by mixed cultures or pure strains have been reported (Larcher and Yargeau 2012, Nguyen et al., 2017). In our study, 80% of sulfamethoxazole were degraded within 25 days with a corresponding half-life of 18 days (Figure 4.2.E and Table 4.1). The half-life of sulfamethoxazole was the highest among the other chemicals that were degraded, this probably due to its antimicrobial effect although its test concentration was low. Sulfamethoxazole degradation is initiated by hydroxylation of the carbon atom attached to the sulfonyl group (ipso-hydroxylation). The most common by-products detected include 3-amino-5-methylisoxazole, and benzoquinone-imine (Birkigt et al., 2015, Jiang et al., 2014). The latter is then transformed to 4-aminophenol.

Tonalide is a musk that is extensively used in fragrances. Above 80% of the tonalide was degraded in 25 days with a half-life of 9 days (Figure 4.2 and Table 4.1).

Table 4.1. Biodegradation rate constants and half-lives of six biodegradable chemicals tested in this study.

Compound	**k (d^{-1})**	**$t_{1/2}$ (days)**	**R^2**
Acetaminophen	1.24	0.56	0.99
Diphenylamine	0.0572	12.12	0.80
Methyl ionene	0.1241	5.59	0.81
Pyriproxyfen	0.0623	11.13	0.89
Sulfamethoxazole	0.0382	18.15	0.72
Tonalide	0.0807	8.59	0.95

On the contrary, concentration of the rest of the chemicals that are not biodegradable such as quinoxyfen (Figure 4.3.A) and simazine (Figure 4.3.B) did not change during the incubation period. Although there is no evidence for the biodegradation of quinoxyfen, simazine, which is a triazine pesticide, is known to be utilized as carbon and nitrogen source by microorganisms (Barra Caracciolo et al., 2005, Blaszak et al., 2011, Kodama et al., 2001, Wan et al., 2014). This suggests that some of the chemicals, like simazine, that are known to be degraded in the environment may not be degraded by every microbial community due to the lack of specific microorganisms.

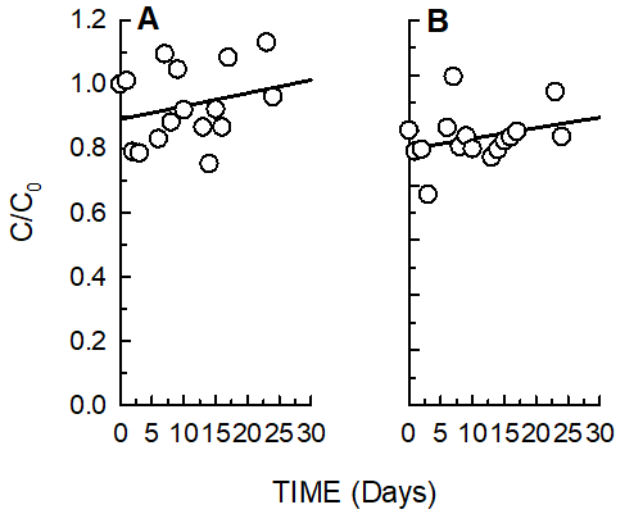


Figure 4.3. Biodegradation profile of (A) Quinoxyfen and (B) Simazine.

In this study, we showed that conventional biodegradation tests may be enhanced by coupling mass spectrometry and become sounder and representative for testing biodegradation of chemicals.

This is the first study that tested the biodegradation of many compound simultaneously at such low concentrations.

4.2. Biodegradation of Micropollutants in River Water

Microcosm biodegradation tests were lasted 30 days. Acetaminophen in the control bottle was not degraded suggesting that contamination was avoided in the course of incubation (Figure 4.4). Furthermore, the biodegradation was ensured by using of amber glass bottles preventing transmission of UV light. Therefore, the decrease in concentration was not caused by photodegradation. Also, using sterile bottles proves that biodegradation of micropollutants was carried out by the river microbial community. Thus, any change in concentration of micropollutants was caused by Ergene river microbial communities. Biodegradation rate constants of each compound in the river water samples were calculated based on the experimental data using Equation 4.1 and summarized in Table 4.2.

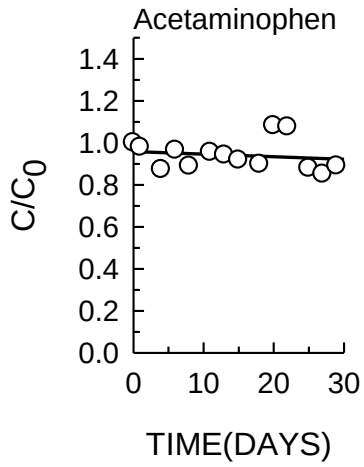


Figure 4.4. Biodegradation profile of control sample.

Table 4.2. Biodegradation rate constants (k values, d^{-1}) of chemicals in all sampling points.

Sampling points / Chemicals	1,2,3-Benzotriazole	2,4-Dihydroxybenzophenone	2-Mercapto-benzothiazole	3-Chloroaniline	4-Chloroaniline	4-Methyl-1H-benzotriazole
4	0.00	0.20	0.16	ND	0.59	0.00
5	0.00	ND	ND	0.86	0.43	0.00
6	0.00	ND	ND	ND	ND	ND
7	0.00	ND	ND	ND	ND	ND
8	0.00	ND	ND	ND	ND	2.92
9	ND	ND	ND	ND	ND	ND
10	0.00	ND	ND	ND	ND	0.00
11	0.00	0.21	ND	ND	ND	0.00
12	0.00	ND	ND	ND	ND	ND
13	0.00	ND	ND	ND	ND	0.00
14	0.00	0.11	ND	ND	ND	0.00
15	ND	ND	ND	ND	ND	ND
16	ND	ND	ND	ND	ND	ND
17	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND
19	0.27	ND	ND	ND	ND	ND
20	0.27	ND	ND	ND	ND	ND
21	0.00	ND	ND	ND	ND	ND
22	ND	ND	ND	ND	ND	ND
23	0.00	0.08	ND	ND	ND	0.00
24	0.00	ND	ND	ND	ND	0.00
25	0.00	ND	ND	ND	ND	0.00
26	ND	ND	ND	ND	ND	ND
28	0.00	0.18	0.00	ND	0.74	0.00
48	ND	ND	ND	0.00	0.00	ND
50	0.00	ND	ND	0.16	0.07	0.00
54	ND	ND	ND	0.46	0.00	ND
55	0.00	ND	ND	ND	ND	ND
65	ND	ND	ND	ND	ND	ND

Table 4.2. Continued.

Sampling points / Chemicals	4-Methylbenzylidenecamphor	4-tert-Octylphenol diethoxylate	5-Methyl-1H-benzotriazole	Acetaminophen	Acetamiprid	Aclonifen
4	7.13	0.17	0.00	7.13	0.00	7.13
5	ND	7.13	ND	7.13	0.00	0.00
6	ND	0.69	0.00	7.13	0.30	0.68
7	ND	ND	0.00	4.09	ND	0.00
8	ND	ND	3.17	3.13	ND	ND
9	ND	ND	ND	0.24	ND	ND
10	ND	ND	0.00	7.13	ND	1.41
11	ND	ND	0.00	1.93	0.00	ND
12	ND	ND	ND	0.52	ND	7.13
13	ND	ND	0.00	7.13	0.00	ND
14	ND	ND	0.00	2.59	ND	ND
15	ND	ND	ND	0.49	0.15	ND
16	ND	ND	ND	0.47	ND	ND
17	ND	0.00	ND	0.51	ND	ND
18	ND	ND	0.00	0.59	ND	1.26
19	ND	ND	7.13	0.35	ND	ND
20	ND	ND	ND	0.16	ND	ND
21	ND	ND	ND	0.36	ND	ND
22	ND	ND	ND	0.17	ND	ND
23	ND	0.00	0.00	5.59	0.00	ND
24	ND	0.00	0.00	0.91	ND	ND
25	ND	0.00	0.00	0.51	0.00	ND
26	ND	ND	ND	0.07	ND	0.00
28	ND	0.00	0.00	3.23	0.00	ND
48	ND	0.05	0.00	7.13	0.00	ND
50	ND	ND	ND	4.02	ND	ND
54	ND	0.05	0.00	4.02	0.00	ND
55	ND	0.05	ND	7.13	ND	ND
65	ND	ND	ND	2.39	ND	ND

Table 4.2. Continued.

Sampling points / Chemicals	AHDI (Phantolide)	Atrazine-desethyl	Azithromycin	Benzyldimethyldodecylammonium	Benzyldimethylhexadecylammonium	Benzyldimethyltetradecylammonium
4	0.34	0.00	ND	0.32	0.17	ND
5	0.26	0.00	ND	0.46	ND	ND
6	0.31	0.00	ND	2.72	ND	ND
7	ND	ND	ND	0.00	ND	0.00
8	0.23	0.09	0.20	0.23	ND	0.23
9	ND	0.00	ND	0.05	ND	0.09
10	ND	ND	ND	0.00	ND	0.96
11	ND	0.00	ND	0.00	ND	0.05
12	ND	0.00	ND	0.00	ND	0.00
13	ND	0.09	ND	0.00	ND	0.14
14	0.39	0.00	ND	0.00	ND	ND
15	ND	0.04	ND	0.00	ND	0.05
16	ND	ND	ND	0.31	ND	0.08
17	ND	ND	ND	0.00	ND	ND
18	ND	ND	ND	0.00	ND	0.00
19	ND	ND	ND	0.00	ND	0.00
20	ND	ND	ND	0.00	ND	0.00
21	ND	0.00	ND	0.00	ND	0.00
22	ND	ND	ND	0.20	ND	0.07
23	ND	ND	ND	0.00	ND	0.00
24	ND	ND	ND	0.00	ND	0.00
25	ND	ND	ND	0.00	ND	0.00
26	ND	ND	ND	0.00	ND	0.00
28	0.12	0.00	ND	1.93	ND	0.06
48	0.13	0.05	ND	0.26	ND	0.00
50	0.19	0.05	ND	0.46	ND	0.06
54	0.23	ND	ND	0.50	ND	0.08
55	0.14	ND	ND	1.67	ND	1.42
65	ND	ND	ND	ND	ND	0.00

Table 4.2. Continued.

Sampling points / Chemicals	Benzyltrimethylammonium	Boisvelone / Iso-Esuper	Carbofuran	Chloramphenicol	Ciprofloxacin	Clarithromycin
4	ND	ND	ND	ND	0.00	0.20
5	ND	ND	ND	ND	0.00	ND
6	ND	ND	ND	ND	0.00	ND
7	ND	ND	ND	ND	0.00	ND
8	0.08	ND	ND	ND	0.00	0.37
9	ND	0.00	0.27	0.10	0.03	ND
10	ND	ND	ND	ND	0.00	ND
11	0.05	ND	ND	ND	0.00	1.76
12	ND	ND	ND	ND	0.00	ND
13	0.05	ND	ND	ND	0.00	ND
14	ND	0.00	ND	ND	0.04	0.47
15	0.07	ND	ND	ND	0.00	ND
16	ND	ND	ND	ND	ND	ND
17	ND	7.13	ND	ND	ND	0.00
18	ND	ND	ND	ND	ND	ND
19	0.07	ND	ND	ND	0.00	ND
20	0.06	ND	ND	ND	ND	ND
21	0.12	ND	ND	ND	ND	ND
22	0.07	ND	ND	ND	ND	ND
23	0.06	ND	ND	ND	0.00	ND
24	ND	ND	ND	ND	0.00	ND
25	0.12	ND	ND	ND	0.00	ND
26	ND	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	0.00	ND
48	ND	ND	ND	ND	0.00	ND
50	ND	ND	ND	ND	ND	ND
54	0.15	ND	ND	ND	ND	ND
55	ND	ND	ND	ND	ND	ND
65	ND	ND	ND	ND	ND	ND

Table 4.2. Continued.

Sampling points / Chemicals	Damascone	Di(2- ethylhexyl)phthalate (DEHP)	Dicyclohexylamine	Erythromycin	Flutriafol	Imazalil
4	ND	ND	0.27	ND	ND	ND
5	ND	ND	0.46	ND	ND	ND
6	ND	ND	ND	ND	ND	ND
7	ND	ND	0.00	ND	ND	ND
8	ND	0.25	0.13	1.91	ND	0.93
9	ND	ND	0.04	ND	ND	0.00
10	ND	ND	0.00	ND	ND	ND
11	ND	0.00	0.00	ND	ND	ND
12	ND	ND	0.16	ND	ND	ND
13	ND	0.00	ND	ND	0.00	ND
14	ND	0.00	ND	ND	ND	ND
15	ND	0.00	0.00	ND	7.13	ND
16	ND	ND	ND	ND	0.00	ND
17	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND
19	ND	ND	ND	ND	ND	ND
20	ND	ND	0.07	ND	ND	ND
21	ND	ND	ND	ND	ND	ND
22	ND	ND	ND	ND	ND	ND
23	ND	ND	ND	ND	ND	ND
24	ND	ND	0.08	ND	ND	ND
25	ND	ND	0.00	ND	ND	ND
26	ND	ND	ND	ND	ND	ND
28	ND	ND	0.46	ND	ND	ND
48	ND	ND	0.00	ND	ND	ND
50	ND	ND	0.21	ND	ND	ND
54	ND	ND	0.33	ND	ND	ND
55	0.09	ND	ND	ND	ND	ND
65	ND	ND	ND	ND	ND	ND

Table 4.2. Continued.

Sampling points / Chemicals	Lenacil	Mepiquat chloride	Monocrotophos	N,N-Diethyl-m-toluamide	N-Benzyldimethylamine	N-Benzylmethylamine
4	ND	0.00	0.34	0.12	ND	0.43
5	ND	0.00	ND	0.00	ND	0.30
6	ND	0.18	ND	ND	ND	ND
7	ND	ND	ND	0.00	ND	ND
8	0.32	1.72	ND	0.07	0.15	ND
9	0.22	0.20	ND	0.00	ND	ND
10	ND	ND	ND	0.03	0.13	ND
11	ND	ND	ND	3.77	0.17	ND
12	ND	ND	ND	0.00	0.08	ND
13	ND	ND	ND	0.00	0.08	0.12
14	ND	ND	ND	4.04	0.14	0.12
15	ND	ND	ND	0.10	0.16	ND
16	ND	ND	ND	0.00	0.04	ND
17	ND	ND	ND	0.08	0.09	ND
18	ND	ND	ND	0.00	ND	ND
19	ND	ND	ND	0.00	0.00	ND
20	ND	ND	ND	0.00	0.00	ND
21	ND	ND	ND	0.05	0.03	ND
22	ND	ND	ND	0.00	0.10	ND
23	ND	ND	ND	ND	ND	ND
24	ND	ND	ND	ND	ND	ND
25	ND	ND	ND	0.00	ND	ND
26	ND	ND	ND	ND	ND	ND
28	ND	0.00	0.07	0.15	0.44	0.39
48	ND	ND	ND	0.00	0.24	0.14
50	ND	ND	ND	0.00	ND	0.57
54	ND	0.07	ND	0.12	ND	ND
55	ND	ND	ND	0.00	ND	ND
65	ND	ND	ND	0.00	ND	ND

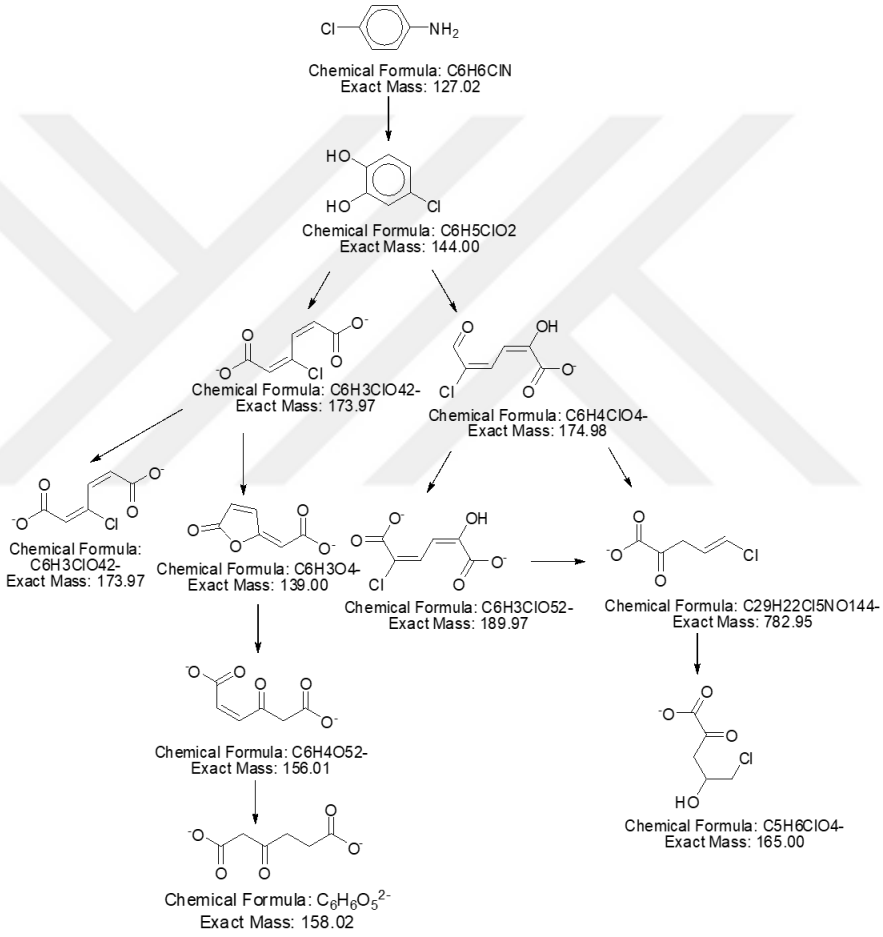
Table 4.2. Continued.

Sampling points / Chemicals	Nonylphenol diethoxylate	Oxybenzone	Piperonylbutoxide	Pirimicarb	Prochloraz	Pyraclostrobin
4	0.20	ND	0.45	ND	ND	ND
5	0.17	0.00	0.16	ND	0.18	ND
6	0.58	ND	0.00	ND	ND	ND
7	ND	ND	7.13	ND	ND	ND
8	0.16	ND	0.20	1.67	ND	ND
9	0.08	ND	0.24	0.72	0.00	ND
10	0.10	0.00	0.10	ND	ND	ND
11	0.17	ND	0.15	ND	0.00	ND
12	ND	ND	0.07	ND	ND	ND
13	ND	ND	0.43	ND	0.00	ND
14	0.24	0.08	0.21	ND	ND	ND
15	ND	ND	ND	ND	ND	ND
16	ND	0.43	ND	ND	ND	ND
17	ND	ND	ND	ND	ND	ND
18	ND	0.05	ND	ND	ND	ND
19	ND	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND	ND
21	ND	ND	ND	ND	ND	ND
22	ND	ND	ND	ND	ND	ND
23	0.07	ND	0.12	7.13	ND	ND
24	0.05	ND	0.08	ND	ND	ND
25	ND	ND	ND	ND	ND	0.04
26	ND	ND	ND	ND	ND	ND
28	0.38	0.17	0.20	ND	ND	ND
48	0.24	0.03	0.18	ND	ND	ND
50	0.33	ND	ND	ND	ND	ND
54	0.26	ND	0.21	ND	ND	ND
55	0.47	ND	ND	7.13	ND	ND
65	ND	ND	ND	ND	ND	ND

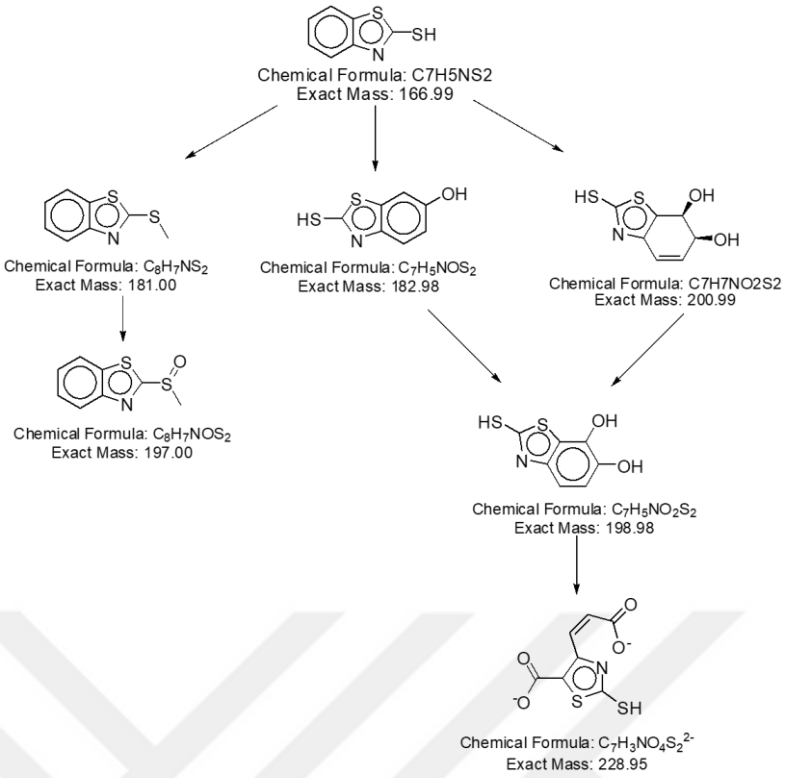
Table 4.2. Continued.

Sampling points / Chemicals	Quinalphos	Spiroxamine	Tetradecyldimethylbenzylammonium	Trifloxystrobin	Tris(2-butoxyethyl) phosphate
4	ND	ND	ND	ND	0.08
5	ND	ND	ND	ND	0.05
6	ND	ND	ND	ND	0.36
7	ND	ND	ND	ND	ND
8	0.65	ND	ND	ND	0.92
9	ND	0.03	ND	ND	ND
10	ND	ND	ND	ND	0.00
11	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	7.13
13	ND	ND	ND	ND	0.00
14	ND	ND	0.09	ND	3.18
15	ND	ND	ND	ND	ND
16	ND	ND	0.10	ND	ND
17	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND
19	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND
21	ND	ND	ND	ND	ND
22	ND	ND	ND	ND	ND
23	ND	ND	ND	ND	0.04
24	ND	ND	ND	ND	ND
25	ND	ND	ND	0.46	0.03
26	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	0.06
48	ND	ND	ND	ND	0.00
50	ND	ND	ND	ND	0.21
54	ND	ND	ND	ND	0.10
55	ND	ND	ND	ND	0.18
65	ND	ND	ND	ND	ND

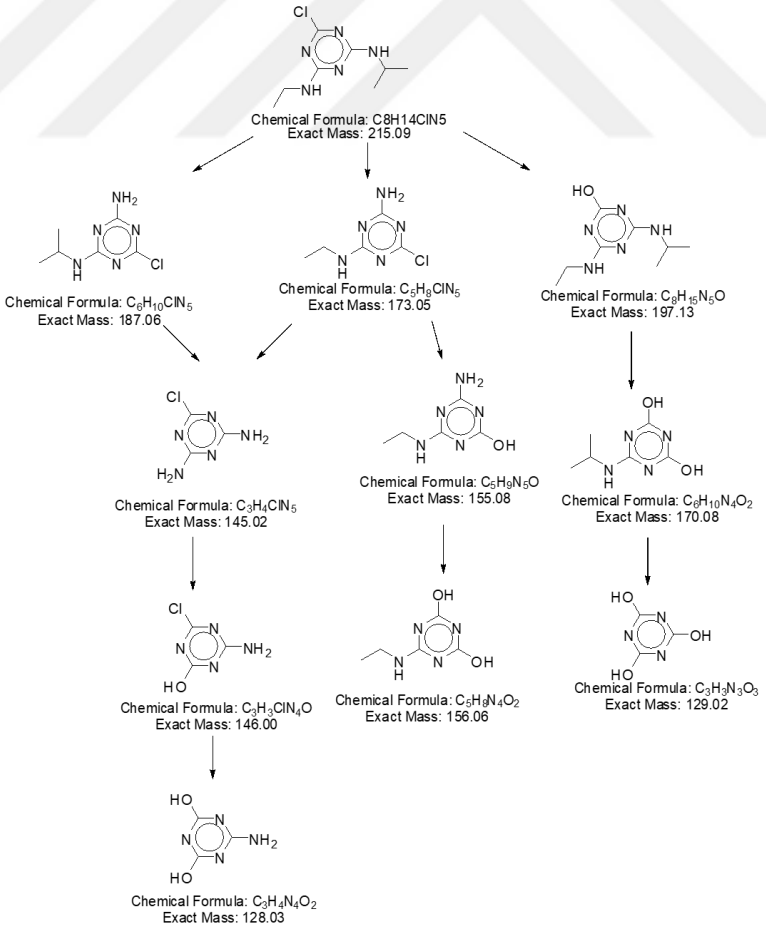
Some of micropollutants biodegraded with different k values at different sampling points. There are several possible reasons of this situation. First of all, the number of microorganisms exist in an environment which have the capability of biodegradation directly affects the k value of a micropollutant. Secondly, at different sampling points, variation of pH value of river water can affect the biodegradation rate. Also, different microorganism communities may degrade a chemical with different rates. Another reason is that there might be different biodegradation pathways. In Figure 4.5, the possible biodegradation pathways of 4-Chloroaniline (A), 2-Mercaptobenzothiazole (B) and Atrazine (C) be examples. Thus, k value showed distribution at different sampling points.



(A)



(B)



(C)

Figure 4.5. Possible biodegradation pathways of Chloroaniline (A), 2-Mercaptobenzothiazole (B) and Atrazine (C).

Sampling Point 4 is located on the downstream of Çorlu Creek close to the Muratlı Province (Figure 4.6). This point is under the pollution stress of domestic discharge, solid waste disposal land leachate, industrial discharge and agricultural runoff.

Figure 4.6. Sampling point 4.

The COD, color, TOC of the water was 804.57 mg/L, 455.00 ADMI, 150.23 mgC/L, respectively. Thirty-three pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.82), 2,4-dihydroxybenzophenone (0.54), 2-mercapto-benzothiazole (10.52), 4-methyl-1H-benzotriazole (4.39), 4-methylbenzylidenecamphor (0.57), 4-tert-Octylphenol diethoxylate (0.10), 5-methyl-1H-benzotriazole (2.35), acetaminophen (3.58), acetamiprid (0.09), aclonifen (0.23), AHDI (Phantolide) (5.24), atrazine-desethyl (0.03), benzyldimethyldodecylammonium (24.73), benzyldimethyltetradecylammonium (4.75), carbendazim (5.08), ciprofloxacin (5.97), clarithromycin (0.35), dicyclohexylamine (0.59), diuron (1.16), hexa(methoxymethyl)melamine (45577.68), mepiquat chloride (0.37), monocrotophos (0.03), N,N-diethyl-m-toluamide (0.09), N-benzylmethylamine (0.67), N-ethyl-p-toluenesulfonamide (0.05), nonylphenol diethoxylate (3.16), ofloxacin (1.79), omethoate (0.33), oxybenzone (0.11), piperonylbutoxide (0.87), sulfamethoxazole (0.31), terbutryn (0.03), tris(2-butoxyethyl) phosphate (22.64). Out of 33 pollutants, 18 of them were degraded (Table 4.2). N,N-diethyl-m-toluamide was degraded at the slowest rate with a half-life of 5.90 days whereas 4-methylbenzylidenecamphor was utilized the fastest with a half-life of 0.10 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole acetamiprid, atrazine-

desethyl, carbendazim, ciprofloxacin, diuron, hexa(methoxymethyl)melamine, mepiquat chloride, N-ethyl-p-toluenesulfonamide, ofloxacin, omethoate, sulfamethoxazole and terbutryn were not degraded.

Sampling Point 5 is located on the İnanlı village close to the Tekirdağ (Figure 4.7). This point is under the pollution stress agricultural runoff, urban waste direct discharge and industrial discharge.

Figure 4.7. Sampling point 5.

The COD, color, TOC of the of the water was, 785.13 mg/L, 585.00 ADMI, 22.83 mgC/L, respectively. Thirty-one number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (4.72), 3-chloroaniline (0.17), 4-chloroaniline (0.06), 4-tert-octylphenol diethoxylate (0.07) , 5-methyl-1H-benzotriazole (3.42), acetaminophen (873600.00), acetamiprid (0.52), aclonifen (0.12), ahdi (phantolide) (6.42), atrazine-desethyl (0.07), benzyldimethyldodecylammonium (4.11), carbendazim (3.07), ciprofloxacin (5.65), dicyclohexylamine (1.96), diuron (1.04), fenamiphos (0.04), hexa(methoxymethyl)melamine (10326.63), mepiquat chloride (0.23), N,N-diethyl-m-toluamide (1.03), N-benzylmethylamine (0.46), N-ethyl-2-tolysulfonamide (0.41), nonylphenol diethoxylate (0.56), norfloxacin (2.70), ofloxacin (1.94), omethoate (0.57), oxybenzone (0.02), piperonylbutoxide (0.05), prochloraz (0.10), sulfamethoxazole (0.96), terbutryn (0.02), tris(2-butoxyethyl) phosphate (0.60). Out of 31 pollutants, 12 of them were degraded (Table 4.2.). Tris(2-butoxyethyl) phosphate was degraded at the slowest rate with a half-life of 13.59 days whereas 4-tert-octylphenol diethoxylate

was utilized the fastest with a half-life of 0.10 days. 1,2,3-benzotriazole, 5-Methyl-1H-benzotriazole, acetamiprid, aclonifen, atrazine-desethyl, carbendazim, ciprofloxacin, diuron, fenamiphos, hexa(methoxymethyl)melamine, mepiquat chloride, N-ethyl-2-tolysulfonamide, N,N-diethyl-m-toluamide, N-ethyl-2-tolysulfonamide, norfloxacin, ofloxacin, omethoate, oxybenzone, sulfamethoxazole and terbutryn were not degraded.

Sampling Point 6 is located on Büyükkarıştıran OIZ (Figure 4.8). This point is under the pollution stress of industrial discharge.

Figure 4.8. Sampling point 6.

The COD, color, TOC of the of the water was 692.82 mg/L, 1119.00 ADMI, 224.23 mgC/L, respectively. Sixteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.59), 4-tert-octylphenol diethoxylate (0.16), 5-methyl-1H-benzotriazole (1.36), acetaminophen (7.97), acetamiprid (0.14), aclonifen (0.35), AHDI (phantolide) (7.80), atrazine-desethyl (0.03), benzyldimethyldodecylammonium (7.82), ciprofloxacin (2.25), diuron (0.95), hexa(methoxymethyl)melamine (221898.40), mepiquat chloride (0.13), nonylphenol diethoxylate (3.43), piperonylbutoxide (0.01), tris(2-butoxyethyl) phosphate (4.69). Out of 16 pollutants, 9 of them were degraded (Table 4.2.). Mepiquat chloride was degraded at the slowest rate with a half-life of 3.86 days whereas benzyldimethyldodecylammonium was utilized the fastest with a half-life of 0.25 days. 1,2,3-benzotriazole, 5-methyl-1H-benzotriazole, atrazine-desethyl, ciprofloxacin, diuron, hexa(methoxymethyl)melamine and piperonylbutoxide were not degraded.

Sampling Point 7 is located on Çiftlikköy village close to the Tekirdağ (Figure 4.9). This point is under the pollution stress of industrial discharges and agricultural runoff.

Figure 4.9. Sampling point 7.

The COD, color, TOC of the of the water was 222.34 mg/L, 78.00 ADMI, 75.73 mgC/L, respectively. Fourteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (8.76), 5-methyl-1H-benzotriazole (0.44), acetaminophen (28.84), aclonifen (0.30), benzyldimethyldodecylammonium (0.13), benzyldimethyltetradecylammonium (0.16), ciprofloxacin (3.17), dicyclohexylamine (0.13), diuron (0.20), hexa(methoxymethyl)melamine (1725.00), N,N-diethyl-m-toluamide (0.14), ofloxacin (4.82), piperonylbutoxide (0.01), tebuconazole (0.37). Out of 14 pollutants, 2 of them were degraded (Table 4.2.). Only piperonylbutoxide was degraded with a half-life of 0.10 days except acetaminophen. Rest of them were not degraded.

Sampling Point 8 is located on Evrensekiz OIKZ close to the Tekirdağ (Figure 4.10). This point is under the pollution stress of industrial discharge.

Figure 4.10. Sampling point 8.

The COD, color, TOC of the of the water was 1219.48 mg/L, 606.00 ADMI, 532.23 mgC/L, respectively. Thirty-four number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (2.40), 4-methyl-1H-benzotriazole (18.20), 5-methyl-1H-benzotriazole (8.14), acetaminophen (37.80), AHDI (phantolide) (5.29), atrazine-desethyl (0.12), azithromycin (0.21), benzyldimethyldodecylammonium (2.73), benzyldimethyltetradecylammonium (1.92), benzyltrimethylammonium (0.23), carbendazim (1.88), ciprofloxacin (8.52), clarithromycin (1.76), di(2- ethylhexyl)phthalate (DEHP) (85.86), dicyclohexylamine (0.91), diuron (0.62), erytromycin (3.83), hexa(methoxymethyl)melamine (1805.76), imazalil (0.80), lenacil (0.61), mepiquat chloride (0.17), N,N-diethyl-m-toluamide (1.17), N-benzyldimethylamine (0.67), N-ethyl-p-toluenesulfonamide (0.30), nonylphenol diethoxylate (0.44), norfloxacin (6.66), ofloxacin (2.29), omethoate (0.61), piperonylbutoxide (0.18), pirimicarb (0.86), sulfamethoxazole (0.56), terbutryn (0.01), tris(2-butoxyethyl) phosphate (4.61) , quinalphos (0.81). Out of 34 pollutants, 23 of them were degraded (Table 4.2.). N,N-diethyl-m-toluamide was degraded at the slowest rate with a half-life of 9.29 days whereas 5-methyl-1H-benzotriazole was utilized the fastest with a half-life of 0.80 days. 1,2,3-benzotriazole, carbendazim, ciprofloxacin, diuron, hexa(methoxymethyl)melamine, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin, omethoate, sulfamethoxazol and terbutryn were not degraded.

Sampling Point 9 is located on Eskibedir village close to the Tekirdağ (Figure 4.11). This point is under the pollution stress of agricultural runoff, industrial discharge and urban wastewater direct discharge.

Figure 4.11. Sampling point 9.

The COD, color, TOC of the of the water was 981.31 mg/L, 600.00 ADMI, 29.22 mgC/L, respectively. Twenty-five number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (7.80), atrazine-desethyl (0.19), benzyldimethyldodecylammonium (0.45), benzyldimethyltetradecylammonium (0.18), boisvelone/iso-esuper (3.47), carbofuran (0.24), chloramphenicol (0.04), ciprofloxacin (51.60), dicyclohexylamine (0.70), hexa(methoxymethyl)melamine (443.21), imazalil (2.21), lenacil (2.06), mepiquat chloride (0.72), N,N-diethyl-m-toluamide (0.05), N-ethyl-p-toluenesulfonamide (0.09), nonylphenol diethoxylate (0.27), norfloxacin (59.45), ofloxacin (11.01), omethoate (2.04), piperonylbutoxide (0.03), pirimicarb (0.11), prochloraz (0.35), propyl paraben (0.03), spiroxamine (0.03), terbuthylazine (0.01). Out of 25 pollutants, 13 of them were degraded (Table 4.2.). Ciprofloxacin was degraded at the slowest rate with a half-life of 25.67 days whereas pirimicarb was utilized the fastest with a half-life of 0.96 days. Atrazine-desethyl, boisvelone/iso-esuper, hexa(methoxymethyl)melamine, imazalil, N,N-diethyl-m-toluamide, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin, omethoate, prochloraz, propyl paraben and terbuthylazine were not degraded.

Sampling Point 10 is located on Durak village close to Lüleburgaz Province (Figure 4.12). This point is under the pollution stress of agricultural runoff and domestic discharge.

Figure 4.12. Sampling point 10.

The COD, color, TOC of the of the water was 137.47 mg/L, 50.00 ADMI, 71.84 mgC/L, respectively. Twenty number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (27.44), 4-methyl-1H-benzotriazole (6.20), 5-methyl-1H-benzotriazole (3.46), acetaminophen (23.08), aclonifen (0.40), benzyldimethyldodecylammonium (0.14), benzyldimethyltetradecylammonium (2.32), ciprofloxacin (2.60), dicyclohexylamine (0.04), diuron (0.09), hexa(methoxymethyl)melamine (404.21), N,N-diethyl-m-toluamide (0.52), N-benzyldimethylamine (2.88), nonylphenol diethoxylate (0.55), norfloxacin (3.24), ofloxacin (1.03), oxybenzone (0.02), piperonylbutoxide (0.11), sulfamethoxazole (0.19), tris(2-butoxyethyl) phosphate (0.37). Out of 20 pollutants, 7 of them were degraded (Table 4.2.). N,N-diethyl-m-toluamide was degraded at the slowest rate with a half-life of 23.10 days whereas aclonifen was utilized the fastest with a half-life of 0.49 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole, benzyldimethyldodecylammonium, ciprofloxacin, dicyclohexylamine, diuron, hexa(methoxymethyl)melamine, norfloxacin, ofloxacin, oxybenzone and sulfamethoxazole were not degraded.

Sampling Point 11 is located on the Düğüncübaşı village close to the Lüleburgaz Province (Figure 4.13). This point is under the pollution stress of agricultural runoff.

Figure 4.13. Sampling point 11.

The COD, color, TOC of the of the water was 120.32 mg/L, 221.00 ADMI, 100.03 mgC/L, respectively. Twenty-seven number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.06), 2,4-dihydroxybenzophnone (0.88), 4-methyl-1H-benzotriazole (3.17), 5-methyl-1H-benzotriazole (1.89), acetaminophen (12.40), acetamiprid (0.31), atrazine-desethyl (0.01), benzyldimethyldodecylammonium (0.16), benzyldimethyltetradecylammonium (0.21), benzyltrimethylammonium (0.38), carbendazim (0.23), ciprofloxacin (5.99), clarithromycin (0.69), di(2- ethylhexyl)phthalate (DEHP) (32.56), dicyclohexylamine (0.09), diuron (0.16), g-methylione (7.12), hexa(methoxymethyl)melamine (610.90), N,N-diethyl-m-toluamide (4.11), N-benzyldimethylamine (0.97), nonylphenol diethoxylate (0.53), norfloxacin (6.23), ofloxacin (1.14), omethoate (0.59), piperonylbutoxide (0.28), prochloraz (0.12) and sulfamethoxazole (3.55). Out of 27 pollutants, 9 of them were degraded (Table 4.2.). Benzyldimethyltetradecylammonium was degraded at the slowest rate with a half-life of 14.20 days whereas N,N-diethyl-m-toluamide was utilized the fastest with a half-life of 0.18 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole, atrazine-desethyl, benzyldimethyldodecylammonium, carbendazim, ciprofloxacin, di(2-ethylhexyl)phthalate(DEHP), dicyclohexylamine, diuron, g-methylione, hexa(methoxymethyl)melamine, norfloxacin, ofloxacin, omethoate, prochloraz and sulfamethoxazole were not degraded.

Sampling Point 12 is located on Düğüncülü close to the Babaeski Province (Figure 4.14). This point is under the pollution stress of agricultural ruonoff.

Figure 4.14. Sampling point 12.

The COD, color, TOC of the of the water was 152.11 mg/L, 633.00 ADMI, 116.03 mgC/L, respectively. Sixteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.35), acetaminophen (20.47), aclonifen (0.30), atrazine-desethyl (0.02), benzyldimethyldodecylammonium (0.15), benzyldimethyltetradecylammonium (0.08), ciprofloxacin (2.68), dicyclohexylamine (0.31), hexa(methoxymethyl)melamine (34.86), N,N-diethyl-m-toluamide (0.06), N-benzyldimethylamine (0.25), norfloxacin (6.20), ofloxacin (0.87), omethoate (0.42), piperonylbutoxide (0.07) and tris(2-butoxyethyl) phosphate (0.04). Out of 16 pollutants, 6 of them were degraded (table 4.2.). piperonylbutoxide was degraded at the slowest rate with a half-life of 9.51 days whereas aclonifen and tris(2-butoxyethyl) phosphate were utilized the fastest with a half-life of 0.10 days. 1,2,3-benzotriazole, atrazine-desethyl, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, ciprofloxacin, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, norfloxacin, ofloxacin, omethoate were not degraded.

Sampling Point 13 is located on Sinanlı town close to the Babaeski Province (Figure 4.15). This point is under the pollution stress of industrial and domestic discharge.

Figure 4.15. Sampling point 13.

The COD, color, TOC of the of the water was 174.53 mg/L, 96.00 ADMI, 52.94 mgC/L, respectively. Thirty-three number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.29), 4-methyl-1H-benzotriazole (1.03), 5-methyl-1H-benzotriazole (0.59), acetaminophen (15.92), acetamiprid (0.10), atrazine-desethyl (0.12), benzyldimethyldodecylammonium (0.08), benzyldimethyltetradecylammonium (0.52), benzyltrimethylammonium (0.36), carbendazim (0.56), ciprofloxacin (1.99), di(2- ethylhexyl)phthalate (DEHP) (63.24), diuron (0.22), flutriafol (0.14), hexa(methoxymethyl)melamine (10496.00), N,N-diethyl-m-toluamide (0.17), N-benzyldimethylamine (0.48), N-benzylmethylamine (0.43), N-ethyl-p-toluenesulfonamide (0.05), norfloxacin (2.24), ofloxacin (0.92), piperonylbutoxide (0.02), prochloraz (0.11), sulfamethoxazole (0.18) and tris(2-butoxyethyl) phosphate (3.38). Out of 33 pollutants, 7 of them were degraded (Table 4.2.). Benzyltrimethylammonium was degraded at the slowest rate with a half-life of 14.69 days whereas piperonylbutoxide was utilized the fastest with a half-life of 1.63 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole, acetamiprid, benzyldimethyldodecylammonium, carbendazim, ciprofloxacin, di(2- ethylhexyl)phthalate (DEHP), diuron, flutriafol, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin, prochloraz, sulfamethoxazole,and tris(2-butoxyethyl) phosphate were not degraded.

Sampling Point 14 is located on Alpullu close to the Babaeski Province (Figure 4.16). This point is under the pollution stress of industrial and domestic discharge.

Figure 4.16. Sampling point 14.

The COD, color, TOC of the of the water was 117.80 mg/L, 57.00 ADMI, 62.51 mgC/L, respectively. Twenty-six number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.18), 2,4-dihydroxybenzophnone (0.57), 4-methyl-1H-benzotriazole (1.07), 5-methyl-1H-benzotriazole (0.77), acetaminophen (14.06), AHDI (phantolide) (9.95), atrazine-desethyl (0.01), benzyldimethyldodecylammonium (0.30), boisvelone / iso-esuper (8.04), carbendazim (0.16), ciproflocacin (6.79), clarithromycin (0.91), di(2- ethylhexyl)phthalate (DEHP) (47.83), hexa(methoxymethyl)melamine (191.30), N,N-diethyl-m-toluamide (5.65), N-benzyldimethylamine (0.24), N-benzylmethylamine (0.10), N-ethyl-p-toluenesulfonamide (0.05), nonylphenol diethoxylate (0.65), norfloxacin (6.60), ofloxacin (1.46), omethoate (0.43), oxybenzone (0.14), piperonylbutoxide (0.07), tetradecyldimethylbenzylammonium (0.43) and tris(2-butoxyethyl) phosphate (0.10). Out of 26 pollutants, 13 of them were degraded (Table 4.2.). Ciprofloxacin was degraded at the slowest rate with a half-life of 16.42 days whereas N,N-diethyl-m-toluamide was utilized the fastest with a half-life of 0.17 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole, atrazine-desethyl, benzyldimethyldodecylammonium, boisvelone/iso-esuper, carbendazim, di(2-ethylhexyl)phthalate (DEHP), hexa(methoxymethyl)melamine, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin and omethoate were not degraded.

Sampling Point 15 is located on Mandıra town close to the Babaeski Province (Figure 4.17). This point is under the pollution stress of domestic discharge.

Figure 4.17. Sampling point 15.

The COD, color, TOC of the of the water was 137.93 mg/L, 140.00 ADMI, 73.00 mgC/L, respectively. Seventeen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (18.35), acetamiprid (0.14), atrazine-desethyl (0.01), benzyldimethyldodecylammonium (0.17,) benzyldimethyltetradecylammonium (0.14), benzyltrimethylammonium (0.26), ciprofloxacin (4.43), di(2- ethylhexyl)phthalate (DEHP) (26.58), dicyclohexylamine (0.08), flutriafol (0.11), Hexa(methoxymethyl)melamine (32.38), N,N-diethyl-m-toluamide (0.31), N-benzyldimethylamine (0.41), N-ethyl-p-toluenesulfonamide (0.04), norfloxacin (5.18), ofloxacin (0.99) and omethoate (0.43). Out of 17 pollutants, 8 of them were degraded (Table 4.2.). Atrazine-desethyl was degraded at the slowest rate with a half-life of 16.12 days whereas flutriafol was utilized the fastest with a half-life of 0.10 days. Benzyldimethyldodecylammonium, ciprofloxacin, di(2- ethylhexyl)phthalate (DEHP), dicyclohexylamine, hexa(methoxymethyl)melamine, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin and omethoate were not degraded.

Sampling Point 16 is located on Karakavak town close to Hayrabolu Province (Figure 4.18). This point is under the pollution stress of agricultural runoff.

Figure 4.18. Sampling point 16.

The COD, color, TOC of the of the water was 119.63 mg/L, 111.00 ADMI, 45.80 mgC/L, respectively. Ten number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (28.97), benzyldimethyldodecylammonium (2.06), flutriafol (0.18), hexa(methoxymethyl)melamine (83.94), N,N-diethyl-m-toluamide (0.14), norfloxacin (7.18), ofloxacin (1.19), oxybenzone (0.28) and tetradecyldimethylbenzylammonium (15.59). Out of 10 pollutants, 5 of them were degraded (Table 4.2.). N-benzyldimethylamine was degraded at the slowest rate with a half-life of 18.73 days whereas oxybenzone was utilized the fastest with a half-life of 1.63 days. Flutriafol, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide and ofloxacin were not degraded.

Sampling Point 17 is located on Nadırlı village close to the Babaeski Province (Figure 4.19). This point is under the pollution stress of agricultural runoff industrial and domestic discharge.

Figure 4.19. Sampling point 17.

The COD, color, TOC of the of the water was 72.51 mg/L, 19.00 ADMI, 28.70 mgC/L, respectively. Ten number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 4-tert-octylphenol diethoxylate (0.12), acetaminophen (30.82), benzyldimethyldodecylammonium (0.15), boisvelone / iso-esuper (0.09), clarithromycin (0.04), hexa(methoxymethyl)melamine (38.45), N,N-diethyl-m-toluamide (0.62), N-benzyldimethylamine (0.95), norfloxacin (4.11) and ofloxacin (1.16). Out of 10 pollutants, 4 of them were degraded (Table 4.2.). N,N-diethyl-m-toluamide was degraded at the slowest rate with a half-life of 8.33 days whereas boisvelone / iso-esuper was utilized the fastest with a half-life of 0.10 days. 4-tert-octylphenol diethoxylate, benzyldimethyldodecylammonium, clarithromycin, hexa(methoxymethyl)melamine, norfloxacin and ofloxacin were not degraded.

Sampling Point 18 is located Katranca village close to the Babaeski Province (Figure 4.20). This point is under the pollution stress of agricultural runoff.

Figure 4.20. Sampling point 18.

The COD, color, TOC of the of the water was 59.02 mg/L, 92.00 ADMI, 25.54 mgC/L, respectively. Eleven number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 5-methyl-1H-benzotriazole (0.17), acetaminophen (32.08), aclonifen (0.10), benzyldimethyldodecylammonium (0.11), benzyldimethyltetradecylammonium (1.67), hexa(methoxymethyl)melamine (77.50), N,N-diethyl-m-toluamide (0.19), norfloxacin (1.62), ofloxacin (0.74), oxybenzone (0.10) and tetradecyldimethylbenzylammonium (3.73). Out of 11 pollutants, 3 of them were degraded (Table 4.2.). Oxybenzone was degraded at the slowest rate with a half-life of 15.30 days whereas aclonifen was utilized the fastest with a half-life of 0.55 days. 5-methyl-1H-benzotriazole, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, norfloxacin, ofloxacin, and tetradecyldimethylbenzylammonium were not degraded.

Sampling Point 19 is located on the Kumköy close to the Pehlivanköy Province (Figure 4.21). This point is under the pollution stress of agricultural runoff.

Figure 4.21. Sampling point 19.

The COD, color, TOC of the of the water was 68.62 mg/L, 81.00 ADMI, 40.10 mgC/L, respectively. Eleven number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.07), 5-methyl-1H-benzotriazole (0.11), acetaminophen (19.12), benzyldimethyldodecylammonium (0.12), benzyldimethyltetradecylammonium (1.58), benzyltrimethylammonium (0.34), ciprofloxacin (1.11), N,N-diethyl-m-toluamide (0.24), N-benzyldimethylamine (0.45), norfloxacin (3.60) and ofloxacin (0.65). Out of 11 pollutants, 4 of them were degraded (Table 4.2.). Benzyltrimethylammonium was degraded at the slowest rate with a half-life of 9.95 days whereas 5-methyl-1H-benzotriazole was utilized the fastest with a half-life of 0.10 days. Benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, ciprofloxacin, N,N-diethyl-m-toluamide, N-benzyldimethylamine, norfloxacin and ofloxacin were not degraded.

Sampling Point 20 is located on Hıdırca village close to the Pehlivanköy Province (Figure 4.22). This point is under the pollution stress of agricultural runoff.

Figure 4.22. Sampling point 20.

The COD, color, TOC of the of the water was 97.67 mg/L, 23.00 ADMI, 53.52 mgC/L, respectively. Ten number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.26), acetaminophen (25.41), benzyldimethyldodecylammonium (0.17), benzyldimethyltetradecylammonium (1.67), benzyltrimethylammonium (0.28), carbendazim (0.10), dicyclohexylamine (0.07), N,N-diethyl-m-toluamide (0.05), N-benzyldimethylamine (0.34) and ofloxacin (0.49). Out of 10 pollutants, 4 of them were degraded (Table 4.2.). Benzyltrimethylammonium was degraded at the slowest rate with a half-life of 10.88 days whereas 1,2,3-benzotriazole was utilized the fastest with a half-life of 2.55 days. Benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, carbendazim, N,N-diethyl-m-toluamide, N-benzyldimethylamine and ofloxacin were not degraded.

Sampling Point 21 is located on Sazlımalkoç village close to the Uzunköprü Province (Figure 4.23). This point is under the pollution stress of agricultural runoff.

Figure 4.23. Sampling point 21.

The COD, color, TOC of the of the water was 73.43 mg/L, 53.00 ADMI, 36.64 mgC/L, respectively. Ten number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.20), acetaminophen (25.57), atrazine-desethyl (0.02), benzyldimethyldodecylammonium (0.19), benzyldimethyltetradecylammonium (1.96), benzyltrimethylammonium (0.29), N,N-diethyl-m-toluamide (0.34), N-benzyldimethylamine (0.77), norfloxacin (3.70) and ofloxacin (0.77). Out of 10 pollutants, 4 of them were degraded (Table 4.2.). N-benzyldimethylamine was degraded at the slowest rate with a half-life of 22.35 days whereas benzyltrimethylammonium was utilized the fastest with a half-life of 5.91 days. 1,2,3-benzotriazole, atrazine-desethyl, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, norfloxacin and ofloxacin were not degraded.

Sampling Point 22 is located on Bayramlı village close to the Uzunköprü Province (Figure 4.24). This point is under the pollution stress of agricultural runoff.

Figure 4.24. Sampling point 22.

The COD, color, TOC of the of the water was 64.51 mg/L, 90.00 ADMI, 30.75 mgC/L, respectively. Nine number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (18.95), benzyldimethyldodecylammonium (2.20), benzyldimethyltetradecylammonium (7.21), benzyltrimethylammonium (0.25), hexa(methoxymethyl)melamine (30.27), N,N-diethyl-m-toluamide (0.14), N-benzyldimethylamine (0.57), norfloxacin (5.23) and ofloxacin (0.56). Out of 9 pollutants, 5 of them were degraded (Table 4.2.). Benzyltrimethylammonium was degraded at the slowest rate with a half-life of 10.43 days whereas benzyldimethyldodecylammonium was utilized the fastest with a half-life of 3.52 days. Hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, norfloxacin and ofloxacin were not degraded.

Sampling Point 23 is located on Uzunköprü close to the Edirne (Figure 4.25). This point is under the pollution stress of domestic discharge and agricultural runoff.

Figure 4.25. Sampling point 23.

The COD, color, TOC of the of the water was 131.07 mg/L, 189.00 ADMI, 51.72 mgC/L, respectively. Twenty number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.80), 2,4-dihydroxybenzophnone (0.16), 4-methyl-1H-benzotriazole (1.13), 4-tert-octylphenoldiethoxylate (0.09), 5-methyl-1H-benzotriazole (0.64), acetaminophen (17.75), acetamiprid (0.10), benzyldimethyldodecylammonium (0.19), benzyldimethyltetradecylammonium (1.91), benzyltrimethylammonium (0.29), carbendazim (0.23), ciprofloxacin (3.06), diuron (0.16), hexa(methoxymethyl)melamine (3123.40), nonylphenol diethoxylate (0.32), norfloxacin (3.70), ofloxacin (0.99), piperonylbutoxide (0.12), pirimicarb (0.06) and tris(2-butoxyethyl) phosphate (1.19). Out of 20 pollutants, 7 of them were degraded (Table 4.2.). Tris(2-butoxyethyl) phosphate was degraded at the slowest rate with a half-life of 16.62 days whereas pirimicarb was utilized the fastest with a half-life of 0.10 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 4-tert-octylphenoldiethoxylate, 5-methyl-1H-benzotriazole, acetamiprid, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, carbendazim, ciprofloxacin, diuron, hexa(methoxymethyl)melamine, norfloxacin and ofloxacin were not degraded.

Sampling Point 24 is located on Uzunköprü close to the Edirne (Figure 4.26). This point is under the pollution stress of agricultural runoff, domestic and industrial discharge.

Figure 4.26. Sampling point 24.

The COD, color, TOC of the of the water was 209.99 mg/L, 169.00 ADMI, 69.74 mgC/L, respectively. Fifteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.73), 4-methyl-1H-benzotriazole (1.56), 4-tert-octylphenoldiethoxylate (0.07), 5-methyl-1H-benzotriazole (0.97), acetaminophen (34.59), azoxystrobin (0.03), benzyldimethyldodecylammonium (0.22), benzyldimethyltetradecylammonium (1.83), carbendazim (0.99), ciprofloxacin (3.01), dicyclohexylamine (0.17), diuron (0.37), hexa(methoxymethyl)melamine (16668.09), N-ethyl-p-toluenesulfonamide (0.07) and nonylphenol diethoxylate (0.21). Out of 15 pollutants, 4 of them were degraded (Table 4.2.). Nonylphenol diethoxylate was degraded at the slowest rate with a half-life of 13.56 days whereas dicyclohexylamine was utilized the fastest with a half-life of 8.26 days. 1,2,3-benzotriazole 4-methyl-1H-benzotriazole, 4-tert-octylphenoldiethoxylate, 5-methyl-1H-benzotriazole, azoxystrobin, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium, carbendazim, ciprofloxacin, diuron, hexa(methoxymethyl)melamine, N-ethyl-p-toluenesulfonamide were not degraded.

Sampling Point 25 is located on Kavacık village to the Uzunköprü Province (Figure 4.27). This point is under the pollution stress of agricultural runoff.

Figure 4.27. Sampling point 25.

The COD, color, TOC of the of the water was 221.42 mg/L, 195.00 ADMI, 93.22 mgC/L, respectively. Twenty-three number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (1.51), 4-methyl-1H-benzotriazole (0.73), 4-tert-octylphenoldiethoxylate (0.07), 5-methyl-1H-benzotriazole (0.55), acetaminophen (31.14), acetamiprid (0.15), azoxystrobin (8.98), benzyldimethyldodecylammonium (0.18), benzyldimethyltetradecylammonium (1.80), benzyltrimethylammonium (0.18), ciprofloxacin (5.89), dicyclohexylamine (0.13), diuron (0.13), hexa(methoxymethyl)melamine (9209.60), N,N-diethyl-m-toluamide (0.21), N-ethyl-p-toluenesulfonamide (0.05), norfloxacin (8.14), ofloxacin (1.34), omethoate (0.55), propiconazole (8/70), pyraclostrobin (0.06), trifloxystrobin (0.10), and tris(2-butoxyethyl) phosphate (2.37). Out of 23 pollutants, 5 of them were degraded (Table 4.2.). Tris(2-butoxyethyl) phosphate was degraded at the slowest rate with a half-life of 24.32 days whereas trifloxystrobin was utilized the fastest with a half-life of 1.52 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, 4-tert-octylphenoldiethoxylate, 5-methyl-1H-benzotriazole, acetamiprid, azoxystrobin, benzyldimethyldodecylammonium, benzyldimethyltetradecylammonium ciprofloxacin, dicyclohexylamine, diuron, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, N-ethyl-p-toluenesulfonamidedid, norfloxacin, ofloxacin, omethoate and propiconazole were not degraded.

Sampling Point 26 is located on Balaban village close to the Uzunköprü Province (Figure 4.28). This point is under the pollution stress of agricultural runoff.

Figure 4.28. Sampling point 26.

The COD, color, TOC of the of the water was 50.55 mg/L, 36.00 ADMI, 37.44 mgC/L, respectively. Six number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (44.70), aclonifen (0.34), benzyldimethyldodecylammonium (0.42), benzyldimethyltetradecylammonium (1.98), norfloxacin (6.02) and ofloxacin (0.95). None of the chemical was degraded except acetaminophen. (Table 4.2.).

Sampling Point 28 is located on İnanlı village close to the Tekirdağ (Figure 4.29). This point is under the pollution stress of domestic and industrial discharge.

Figure 4.29. Sampling point 28.

The COD, color, TOC of the of the water was 698.65 mg/L, 267.00 ADMI, 190.93 mgC/L, respectively. Thirty-four number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (3.85), 2,4-dihydroxybenzophenone (0.42), 2-mercapto-benzothiazol (2.48), 4-chloroaniline (0.31), 4-methyl-1H-benzotriazole (6.94), 4-tert-octylphenoldiethoxylate (0.10), 5-methyl-1H-benzotriazole (4.21), acetaminophen (17.90), acetamiprid (0.25), AHDI (phantolide) (4.25), atrazine-desethyl (0.07), azoxystrobin (0.01), benzyldimethyldodecylammonium (14.75), benzyldimethyltetradecylammonium (7.28), carbendazim (2.35), ciprofloxacin (6.86), dicyclohexylamine (0.85), diuron (1.43), hexa(methoxymethyl)melamine (16039.00), mepiquat chloride (0.29), monocrotophos (0.03), N,N-diethyl-m-toluamide (1.53), N-benzyldimethylamine (0.44), N-benzylmethylamine, N-ethyl-p-toluenesulfonamide (0.20), nonylphenol diethoxylate (1.22), norfloxacin (2.47), ofloxacin (6.86), omethoate (0.40), oxybenzone (0.08), piperonylbutoxide (0.23), sulfamethoxazole (0.81), terbutryn (0.02) and tris(2-butoxyethyl) phosphate (28.16). Out of 34 pollutants, 15 of them were degraded (Table 4.2.). Monocrotophos was degraded at the slowest rate with a half-life of 9.92 days whereas 4-chloroaniline was utilized the fastest with a half-life of 0.94 days. 1,2,3-benzotriazole, 2-mercapto-benzothiazol, 4-methyl-1h-benzotriazole, 4-tert-octylphenoldiethoxylate, 5-methyl-1h-benzotriazole, acetamiprid, atrazine-desethyl, azoxystrobin, ciprofloxacin, diuron, hexa(methoxymethyl)melamine, mepiquat chloride, N-ethyl-p-toluenesulfonamide, norfloxacin, ofloxacin, omethoate, sulfamethoxazole and terbutryn were not degraded.

Sampling Point 48 is located on Çorlu close to the Tekirdağ (Figure 4.30). This point is under the pollution stress of industrial and domestic discharge.

Figure 4.30. Sampling point 48.

The COD, color, TOC of the of the water was 738.49 mg/L, 601.00 ADMI, 48.33 mgC/L, respectively. Twenty-four number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 3-chloroaniline (0.51), 4-chloroaniline (0.32), 4-tert-octylphenoldiethoxylate (0.30), 5-methyl-1H-benzotriazole (0.86), acetaminophen (19.61), acetamiprid (0.04), AHDI (phantolide) (5.58), atrazine-desethyl (0.06), benzyldimethyldodecylammonium (2.37), benzyldimethyltetradecylammonium (2.02), carbendazim (0.40), ciprofloxacin (2.31), dicyclohexylamine (0.10), diuron (0.85), hexa(methoxymethyl)melamine (107228.30), N,N-diethyl-m-toluamide (0.49), N-benzyldimethylamine (0.83), N-ethyl-p-toluenesulfonamide (0.05), nonylphenol diethoxylate (1.71), ofloxacin (1.50), oxybenzone (0.19), piperonylbutoxide (0.41), terbutryn (0.01) and tris(2-butoxyethyl) phosphate (142.45). Out of 24 pollutants, 10 of them were degraded (Table 4.2.). Oxybenzone was degraded at the slowest rate with a half-life of 21.26 days whereas benzyldimethyldodecylammonium was utilized the fastest with a half-life of 2.63 days. 3-chloroaniline, 4-chloroaniline, 5-methyl-1H-benzotriazole, acetamiprid, benzyldimethyltetradecylammonium, carbendazim, ciprofloxacin, dicyclohexylamine, diuron, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide, N-ethyl-p-toluenesulfonamide, ofloxacin, terbutryn and tris(2-butoxyethyl) phosphate were not degraded.

Sampling Point 50 is located on Misinli town close to the Çorlu Province (Figure 4.31). This point is under the pollution stress of agricultural runoff, industrial and domestic discharge.

Figure 4.31. Sampling point 50.

The COD, color, TOC of the of the water was 1054.29 mg/L, 784.00 ADMI, 59.71 mgC/L, respectively. Eighteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.55), 3-chloroaniline (0.95), 4-chloroaniline (0.77), 4-methyl-1H-benzotriazole (0.64), acetaminophen (12.95), AHDI (phantolide) (6.66), atrazine-desethyl (0.08), benzyldimethyldodecylammonium (14.22), benzyldimethyltetradecylammonium (5.64), carbendazim (0.41), dicyclohexylamine (3.81), diuron (0.91), hexa(methoxymethyl)melamine (78086.24), N,N-diethyl-m-toluamide (0.06), N-benzylmethylamine (0.11), nonylphenol diethoxylate (11.47), ofloxacin (1.09) and tris(2-butoxyethyl) phosphate (195.59). Out of 18 pollutants, 11 of them were degraded (Table 4.2.). Atrazine-desethyl was degraded at the slowest rate with a half-life of 15.13 days whereas N-benzylmethylamine was utilized the fastest with a half-life of 1.22 days. 1,2,3-benzotriazole, 4-methyl-1H-benzotriazole, carbendazim, diuron, hexa(methoxymethyl)melamine, N,N-diethyl-m-toluamide and ofloxacin, were not degraded.

Sampling Point 54 is located on Esenler town close to the Çorlu Province (Figure 4.32). This point is under the pollution stress of agricultural runoff and domestic discharge.

Figure 4.32. Sampling point 54.

The COD, color, TOC of the of the water was 706.43 mg/L, 472.00 ADMI, 104.83 mgC/L, respectively. Twenty-six number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (12.98), 3-chloroaniline (0.34), 4-chloroaniline (0.24), 4-tert-octylphenoldiethoxylate (0.21), 5-methyl-1H-benzotriazole (3.30), acetaminophen (16.07), acetamiprid (0.48), AHDI (phantolide) (8.98), benzyldimethyldodecylammonium (14.51), benzyldimethyltetradecylammonium (6.60), benzyltrimethylammonium (0.13), carbendazim (2.04), dicyclohexylamine (0.84), diuron (1.41), hexa(methoxymethyl)melamin (11796.10), mepiquat chloride (0.30), N,N-diethyl-m-toluamid (0.75), N-ethyl-p-toluenesulfonamide (0.42), nonylphenol diethoxylate (1.67), ofloxacin (1.82), oxybenzone (0.12), piperonylbutoxide (0.06), sulfamethoxazole (0.56), terbutryn (0.02), triphenylphosphineoxide (3.17), and tris(2-butoxyethyl) phosphate (0.95). Out of 26 pollutants, 14 of them were degraded (Table 4.2.). 4-tert-octylphenol diethoxylate was degraded at the slowest rate with a half-life of 14.00 days whereas 3-chloroaniline was utilized the fastest with a half-life of 1.50 days. 1,2,3-benzotriazole, 4-chloroaniline, 5-methyl-1H-benzotriazole, acetamiprid, carbendazim, diuron, hexa(methoxymethyl)melamin, N-ethyl-p-toluenesulfonamide, ofloxacin, sulfamethoxazole, terbutryn and triphenylphosphineoxide were not degraded.

Sampling Point 55 is located on Vakıflar village close to the Ergene Province (Figure 4.33). This point is under the pollution stress of agricultural runoff and industrial discharge.

Figure 4.33. Sampling point 55.

The COD, color, TOC of the of the water was 922.14 mg/L, 1024.00 ADMI, 77.73 mgC/L, respectively. Fifteen number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), 1,2,3-benzotriazole (0.77), 4-tert-octylphenoldiethoxylate (0.47), acetaminophen (15.29), AHDI (Phantolide) (4.01), benzyldimethyldodecylammonium (4.33), benzyldimethyltetradecylammonium (23.28), damascone (1132.40), diuron (0.80), Hexa(methoxymethyl)melamin (40708.31), N,N-diethyl-m-toluamid (0.07), nonylphenol diethoxylate (11.09), norfloxacin (4.04), ofloxacin (1.54), pirimicarb (0.09) and tris(2-butoxyethyl) phosphate (0.60). Out of 15 pollutants, 9 of them were degraded (Table 4.2.). 4-tert-octylphenol diethoxylate was degraded at the slowest rate with a half-life of 14.72 days whereas pirimicarb was utilized the fastest with a half-life of 0.10 days. 1,2,3-benzotriazole, diuron, N,N-diethyl-m-toluamide and ofloxacin were not degraded.

Sampling Point 65 is located on Beyazköy village close to the Saray Province (Figure 4.34). This point is under the pollution stress of industrial discharge and agricultural runoff.

Figure 4.34. Sampling point 65.

The COD, color, TOC of the of the water was 84.86 mg/L, 24.00 ADMI, 23.63 mgC/L, respectively. Six number of pollutants were detected in the sample taken from that point. Those pollutants include (initial concentration, µg/L), acetaminophen (27.87), benzyldimethyltetradecylammonium (1.53), g-methylione, (5.91) hexa(methoxymethyl)melamin (141.74), N,N-diethyl-m-toluamide (0.13) and N-ethyl-p-toluenesulfonamide (0.12). None of the chemical was degraded except acetaminophen. (Table 4.2.).

In Table 4.3, detection frequency of chemicals is given along with their correspondent k values. Furthermore, in Figure 4.35, clustering of contaminants and sampling points based on detection frequency and biodegradation rate of contaminants can be seen on a heatmap. As can be seen, benzyldimethyldodecylammonium was the most frequently detected chemical among all sampling points with a mean degradation rate constant of 0.33±0.67. On the other hand, azithromycin was detected only once (sampling point 8) with a k value of 0.20. Although, 1,2,3-benzotriazole was one of the most detected micropollutant (19 times), it was biodegraded at only 2 sampling points with a very low mean k value (0.03±0.67). On the heatmap, Z-score indicates whether any k value of each chemical in a sampling point is above or below of the mean k value of a particular chemical in all sampling points. If the Z-score is 0, it shows us that the score of the data point is the same as the mean score. It may also be negative or positive. If it is negative, it means the data point score is below the mean. If it is positive, on the other hand, the score of the data point is above the mean. The Z-score is calculated as in the Equation 4.3:

$$Z = \frac{X - \mu}{\sigma} \tag{4.3}$$

where X is the value obtained for a chemical in a certain sample, μ is the mean of the k values obtained in each sampling point and σ is the standard deviation of the k values.

If the colors are the same at the sampling points where the chemical is seen, the chemical does not show variation at those points. It means the rate of biodegradation does not show spatial variation. For example, ciprofloxacin was detected at 18 sampling points. In sampling points 9 and 14, it has a k value above the mean represented by red color. In other 16 sampling points where it is represented by similar color, it has a k value below the mean. It was not detected in rest of the 11 sampling points where it is shown by white color. Similarly, N,N-diethyl-m-toluamide was detected at 25 sampling points. At 23 sampling points N,N-diethyl-m-toluamide was biodegraded with similar k value but at sampling point 11 and 14, N,N-diethyl-m-toluamide was degraded faster than the others. On the other hand, biodegradation rate constant of nonylphenol diethoxylate has too much variations at 15 sampling points. In Figure 4.34, micropollutants and the sampling points were also clustered by using average linkage clustering method. Distance measurement was performed by using the Euclidian method. Clustering of contaminants shows biodegradation profile similarities of chemicals whereas clustering of sampling points shows biodegradation profile similarities of sampling points according to z scores. Sampling point 13 and 48 are under the pollution stress of industrial and domestic discharge. They were clustered at the first step. Similarly, sampling point 50 and 54 were clustered at the first step. Both are under the stress of agricultural runoff and industrial discharge. Although, sampling point 11 and 14 are under the stress of agricultural runoff and industrial/domestic discharge respectively, these sampling points were clustered at first step. This situation can be explained by z-scores of detected micropollutants are closer to each other. Dicyclohexylamine (surfactant) and 4-chloroaniline (an ingredient for production of pesticides, dyes and pharmaceuticals) were clustered at the first step due to z-score distribution over all sampling points are close to each other. Similarly, tris(2-butoxyethyl) phosphate (plasticizer) and aclonifen (herbicide), erythromycin (antibiotic) and mepiquat chloride (plant growth regulater), imazalil (fungicide) and quinalphos (insecticide) were clustered at the first step even they have different molecular structure and different properties.

Table 4.3. Detection frequency of chemicals in Ergene River and the range of k values (d^{-1}) meausured.

Chemicals	# of point detected	Min	Median	Max	Mean	STDV (±)
1,2,3-Benzotriazole	19	0.00	0.00	0.27	0.03	0.09
2,4-Dihydroxybenzophenone	5	0.08	0.18	0.21	0.16	0.06
2-Mercapto-benzothiazole	2	0.00	0.08	0.16	0.08	0.11
3-Chloroaniline	4	0.00	0.31	0.86	0.37	0.38
4-Chloroaniline	6	0.00	0.25	0.74	0.30	0.32
4-Methyl-1H-benzotriazole	12	0.00	0.00	2.92	0.24	0.84
4-Methylbenzylidenecamphor	1	7.13	7.13	7.13	7.13	N/A
4-tert-Octylphenol diethoxylate	11	0.00	0.05	7.13	0.74	2.13
5-Methyl-1H-benzotriazole	16	0.00	0.00	7.13	0.64	1.90
Acetaminophen	29	0.07	2.39	7.13	2.97	2.80
Acetamiprid	11	0.00	0.00	0.30	0.04	0.10
Aclonifen	8	0.00	0.97	7.13	2.20	3.09
AHDI (Phantolide)	10	0.12	0.23	0.39	0.23	0.09
Atrazine-desethyl	14	0.00	0.00	0.09	0.02	0.04
Azithromycin	1	0.20	0.20	0.20	0.20	N/A
Benzyldimethyldodecylammonium	28	0.00	0.00	2.72	0.33	0.67
Benzyldimethylhexadecylammonium	1	0.17	0.17	0.17	0.17	N/A
Benzyldimethyltetradecylammonium	24	0.00	0.02	1.42	0.14	0.34
Benzyltrimethylammonium	11	0.05	0.07	0.15	0.08	0.03
Boisvelone / Iso-Esuper	3	0.00	0.00	7.13	2.38	4.12
Carbofuran	1	0.27	0.27	0.27	0.27	N/A
Chloramphenicol	1	0.10	0.10	0.10	0.10	N/A
Ciprofloxacin	18	0.00	0.00	0.04	0.00	0.01
Clarithromycin	5	0.00	0.37	1.76	0.56	0.69
Damascone	1	0.09	0.09	0.09	0.09	N/A
Di(2- ethylhexyl)phthalate (DEHP)	5	0.00	0.00	0.25	0.05	0.11
Dicyclohexylamine	16	0.00	0.08	0.46	0.14	0.16
Erythromycin	1	1.91	1.91	1.91	1.91	N/A
Flutriafol	3	0.00	0.00	7.13	2.38	4.12
Imazalil	2	0.00	0.46	0.93	0.46	0.66
Lenacil	2	0.22	0.27	0.32	0.27	0.07
Mepiquat chloride	7	0.00	0.07	1.72	0.31	0.63
Monocrotophos	2	0.07	0.20	0.34	0.20	0.19
N,N-Diethyl-m-toluamide	25	0.00	0.00	4.04	0.34	1.07
N-Benzyldimethylamine	14	0.00	0.11	0.44	0.13	0.12
N-Benzylmethylamine	7	0.12	0.30	0.57	0.30	0.18
Nonylphenol diethoxylate	15	0.05	0.20	0.58	0.23	0.15
Oxybenzone	7	0.00	0.05	0.43	0.11	0.15

Table 4.3. Cont'd.

Chemicals	# of point detected	Min	Median	Max	Mean	STDV (±)
Piperonylbutoxide	16	0.00	0.19	7.13	0.62	1.74
Pirimicarb	4	0.72	4.40	7.13	4.16	3.45
Prochloraz	4	0.00	0.00	0.18	0.04	0.09
Pyraclostrobin	1	0.04	0.04	0.04	0.04	N/A
Quinalphos	1	0.65	0.65	0.65	0.65	N/A
Spiroxamine	1	0.03	0.03	0.03	0.03	N/A
Tetradecyldimethylbenzylammonium	2	0.09	0.09	0.10	0.09	0.00
Trifloxystrobin	1	0.46	0.46	0.46	0.46	N/A
Tris(2-butoxyethyl) phosphate	15	0.00	0.08	7.13	0.82	1.93

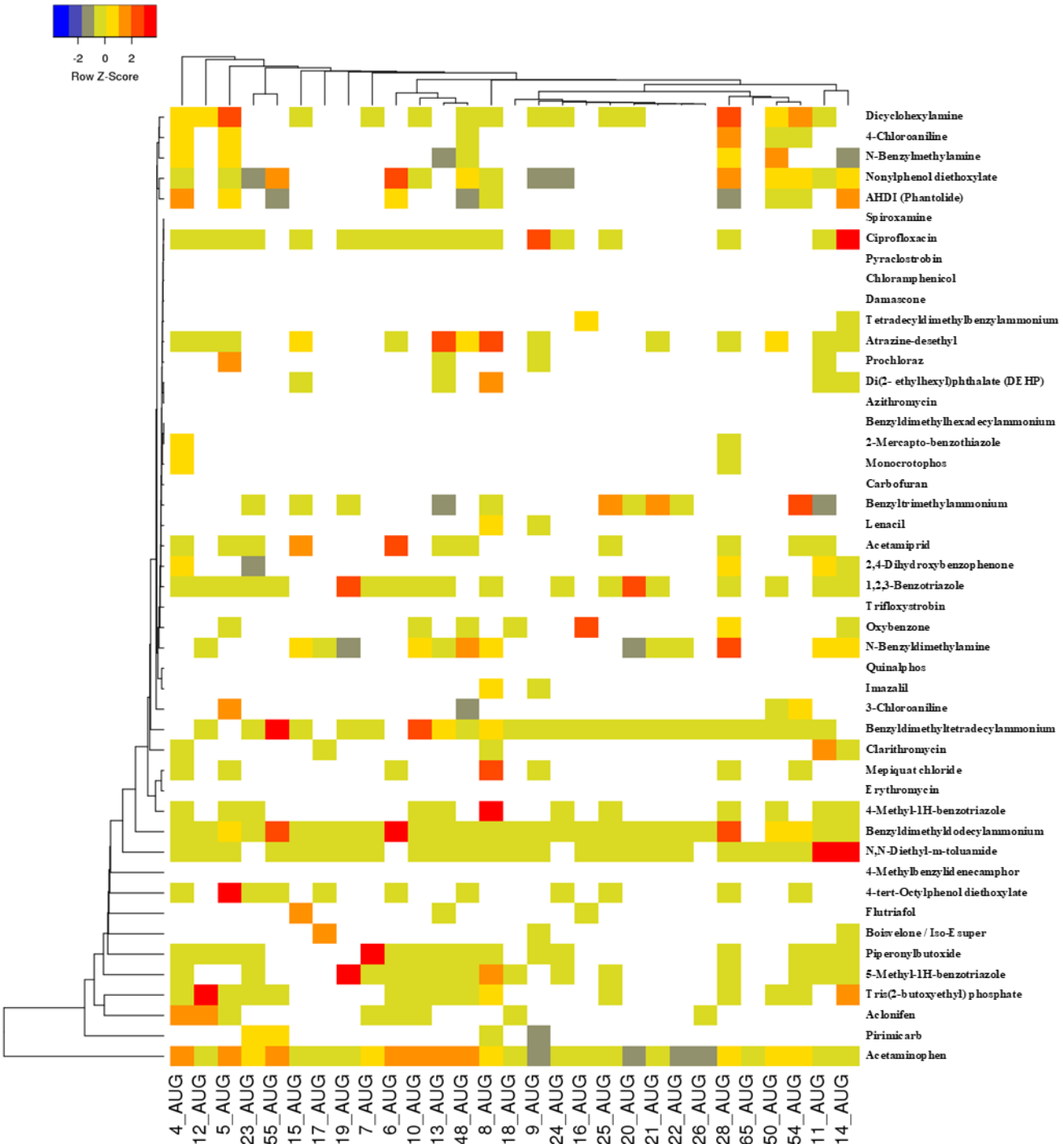


Figure 4.35. Clustering of contaminants and sampling points based on detection frequency and biodegradation rate of contaminants.

Boxplot, in Figure 4.36, shows biodegradation profile of micropollutants. In the boxplot, circles, red lines, black lines and whiskers represent outliers, mean k value, median, minimum and maximum k value, respectively. As expected, acetaminophen was biodegraded at all sampling points with relatively high mean k value. On the other hand, carbofuran, erythromycin, quinalphos trifloxystrobin was detected and biodegraded at only one sampling point. Although, 1,2,3-benzotraiazole was

detected at 19 sampling points, it was biodegraded at only 2 sampling points. Thus, mean k value was calculated low. Pirimicarb was detected and biodegraded at four sampling points and degraded in all of them. Tris(2-butoxyethyl) phosphate has a relatively low mean k values whereas it was rarely biodegraded with high k value.

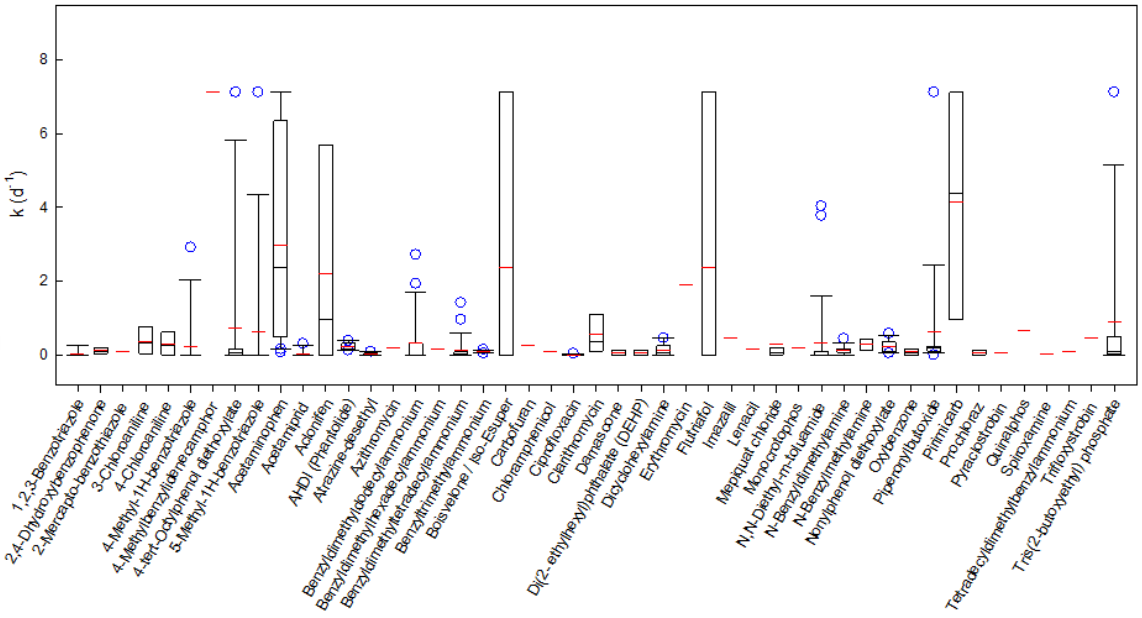


Figure 4.36. Biodegradation profile of micropollutants.

1,2,3-Benzotriazole is generally used as corrosion inhibitor, ultraviolet light stabilizer for plastics and antifoggant in photography. Many benzotriazoles may persist in the environment for a long time because it is resistant to UV light (Kowalska et al., 2015). Liu, et al. (2011) reported that in batch experiment, 1,2,3-Benzotriazole was degraded by activated sludge microorganism with a half-life of 114 days in aerobic condition and at room temperature (Liu and Ying et al., 2011). In this study, we calculated half-life of this chemical as 2.55 days at 2 sampling points.

2,4-Dihydroxybenzophenone (DHBP) which is an aromatic ketone and generally used for the synthesis of pharmaceutical agents (drug and pesticides), perfumery and manufacturing dyes (Trivedi et al., 2015). We detected degradation of DHBP at 5 sampling points. Half-life of this compound was calculated as around 3.25-9.13 days.

2-Mercapto-benzothiazole is a commercial compound used primarily as an ingredient in petroleum products and production of rubber (Whittaker et al., 2004, De Wever et al., 1998). Many studies show this compound and its byproducts are very harmful for living organisms. This compound is not expected to be biodegraded by microorganisms, but it is sensitive to direct photolysis. Its half-

life was reported as <1 day to <1 h (Whittaker et al., 2004). In our study, half-life of 2-mercapto-benzothiazole was calculated as 4.33 days at sampling point 5.

Chloramines are amines that are extensively used in production of pharmaceuticals, dyes, rubber and photography chemicals (Choy et al., 2005). Zhang et al. (2010) reported that by using activated sludge microorganisms, biodegradation rate was calculated as 13.0 ± 0.08 mg/h for 3-chloroaniline and 12.6 ± 0.08 mg/h for 4-chloroaniline in the batch test. In our study, 3-chloroaniline was detected in 3 sampling points and their half-lives were calculated as around 0.81-4.2 days. 4-chloroaniline was detected in 4 sampling points and their half-lives were calculated as around 0.94-10.40 days.

4-Methyl-1H-benzotriazole and 5-methyl-1H-benzotriazole are generally formed by after ozonation processes in the water (Müller et al., 2012). Half-life of these compounds was reported 8.5 days for 4-methyl-1H-benzotriazole and 0.9 days for 5-methyl-1H-benzotriazole in activated sludge (Hunstca et al., 2014). We detected 4-methyl-1H-benzotriazole at sampling point 8 and calculated its half-life as 0.24 days. 5-Methyl-1H-benzotriazole was biodegraded at only sampling points 8 and 9 and half-lives were calculated as 2.22 and 0.04 days, respectively.

4-methylbenzylidenecamphor has an endocrine disrupter effect and it can accumulate in the environment. In WWTPs, it cannot be degraded by conventional techniques (Ji et al., 2016). In sample point 4, this compound was biodegraded and its half-life was calculated as 0.01 days.

4-tert-Octylphenol diethoxylate is an endocrine disrupting compound degraded by only photocatalytic reactions in the literature (Błędzka et al., 2009). 4-tert-Octylphenol diethoxylate was biodegraded in 6 samples and half-lives were calculated as around 0.69-14.71 days.

Acetamiprid is used as a pesticide, especially to protect crops and in batch experiments, its half-life was reported as about 2.8–14 days in the soil (Singh et al., 2008). This compound was biodegraded in sampling points 6 and 15. Half-lives were calculated as 2.28 and 4.53 days, respectively.

Aclonifen is widely used as an herbicide and generally used to protect sunflowers. Laboratory experiments show its half-life as 40 to 49 days in soil samples at different incubation conditions including different temperature and different soil moisture (Vischetti et al., 2002). This compound was biodegraded at 5 sampling points and half-lives were calculated as around 0.01-0.55 days.

AHDI (Phantolide) is a polycyclic synthetic musk compound which is extensively used in personal care and cosmetic products. Due to not being completely eliminated in treatment plants, it reaches in aquatic environments (Tumova et al., 2019). We detected biodegradation of this compound at 10 sampling points and their half-lives were calculated as around 1.80- 5.56 days.

Atrazine-desethyl is a degradation by-product of atrazine which is an endocrine disrupting herbicide. It shows an equal toxicity to its parent compound (Khan et al., 2017). Atrazine can be degraded in surface water by photolysis and microorganisms via N-dealkylation and hydrolysis of the chloro substituent; the corresponding half-lives are greater than 100 days at 20°C (USEPA, 1988). We detected biodegradation of this compound at 3 sampling points and their half-lives were calculated as around 7.49-16.42 days.

Azithromycin is an antibiotic that excessively found in water systems. Vermillion Maier et al. (2018) used to American River soils and water to determine degradation of this micropollutant in microcosms simulating aerobic California watershed condition. They reported, under aerobic conditions, the degradation rate constant, k, and half-life of azithromycin are 0.0084 ± 0.0039 day^{-1} and 82.52 ± 56.54 days, respectively. This compound was biodegraded at sampling point 8 and half-life was calculated as 3.47 days.

Boisvelone / Iso-Esuper is a very common perfume ingredient that is used in soap, shampoo, cologne, liquid detergent. Bester et al., (2003) reported boisvelone / iso-esuper is eliminated from the wastewater with 56–64% percentage during waste water treatment processes. The elimination process is done by sorption to sludge. In our study, we detected biodegradation of this chemical at sampling point 17 and half-life was calculated as 0.10 days.

Carbofuran is a broad spectrum insecticide and is generally used to protect corn, grape and strawberries (Trotter et al., 1991). According to DPR Pesticide Chemistry Database (2002), carbofuran is biodegraded in aerobic conditions in 22 days. We detected biodegradation at sampling point 9 and half-life was calculated as 2.54 days.

Chloramphenicol is a broad spectrum antibiotic which is widely used to treat food-producing animals (Marni et al., 2010). Solution of chloramphenicol is degraded at room temperature for 4 days by sunlight in batch experiment (Shih., 1971). In our experiment, this compound was biodegraded at sampling point 9 and half-life was calculated as 7.1 days.

Ciprofloxacin is a broad spectral antibiotic and extensive consumption of this antibiotic has resulted in their accumulation in environment. Therefore drug-resistant microorganisms have emerged (Liao et al., 2016). Biodegradation of ciprofloxacin determined in pure fungal cultures (Wetzstein et al., 1999; Parshikov et al., 2001), but reactions appear to be slow and complete mineralization has not been reported. At sampling point 9, this compound was biodegraded and half-life was calculated as 25.67 days.

Clarithromycin is an antibiotic which is used to fight causative organisms such as diphtheria, pertussis and anthrax. When it reaches to the WWTPs, it cannot be eliminated easily. Mineralization of clarithromycin by ozone would require 100 times as much ozone (Lange et al., 2006). At 4 sampling points this compound was biodegraded and half-lives were calculated as around 0.39-3.38 days.

Chang et al. (2005) reported di(2- ethylhexyl)phthalate (DEHP) was biodegraded from river sediment in Taiwan in anerobic conditions by *Sphigomonas* sp. DK4. Half-life was determined as 3.01 days under optimal conditions of 30°C and pH 7.0. Similarly, at sampling point 8, half-life of this compound was calculated as 2.74 days.

Dicyclohexylamine is primarily used for production of soap, detergents and rubber (Lewis., 1993). According to SIDS Initial Assessment Report in the atmosphere, dicyclohexylamine was degraded by photochemically and half-life was calculated as 2.9 hours. In our study, this compound was biodegraded at 10 sampling points. Half-life was calculated as around 17.16-1.50 days.

Erythromycin is a macrolide antibiotic and generally cannot be removed by traditional wastewater treatment methods. Removal of this compound requires advanced oxidation processes (Kolplin et al., 2002). *Pseudomonas aeruginosa* 3011 can biodegrade erythromycin in only 24 hours. The pure bacterial culture was able to biodegrade 33.43±5.7% of erythromycin in laboratory experiments (Šabić et al., 2015). This compound was biodegraded at sampling point 8 and half-life was calculated as 0.36 days.

Flutriafol is a fungicide used for control of fungal diseases on fruits and vegetables. Zhang et al. (2014) reported the half-life of stereoisomers of this compound in grape. Half-lives were calculated as 5.59 and 6.98 for the (−) and (+) flutriafol, respectively. At sampling point 15, flutriafol was biodegraded and half-life was calculated as 0.10 days.

Imazalil is a fungicide used to control wide range of fungi on fruits and vegetables. In acid to neutral aqueous solutions, imazalil is stable for at least eight weeks at 40℃ (Food and Agriculture Organization of the United Nations., 1977). We detected biodegradation of this compound at sampling point 8 and half-life was calculated as 0.75 days.

Lenacil is a diazine herbicide which is used for selective weed control. Zhang et al. (1999) monitored degradation of lenacil in three soils and in two sediments systems for 100 days. They reported that lenacil was stable in the dark and at pH 5 and 7 but at pH 9 under irradiation, half-life was calculated in three soils ranged from 81 to 150 days and in two sediments ranged from 32 to 105 days. We found biodegradation of this compound at sampling points 8 and 9. Half-lives were calculated as 2.14 and 3.12 days, respectively.

Mepiquat chloride is a growth regulator globally used in cotton (Wang et al., 2014). No data was reported for biodegradation of mepiquat chloride in aquatic environment (USEPA., 2002). However, at 4 sampling points, mepiquat chloride was biodegraded. Half-lives were calculated as around 0.40-9.67 days.

Monocrotophos is a pesticide. It is stable at room temperature and half-life in solution is 23 days at pH 7 (USEPA., 1985). We detected biodegradation of this compound at sampling point 4 and 28. Both of them are under the pollution stress of domestic and industrial discharge. Half-lives were calculated as 2.05 and 9.92.

N,N-diethyl-m-toluamide is an ingredient of insecticides. Almost 30% of the U.S. population consumes products that contains N,N-diethyl-m-toluamide (USEPA 1998). Based on ready biodegradation tests; N,N-diethyl-m-toluamide, at 100 mg/L, is not biodegraded under aerobic conditions with a sewage inoculum and the Japanese MITI test in 4 weeks (NITE-CHRIP, 2016). We detect biodegradation of this compound at 9 different sampling points and half-lives were calculated as around 0.18-23.10 days.

Nonylphenol diethoxylate is a surfactant used for industrial processes such as pulp and paper processing, oil and gas recovery and steel manufacturing (Bettinetti et al., 2002). Jonkers et al. (2001) reported aerobic biodegradation kinetics of nonylphenol diethoxylate in a laboratory scale bioreactor filled with river water. The concentration of nonylphenol diethoxylate reduced to 50% after 10 h and over 99% of the initial nonylphenol diethoxylate was degraded after 4 days. Biodegradation of this compound was observed at 15 sampling points. Half-lives were calculated as around 1.20-13.56 days.

Oxybenzone is generally used as an UV light absorber in sunscreen products and plastics. In batch experiment, oxybenzone was biodegraded by microbial community of activated sludge and digester sludge in aerobic and anaerobic conditions with half-lives of 4.2 and 10.7 days, respectively (Liu et al., 2012). We detected oxybenzone at 5 sampling points. Half-lives were calculated as around 1.63-21.26 days.

Piperonylbutoxide is used in bug sprays to prolong the effects of the natural insecticides (Arnold et al., 1998). Waster et al. (1994) reported biodegradation of piperonylbutoxide in aqueous environments at three sites, and the half-life as around 0.55-1.64 days. We detected biodegradation of this compound at 15 sampling points and half-lives were calculated as around 0.01-9.51 days.

Pirimicarb is used as an insecticide in worldwide to protect fruits and vegetables (Pirisi et al., 1996). In aqueous solution only, photodegradation was reported with half-life of 30 min at 254 nm (Chen et al., 2009). We detected biodegradation of this at 4 sampling points. Half-lives were calculated as around 0.01-0.9 days.

Prochloraz is a broad spectrum fungicide. In aqueous solution half-life of prochloraz was reported as 18.35 and 19.17 days at pH 4.0, 22.6 and 25.1 days at pH 7.0 and 15.8 and 16.6 days at pH 9.2 (Aktar et al., 2008). We observed biodegradation of this compound at sampling point 5 with half-life of 3.94 days.

Pyraclostrobin is a fungicide that is generally used to protect crops. Chen et al. (2018) used sequential enrichments with pyraclostrobin as a sole carbon source. Two microbial communities (HI2 and HI6) capable of catabolizing pyraclostrobin were isolated from Hawaiian soils. More than 99% of pyraclostrobin was degraded by the soil microorganisms in 5 days. We detected biodegradation of this micropollutant at sampling point 25 with a half-life of 16.39 days.

Quinalphos is the toxic organophosphate which is biodegraded by the natural soil microorgansims. *Bacillus* and *Pseudomonas* spp., which is isolated from contaminated soil samples are capable of degrading quinalphos from aqueous streams. Batch experiments were performed to determine the natural and induced biodegradation of quinalphos in the aqueous medium. Isolated microorganisms degraded >80% of quinalphos in 17 days. (Dhanjal et al., 2014). We observed biodegradation of this compound at sampling point 8 and half-life was calculated as 1.06 days.

Spiroxamine is a protective and eradicative fungicide that is used for cereals and grapes (Rosales-Conrado, 2009). Rosales-Conrado, (2009) conducted biodegradation experiment in water at different pH values. Degradation was observed at both pH 4 and 14 with half-life of 37 and 10 days, respectively. In our work, spiroxamine biodegradation was detected at sampling point 9 with a half-life 20.33 days.

Trifloxystrobin is a broad spectrum agricultural fungicide. It was biodegraded in vitro conditions in soil with half-lives ranging from 1.8 to 5 days in dark (Benerjee et al., 2007). We detected biodegradation of trifloxystrobin at sampling point 25 and half-life was calculated as 1.52 days.

Tris(2-butoxyethyl) phosphate is used in floor polishes, rubber and plastics. This compound is classified as readily biodegradable. Semi-continuous sludge laboratory tests show substantial elimination of tris(2-butoxyethyl) phosphate (>80%). In estuarine water, half-life of this compound was reported as 50 days (Benson et al., 2000). We detected this compound at 12 different sampling points and half-life was calculated as around 0.22 to 24.32 days.

In this region, most of the OIZs are in the upstream of the river. They discharge their wastewaters into the river. On the other hand, most of the agricultural areas are in the downstream of the river. Since the river water is used in irrigational activities, most of the micropollutants, even they are biodegradable, can reach agricultural areas and contaminate the agricultural products. The arrival time of each micropollutant from any sampling point to the agricultural areas can be estimated via the velocity of water. The risk analysis can be done according to the biodegradation rate constants of chemicals and the sampling point distances to the agricultural areas. In this work, the risk analysis of biodegradable micropollutants detected at sampling points 4 and 5 which can be reached to the sampling point 3 were done according to Equation 4.4.

$$Risk = \frac{2\ x\ t_{1/2}}{t_{reach}} \tag{4.4}$$

where $t_{1/2}$ is the half-life of chemicals and t_{reach} (days) is the time of each chemical to reach from its sampling point to the sampling point 3. The sampling point 3 is located in the downstream of the river and used for irrigational activities. In Equation 4.4, $t_{1/2}$ is multiplied by 2 because 25% of the remaining micropollutants reaching to the sampling point 3 is considered as an critical metric for contamination risk of irrigational activities. In Table 4.4 and Table 4.5, the risk analysis of each biodegradable micropollutants detected in sampling points 4 and 5 can be seen, respectively. If the

risk is calculated above 1, the micropollutants are highlighted with red color as the high risky chemicals. The moderate risky micropollutants which are between 0.5 and 1 is shown with yellow. If it is below 0.5, it is highlighted as green color which represents the least risky micropollutants.

Table 4.4. Risk analysis of biodegradable micropollutants detected in sampling point 4.

Chemicals	$t_{1/2}$	Risk
2,4-Dihydroxybenzophenone	3.38	1.48
2-Mercapto-benzothiazole	4.33	1.89
4-Chloroaniline	1.18	0.52
4-Methylbenzylidenecamphor	0.10	0.04
4-tert-Octylphenol diethoxylate	4.02	1.76
Acetaminophen	0.10	0.04
Aclonifen	0.10	0.04
AHDI (Phantolide)	2.03	0.89
Benzyldimethyldodecylammonium	2.17	0.95
Benzyldimethylhexadecylammonium	4.16	1.82
Clarithromycin	3.38	1.48
Dicyclohexylamine	2.57	1.12
Monocrotophos	2.05	0.90
N,N-Diethyl-m-toluamide	5.90	2.58
N-Benzylmethylamine	1.61	0.70
Nonylphenol diethoxylate	3.45	1.50
Piperonylbutoxide	1.55	0.68
Tris(2-butoxyethyl) phosphate	8.71	3.80

Table 4.5. Risk analysis of biodegradable micropollutants detected in sampling point 5.

Chemicals	$t_{1/2}$	Risk
3-Chloroaniline	0.81	0.38
4-Chloroaniline	1.59	0.74
4-tert-Octylphenol diethoxylate	0.10	0.05
Acetaminophen	0.10	0.05
AHDI (Phantolide)	2.63	1.23
Benzyldimethyldodecylammonium	1.51	0.70
Dicyclohexylamine	1.50	0.70
N-Benzylmethylamine	2.31	1.08
Nonylphenol diethoxylate	4.00	1.87
Piperonylbutoxide	4.40	2.05
Prochloraz	3.94	1.84
Tris(2-butoxyethyl) phosphate	13.59	6.34

On the other hand, the rest of the other chemicals were not biodegraded during the incubation processes. These chemicals were fungicides (azoxystrobin, carbendazim, propiconazole and tebuconazole), herbicides (diuron, N-ethyl-p-toluenesulfonamide, terbuthylazine, terbutryn), insecticides (fenamiphos, omethoate), antibotics (norfloxacin, ofloxacin, sulfamethoxazole), preservative (terbutryn), fragrance (g-methylone), organophosphorus compound (triphenylphosphineoxide) and ingredient in the production of coating and plasticizers (hexa(methoxymethyl)melamine). Among these resistant micropollutants diuron, omethoate and terbutryn are also classified as PSs, because of the potential of high toxicity and resistance of degradation in the environment. Ofloxacin was one of the most detected micropollutant which was

detected at 28 sampling points and its concentration did not change for 30 days. Hexa(methoxymethyl)melamine is an emerging contaminant generally used in production of plastics, coils and automobiles (Dsikowitzky et al., 2015). We found this compound in 25 samples with a high concentration and it was not biodegraded. Also, Dsikowitzky et al. (2015) reported that in German rivers, this compound was occurred with relatively high concentrations in 60 out of 117 water samples taken from rivers.

5. CONCLUSIONS

In this study, a high-throughput method was developed to test biodegradability of chemicals. The method integrates triple quad mass spectroscopy to measure many chemicals simultaneously at very low concentrations which enabled us to test biodegradation of multiple chemicals simultaneously at non-toxic environmentally relevant low concentrations in a single flask. These chemicals include, antibiotics, industrial chemicals, pharmaceuticals, agricultural chemicals and personal care products. Only 7 out of 32 chemicals tested were degraded above 60 percent.

This high-throughput method was used to test the biodegradability of micropollutants present in the Ergene River by the native microorganisms. As a result of several measurements, biodegradation was only observed for 47 chemicals out of 64. Chemicals which were biodegraded were further analyzed and their decay rate constants were calculated. To verify our results, biodegradability of each chemical was compared with the results in literature. Their half-life was also compared. For some of the chemicals, our results are consistent with ones in the literature. However, some chemicals which are known as non-biodegradable or have no evidence about biodegradability, were found to be biodegradable. Biodegradation rate constants and half-lives were calculated as around 0.03-7.13 d^{-1} and 0.10-25.67 days, respectively.

The findings of this thesis indicated most of the emerging contaminants cannot be eliminated by activated sludge processes. Thus, they may reach to surface water and stay which cause risk of continuous pollution of Ergene River. Moreover, even some micropollutants were biodegraded, they may reach to the agricultural areas via irrigation activities before they were degraded.

For future studies, unknown analysis should be done to monitor different micropollutants. Also, biotransformation products should be analyzed because of the high toxicity potential. Carcinogenicity and mutagenicity of micropollutants and biotransformation products should be examined.

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APPENDIX A: MRM TRANSITIONS OF SELECTED CHEMICALS

Table A.1. MRM transitions of detected chemicals

Compound	RT	DP	Q1
1,2,3-Benzotriazole	2.87	61	120.0
2-Mercapto-benzothiazole	3.38	71	167.9
2,4-Dihydroxybenzophenone	4.56	61	215.0
3-Chloroaniline	2.83	51	128.0
4-Chloroaniline	2.83	56	128.0
4-Methyl-1H-benzotriazole	3.09	46	134.0
4-Methylbenzylidenecamphor	7.10	81	255.1
4-tert-Octylphenol diethoxylate	7.04	61	312.2
5-Methyl-1H-benzotriazole	3.08	56	134.0
5,6-Dimethyl-1H-benzotriazole monohydrate	3.34	81	148.1
Acetaminophen	2.65	56	152.0
Acetamiprid	2.99	76	223.1
Aclonifen	6.16	61	265.0
AHDI (Phantolide)	7.33	71	245.2
Alachlor	5.77	21	270.0
Amoxicillin	0.51	16	366.1
Atrazine	4.06	21	216.1
Atrazine-desethyl	3.09	56	188.2
Azithromycin	2.80	86	749.5
Azoxystrobin	5.20	76	404.1
Benzyldimethyldodecylammonium	5.75	11	304.3
Benzyldimethylhexadecylammonium	6.72	101	360.4
Benzyldimethyltetradecylammonium	6.39	96	332.3
Benzyltrimethylammonium	0.50	66	150.1
Boisvelone / Iso-Esuper	7.43	71	235.2
Cadusafos	6.62	66	271.1
Carbazole	5.29	76	168.0
Carbendazim	2.73	71	192.0
Carbofuran	3.45	76	222.1
Chlorfenvinphos	6.30	66	358.9
Chlorpyrifos	7.16	56	349.9
Ciprofloxacin	2.72	76	332.2
Clarithromycin	3.75	46	748.4
Cyprodinil	5.05	91	226.1
Damascone	6.19	41	193.0
Di(2- ethylhexyl)phthalate (DEHP)	8.36	61	391.3
Dichlorvos	3.36	61	220.9
Dicyclohexylamine	2.78	61	182.2
Dimethoate	2.96	66	230.1
Diphenylamine	5.52	71	170.0
Diuron	4.22	61	233.0
Doxycycline	2.91	86	445.1
Drometrizole	6.97	76	226.1
Erythromycin	3.18	21	734.5
Fenamiphos	6.02	71	304.0
Flutolanil	5.44	86	324.0
Flutriafol	4.00	71	302.0
g-Methylionone	6.85	41	207.1
Galaxolide	7.54	91	257.1
Hexa(methoxymethyl)melamine	3.7	26	391.0
Hexylcinnamaldehyde	7.18	66	217.1
Imazalil	3.17	56	297.0
Lenacil	4.14	66	235.1
Mepiquat chloride	0.50	46	113.9
Monocrotophos	2.82	56	224.2

Table A.1. MRM transitions of detected chemicals – Cont'd

Compound	RT	DP	Q1
N-Benzyldimethylamine	0.51	41	136.1
N-Benzylmethylamine	0.51	36	122.2
N-Ethyl-p-toluenesulfonamide	3.29	46	200.0
N,N-Diethyl-m-toluamide	4.10	71	192.1
Norfloxacin	2.71	71	320.2
Ofloxacin	2.70	46	362.2
Omethoate	2.66	51	213.9
Oxybenzone	6.00	61	229.1
Penconazole	6.17	81	284.2
Piperonylbutoxide	6.99	16	356.2
Pirimicarb	2.96	66	238.7
Prochloraz	5.99	46	376.0
Propazine	5.02	46	229.9
Propetamphos	5.55	56	282.2
Propiconazole	6.30	96	342.1
Pyraclostrobin	6.45	36	388.0
Pyridaben	7.64	66	365.1
Quinalphos	6.13	61	299.0
Quinoxyfen	7.07	111	307.9
Simazine	3.49	41	202.1
Spiroxamine	3.85	71	298.0
Sulfamethoxazole	2.85	46	254.0
Tebuconazole	6.17	91	308.2
Terbuthylazine	5.23	76	230.1
Terbutryn	4.09	61	242.0
Tetradecyldimethylbenzylammonium	2.85	36	229.1
Tonalide	7.54	71	259.1
Triazophos	5.65	66	314.0
Trifloxystrobin	6.73	61	409.1
Triphenylphosphineoxide	5.05	96	279.1
Tris(2-butoxyethyl) phosphate	6.89	26	399.2

APPENDIX B: CONCENTRATION CHANGES DURING THE INCUBATION PERIOD

Figure B.1. Biodegradation profile of chemicals at sampling point 4.

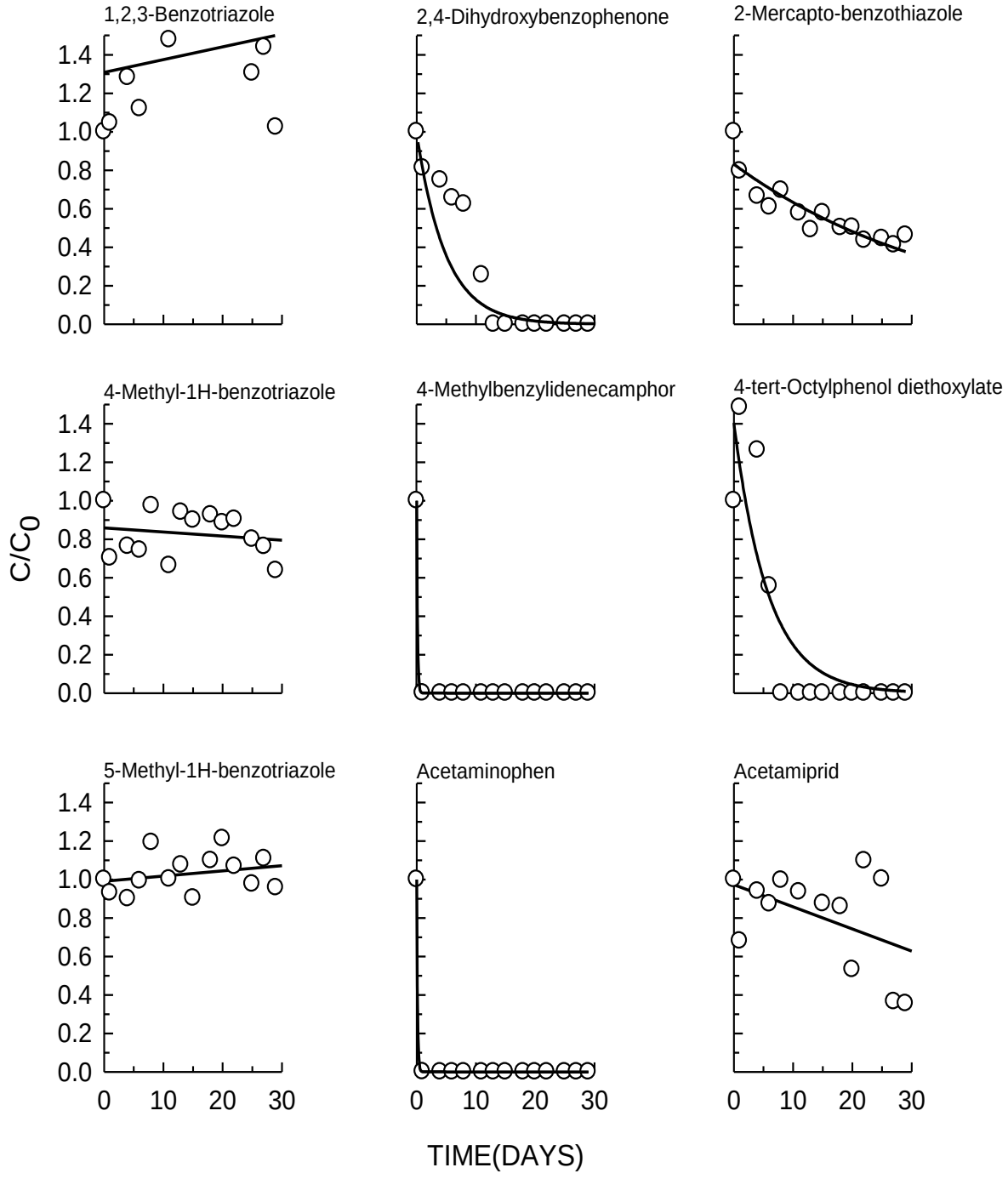


Figure B.1. Biodegradation profile of chemicals at sampling point 4 – Cont'd.

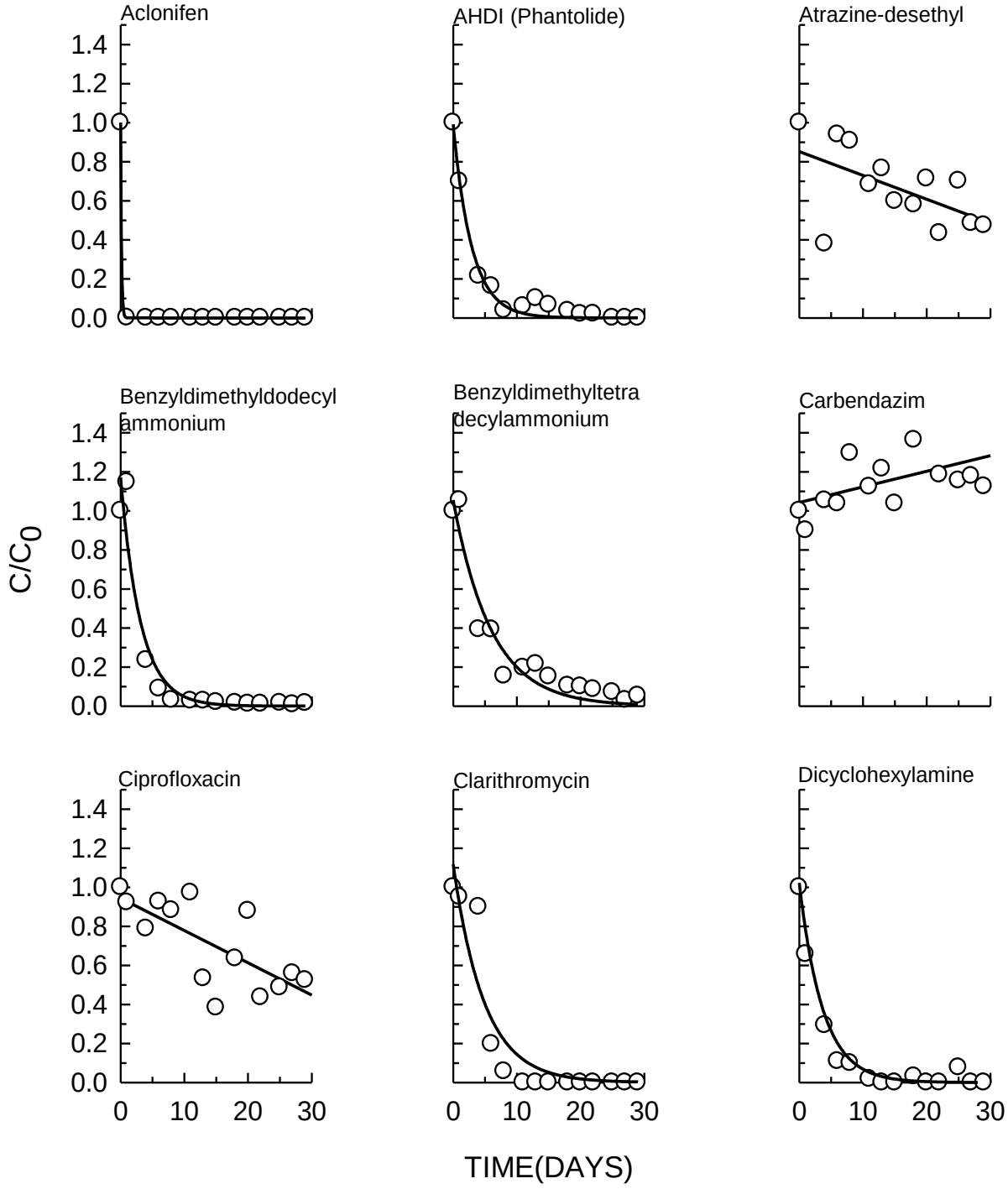


Figure B.1. Biodegradation profile of chemicals at sampling point 4– Cont'd.

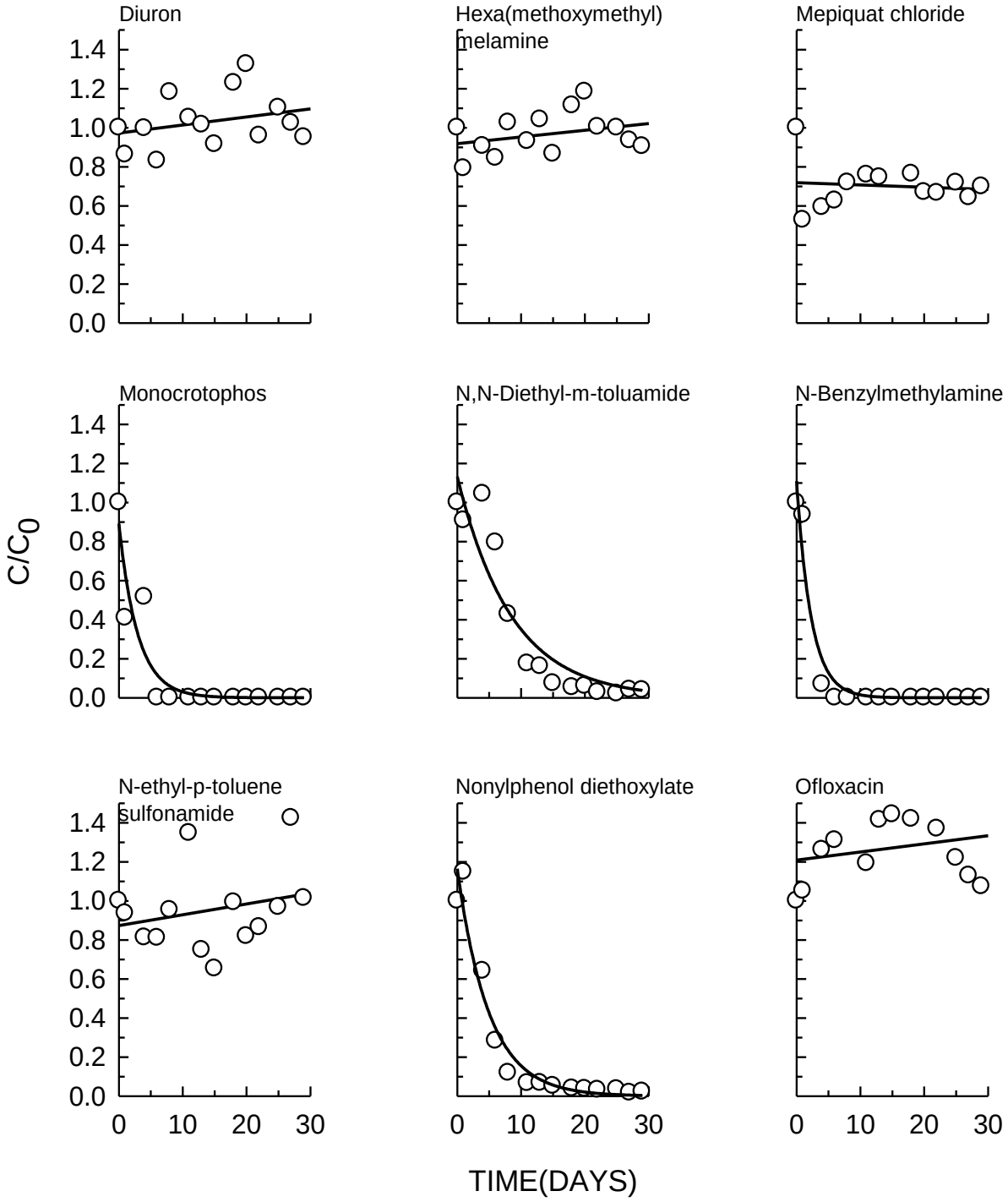


Figure B.1. Biodegradation profile of chemicals at sampling point 4 – Cont'd.

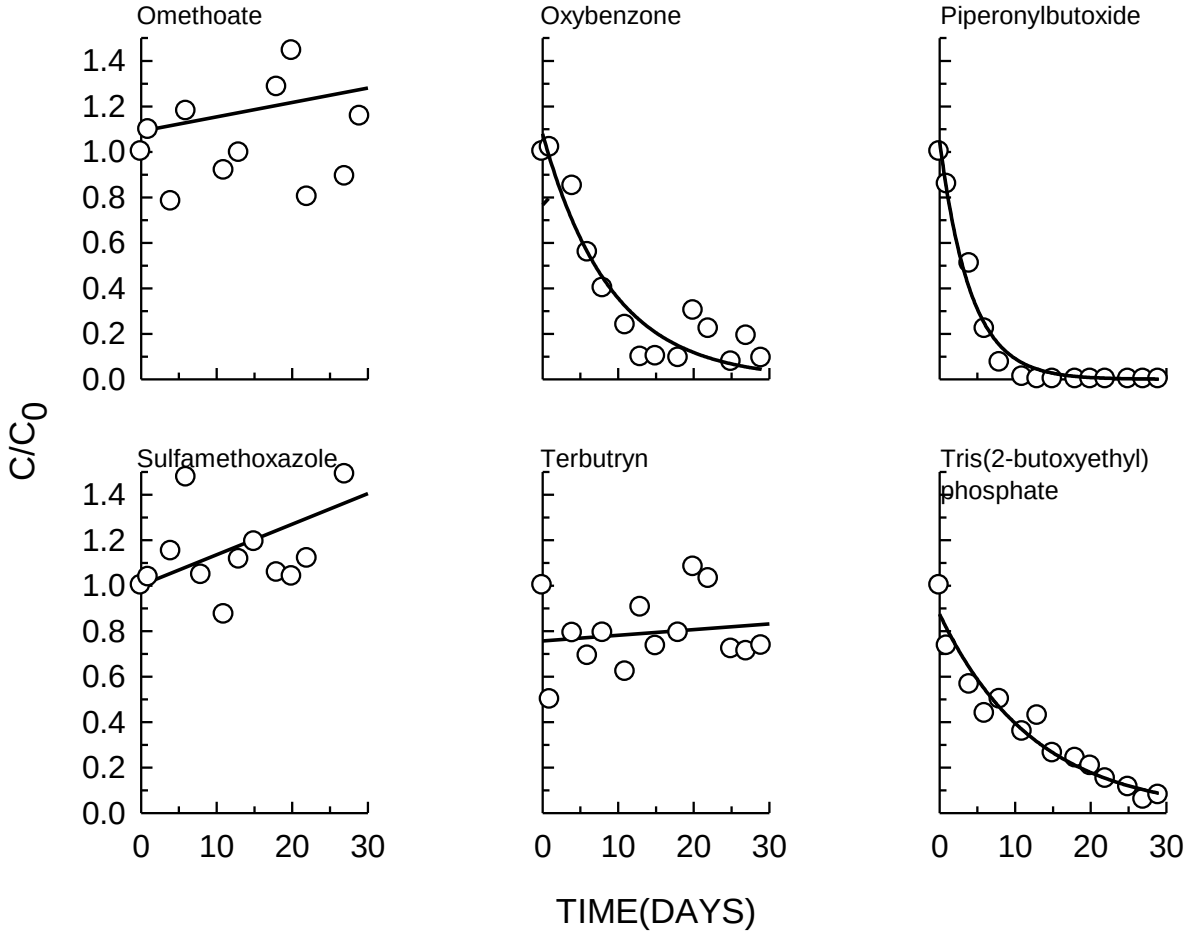


Figure B.2. Biodegradation profile of chemicals at sampling point 5.

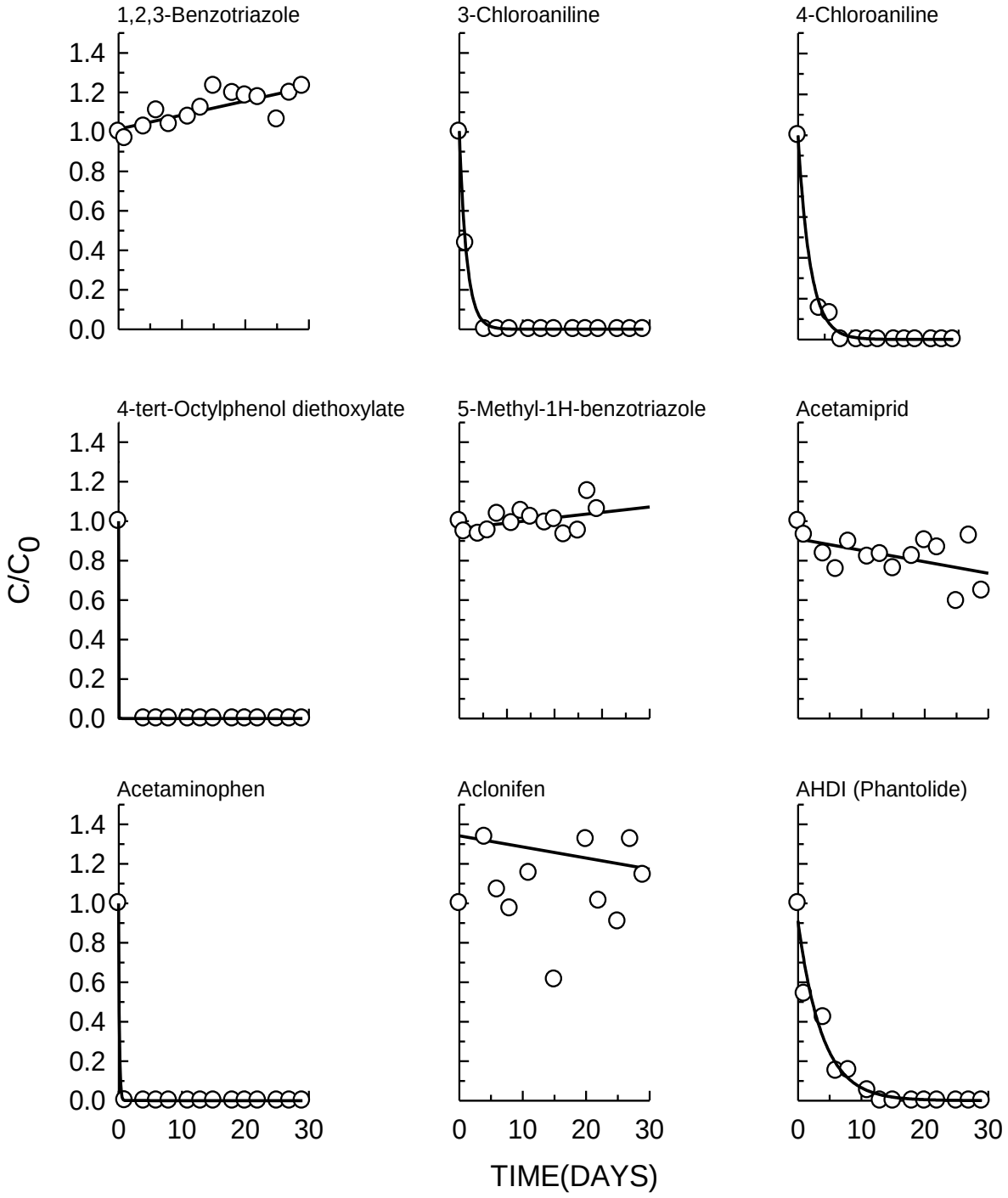


Figure B.2. Biodegradation profile of chemicals at sampling point 5 – Cont'd.

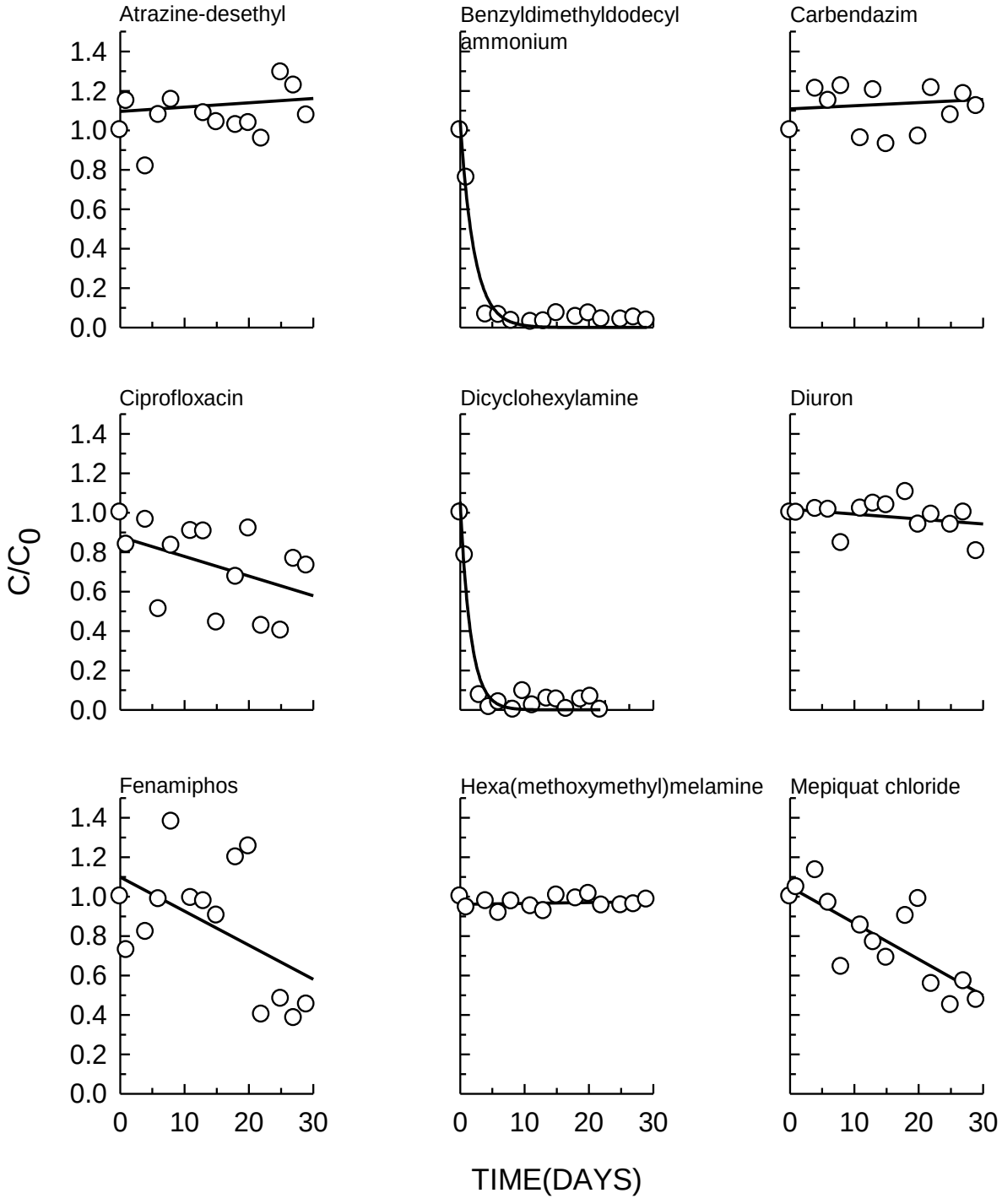


Figure B.2. Biodegradation profile of chemicals at sampling point 5 – Cont'd.

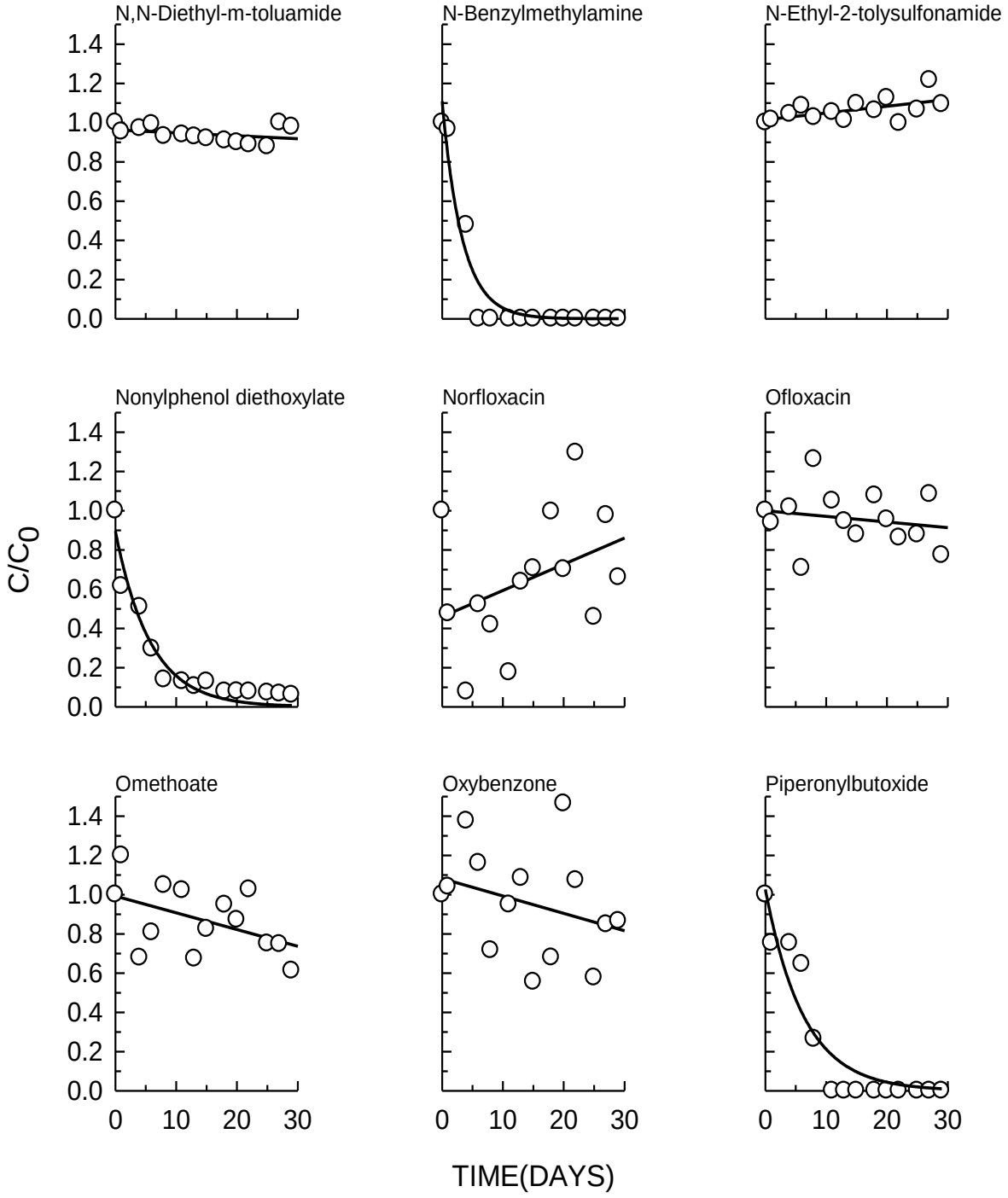


Figure B.2. Biodegradation profile of chemicals at sampling point 5 – Cont'd.

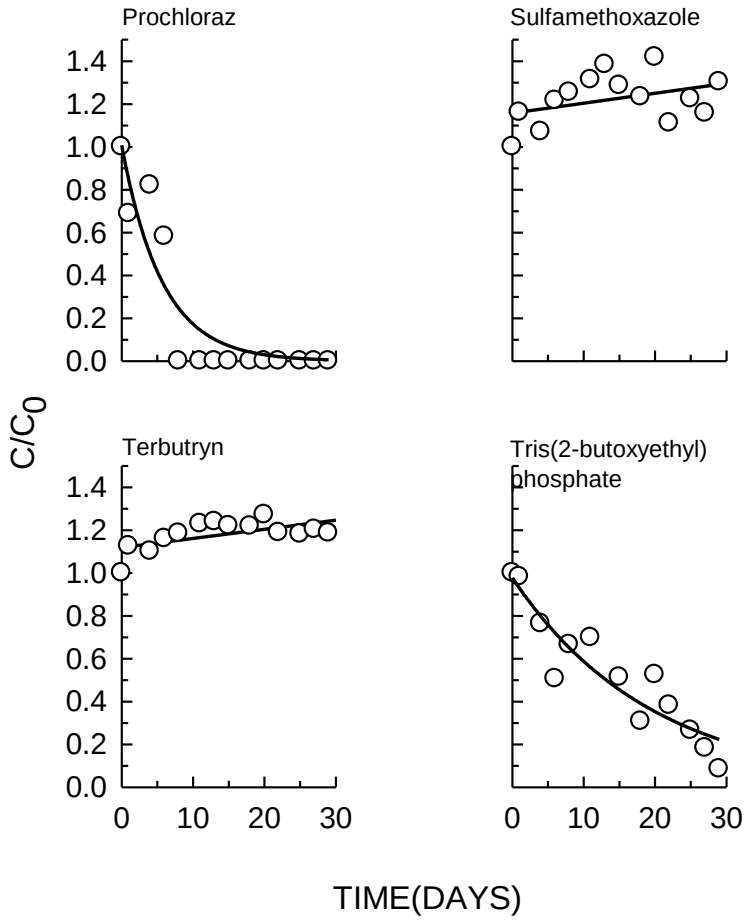


Figure B.3. Biodegradation profile of chemicals at sampling point 6.

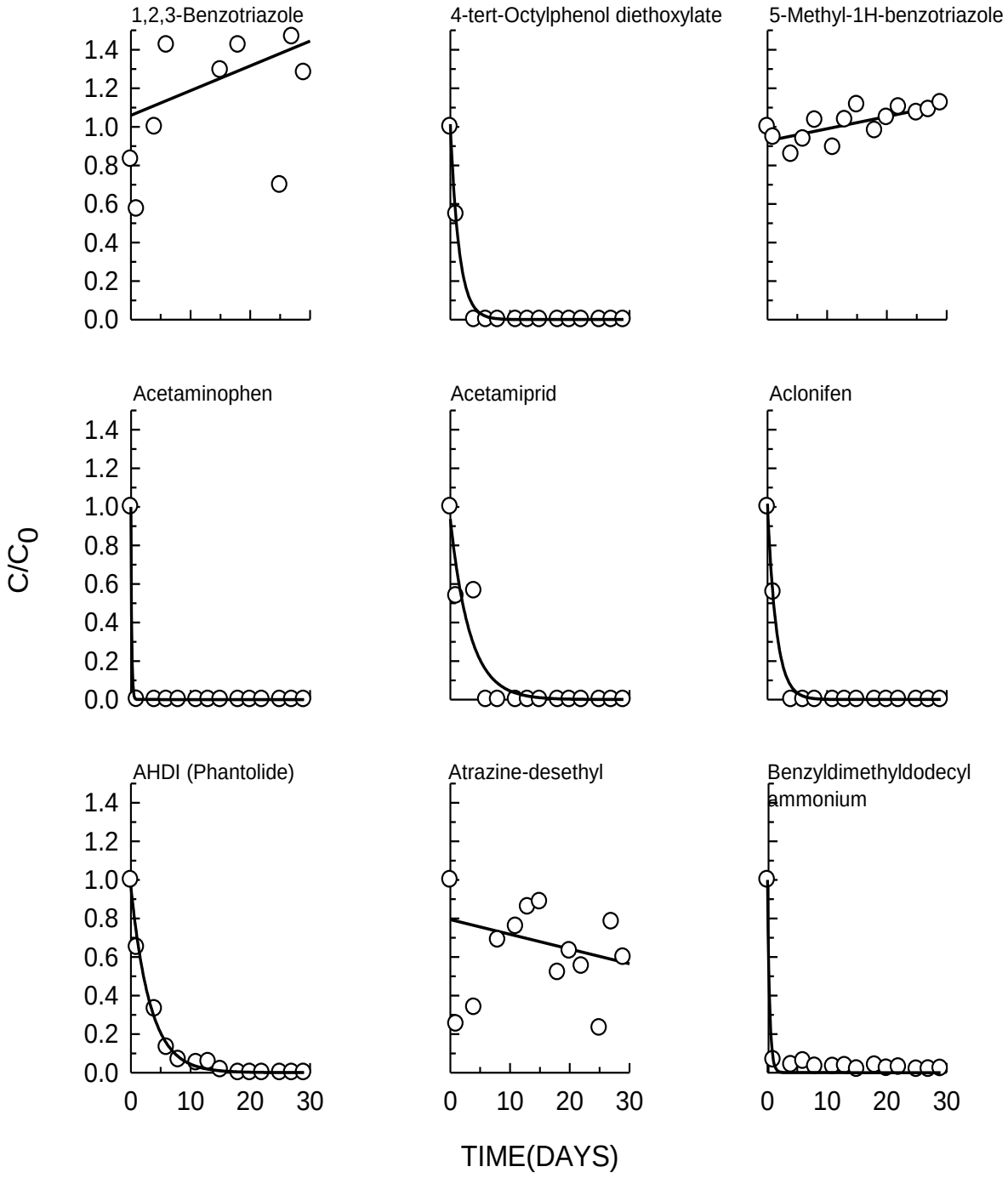


Figure B.3. Biodegradation profile of chemicals at sampling point 6 – Cont'd.

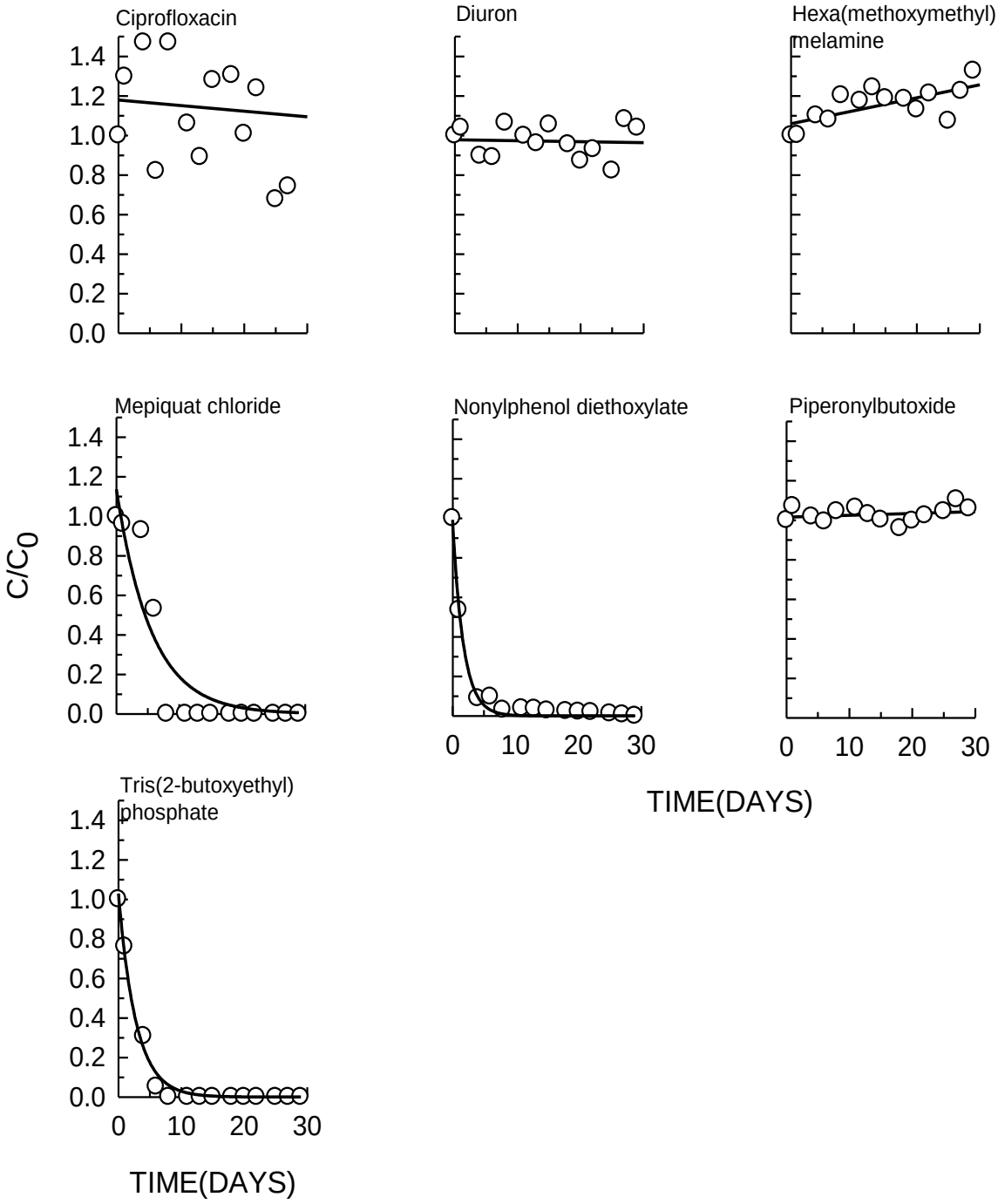


Figure B.4. Biodegradation profile of chemicals at sampling point 7.

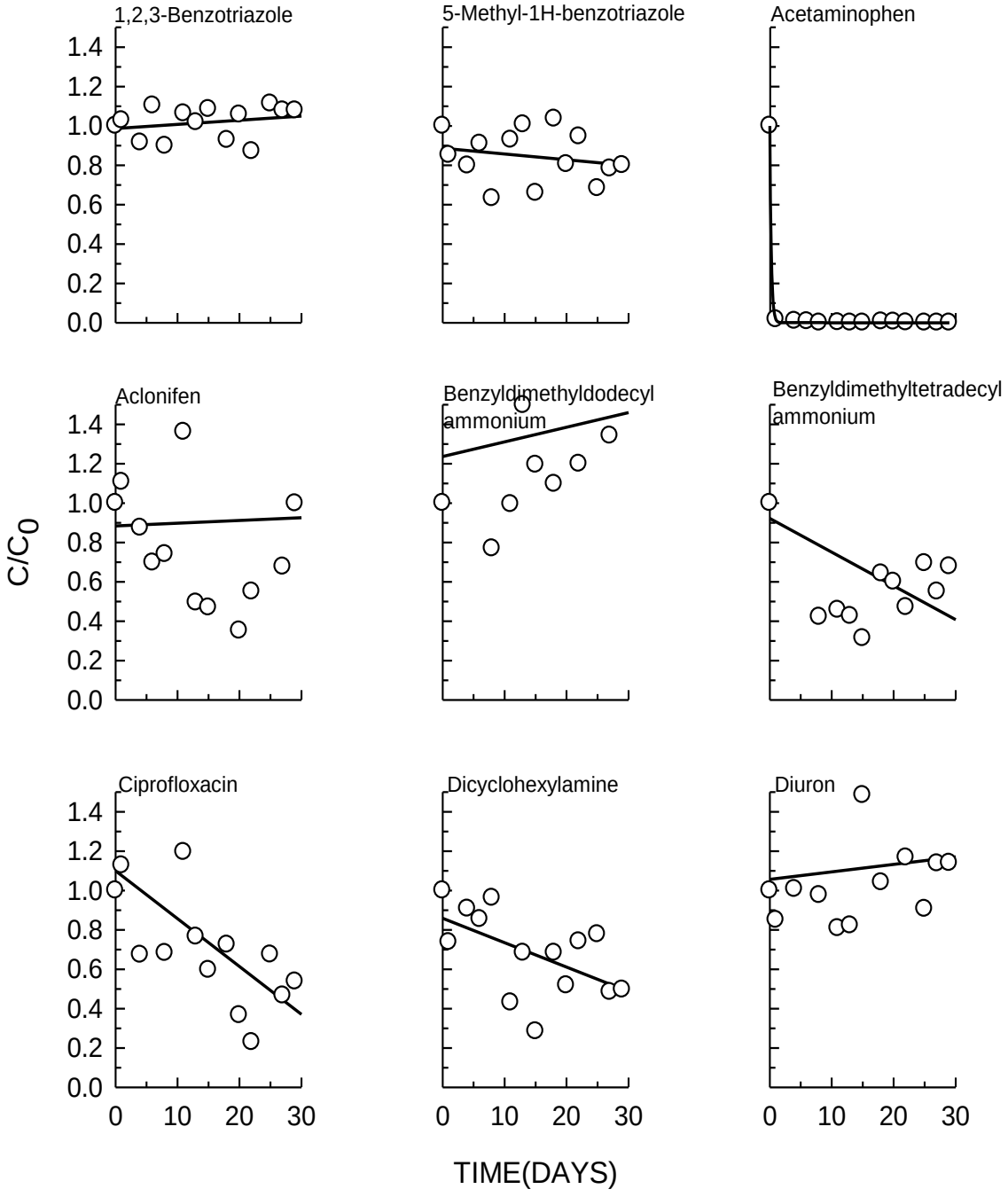


Figure B.4. Biodegradation profile of chemicals at sampling point 7– Cont'd.

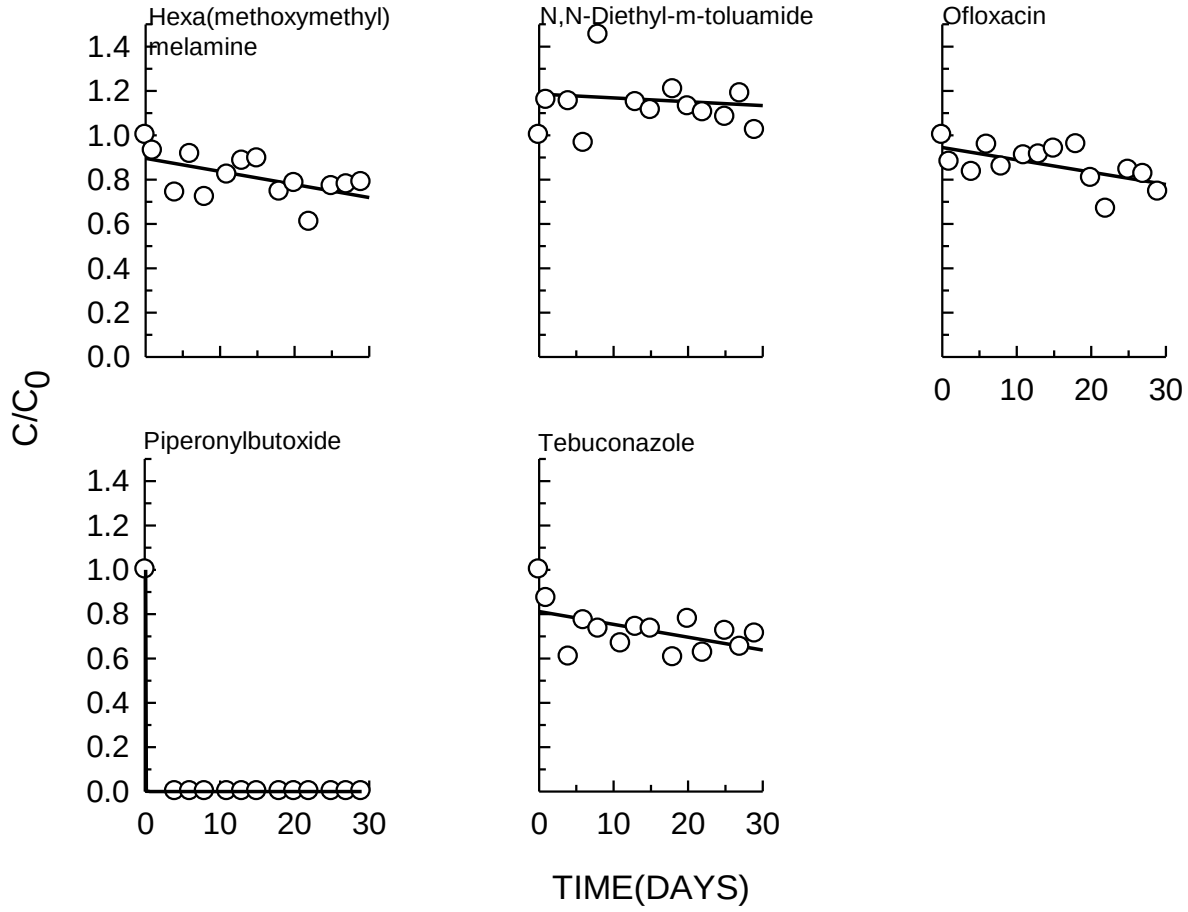


Figure B.5. Biodegradation profile of chemicals at sampling point 8.

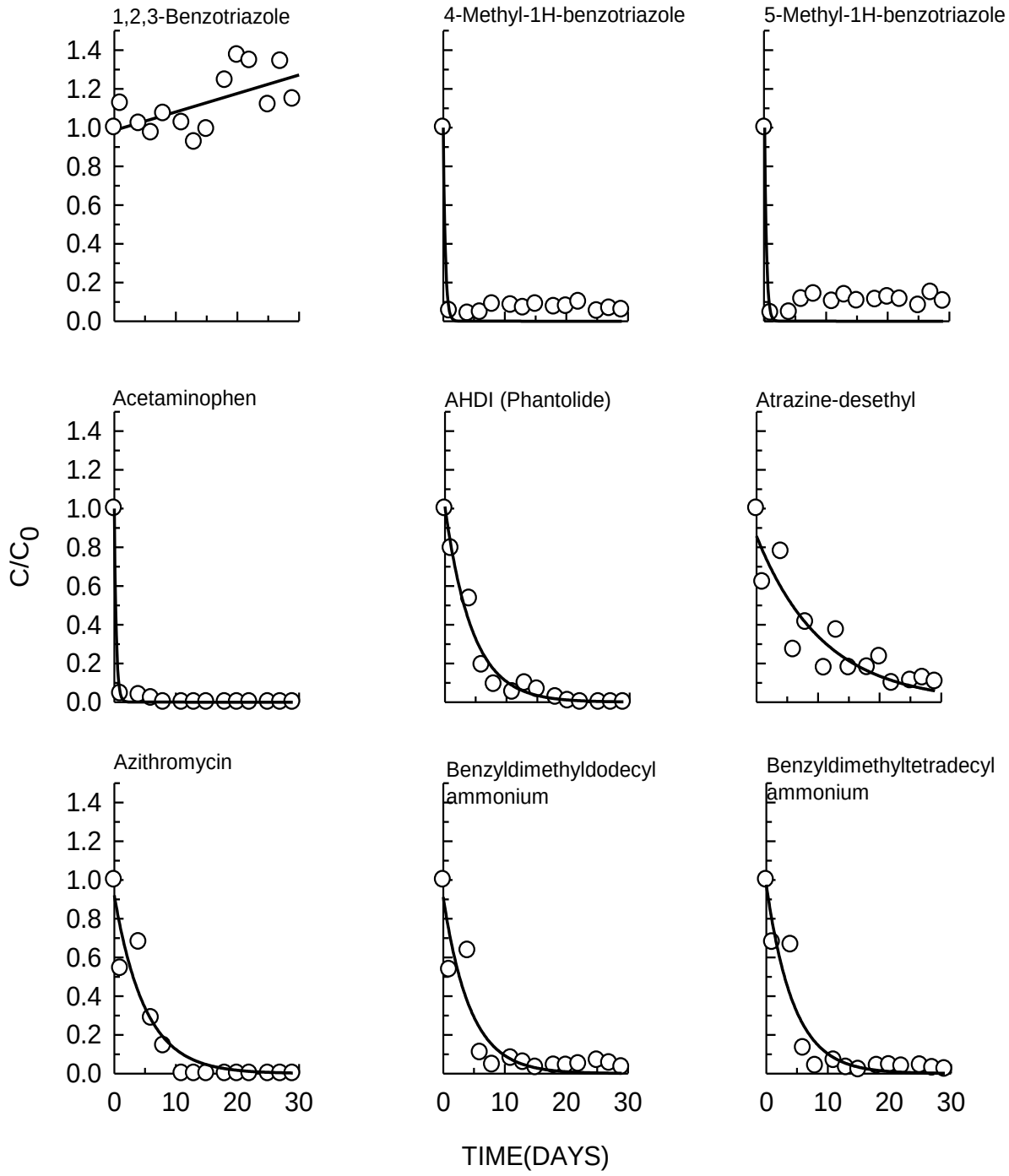


Figure B.5. Biodegradation profile of chemicals at sampling point 8 – Cont'd.

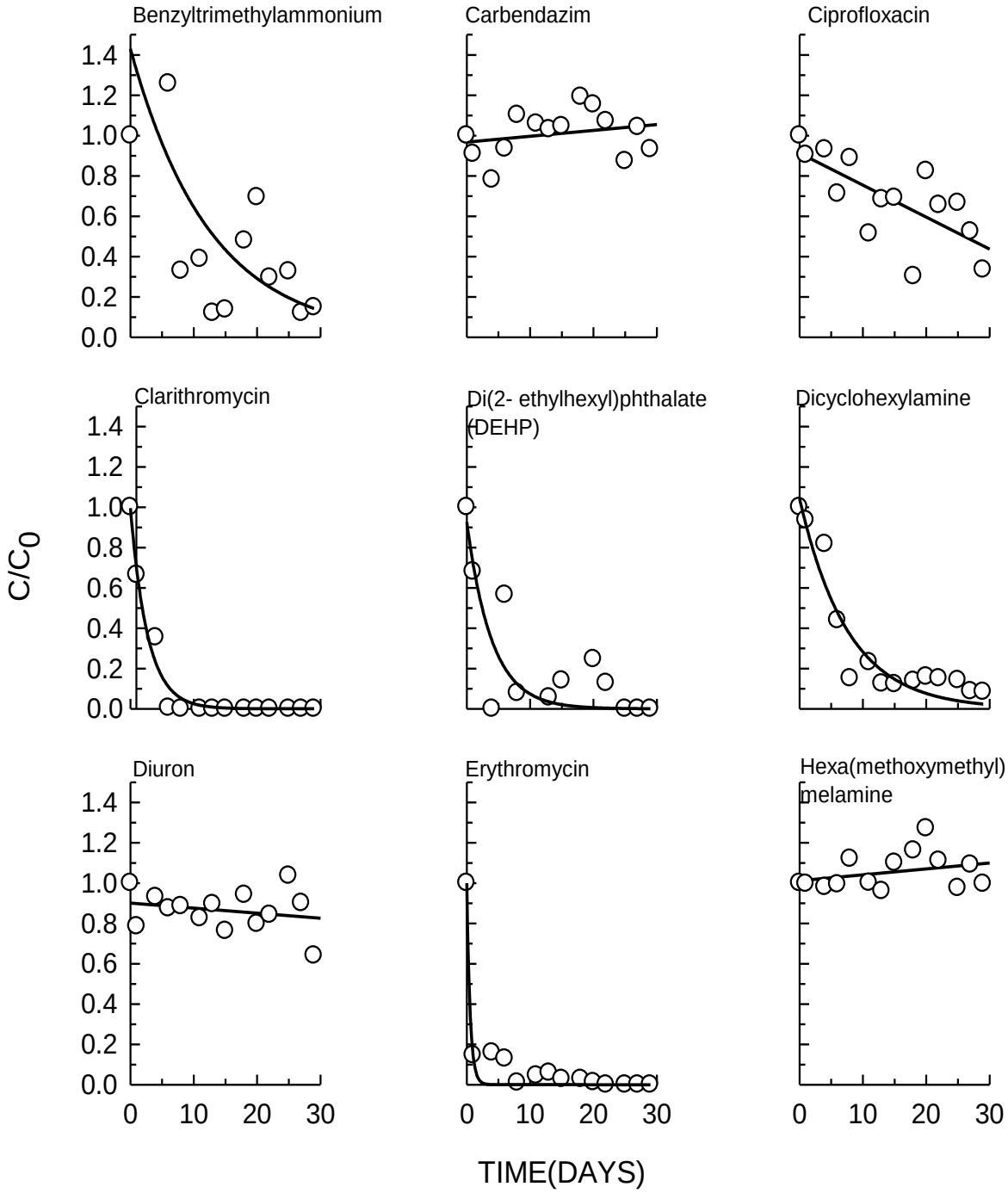


Figure B.5. Biodegradation profile of chemicals at sampling point 8 – Cont'd.

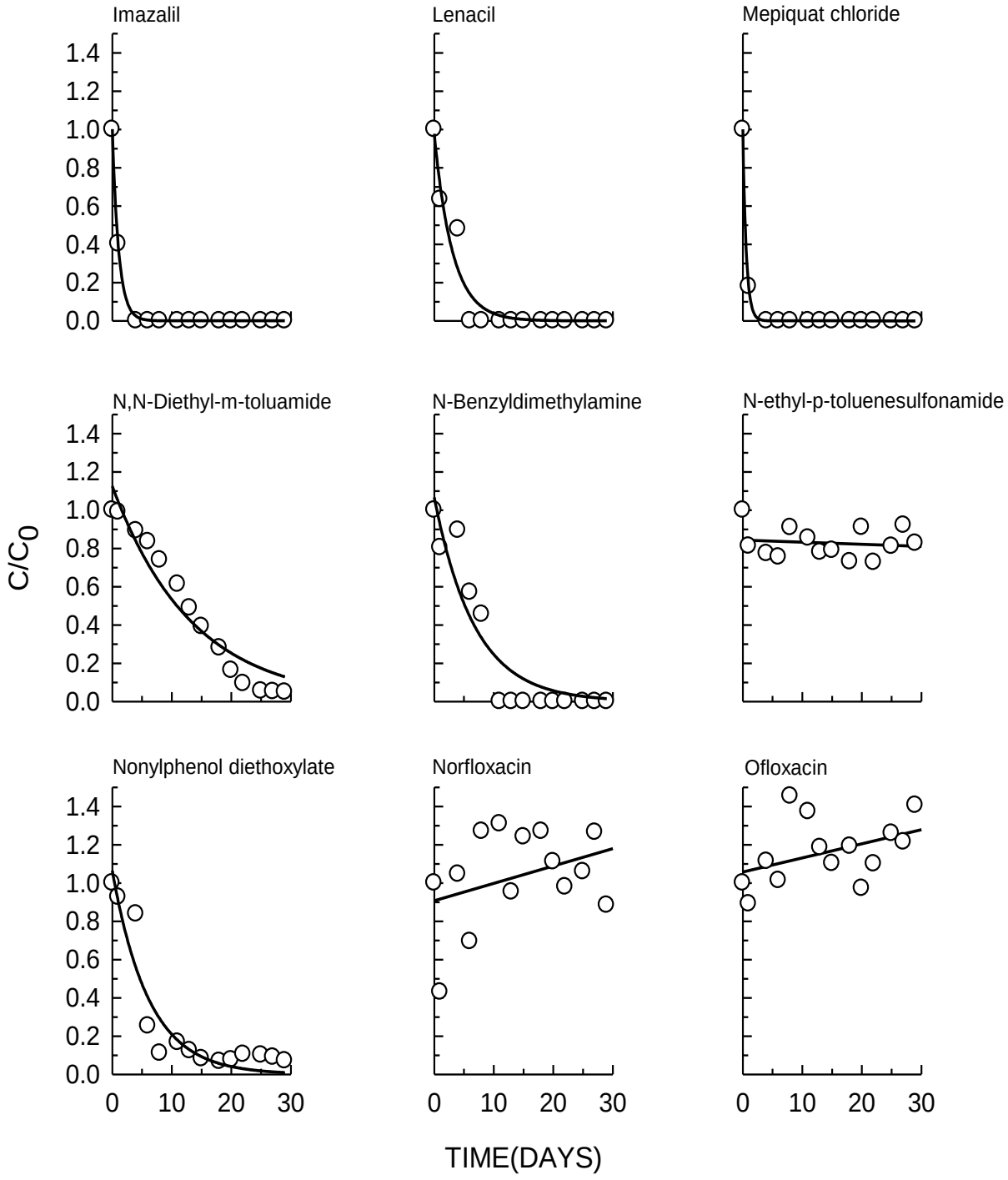


Figure B.5. Biodegradation profile of chemicals at sampling point 8 – Cont'd.

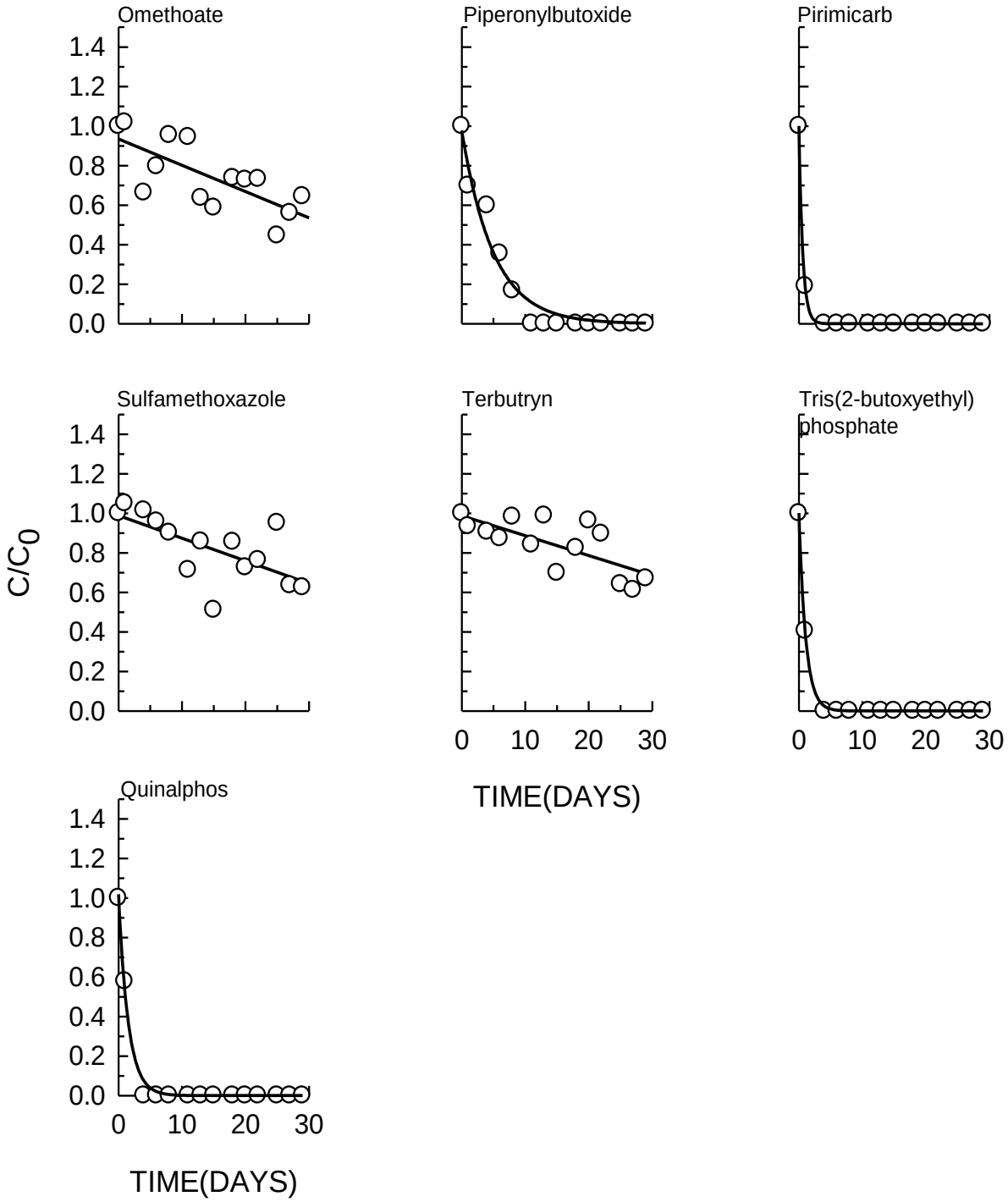


Figure B.6. Biodegradation profile of chemicals at sampling point 9.

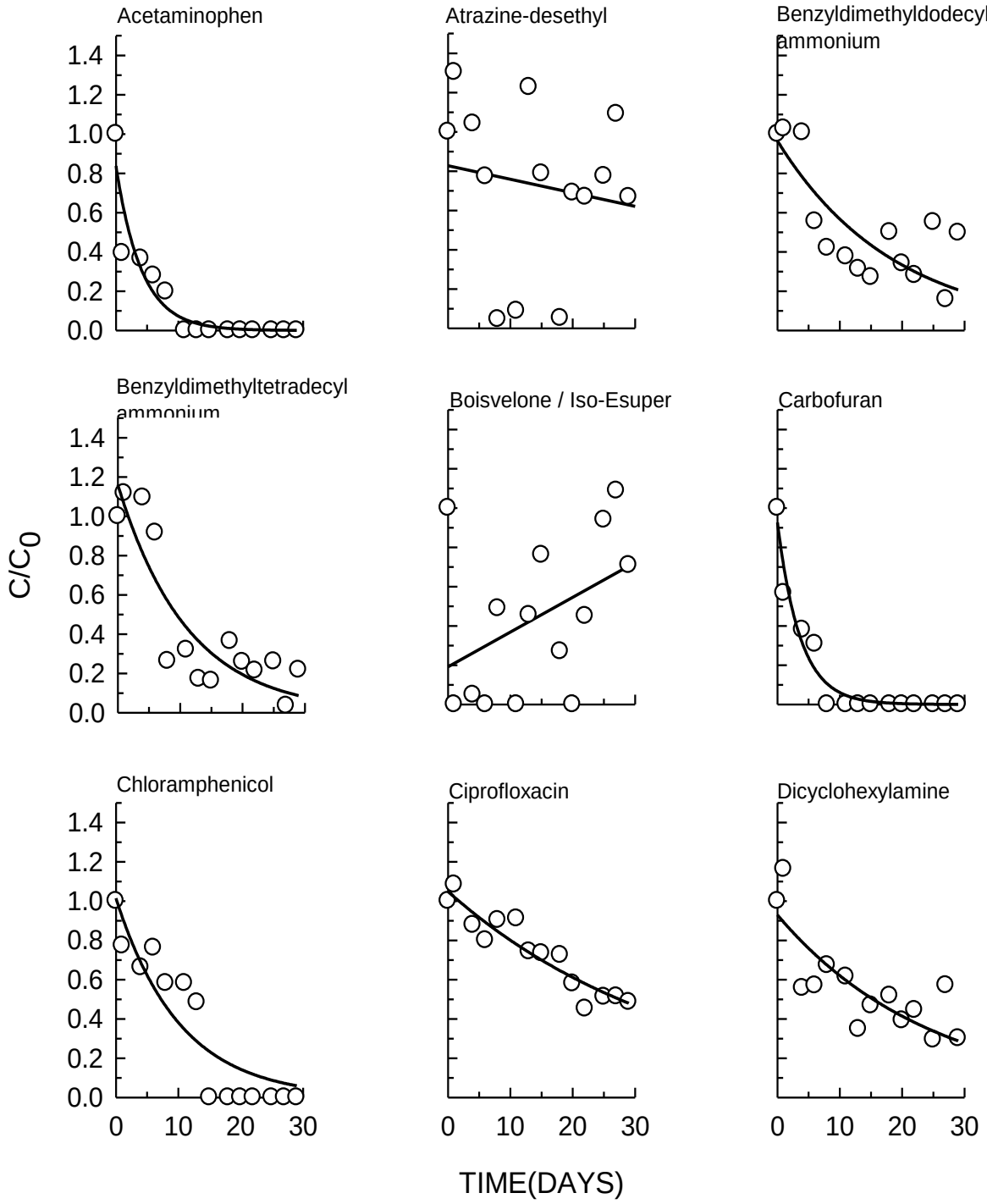


Figure B.6. Biodegradation profile of chemicals at sampling point 9 – Cont'd.

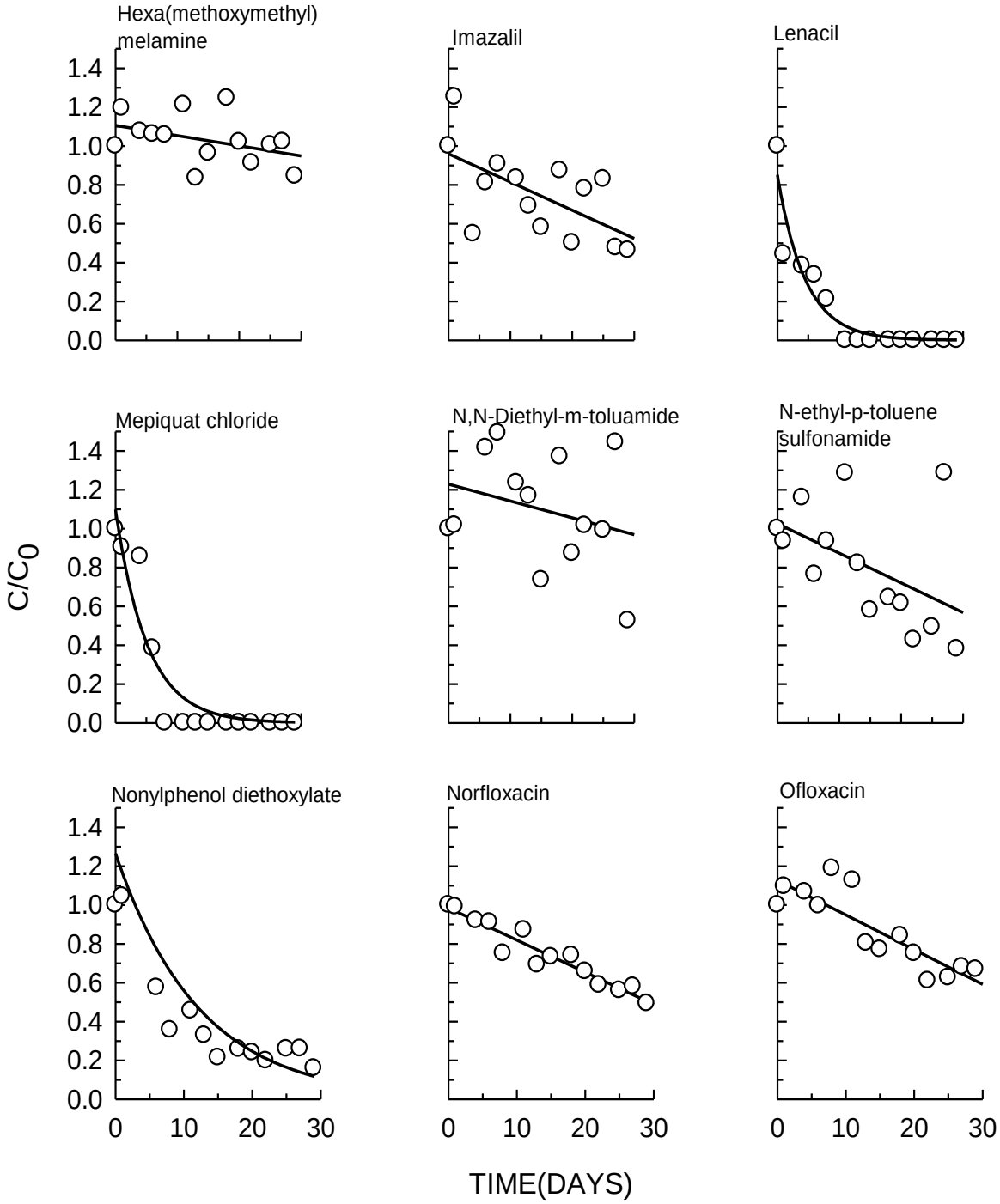


Figure B.6. Biodegradation profile of chemicals at sampling point 9 – Cont'd.

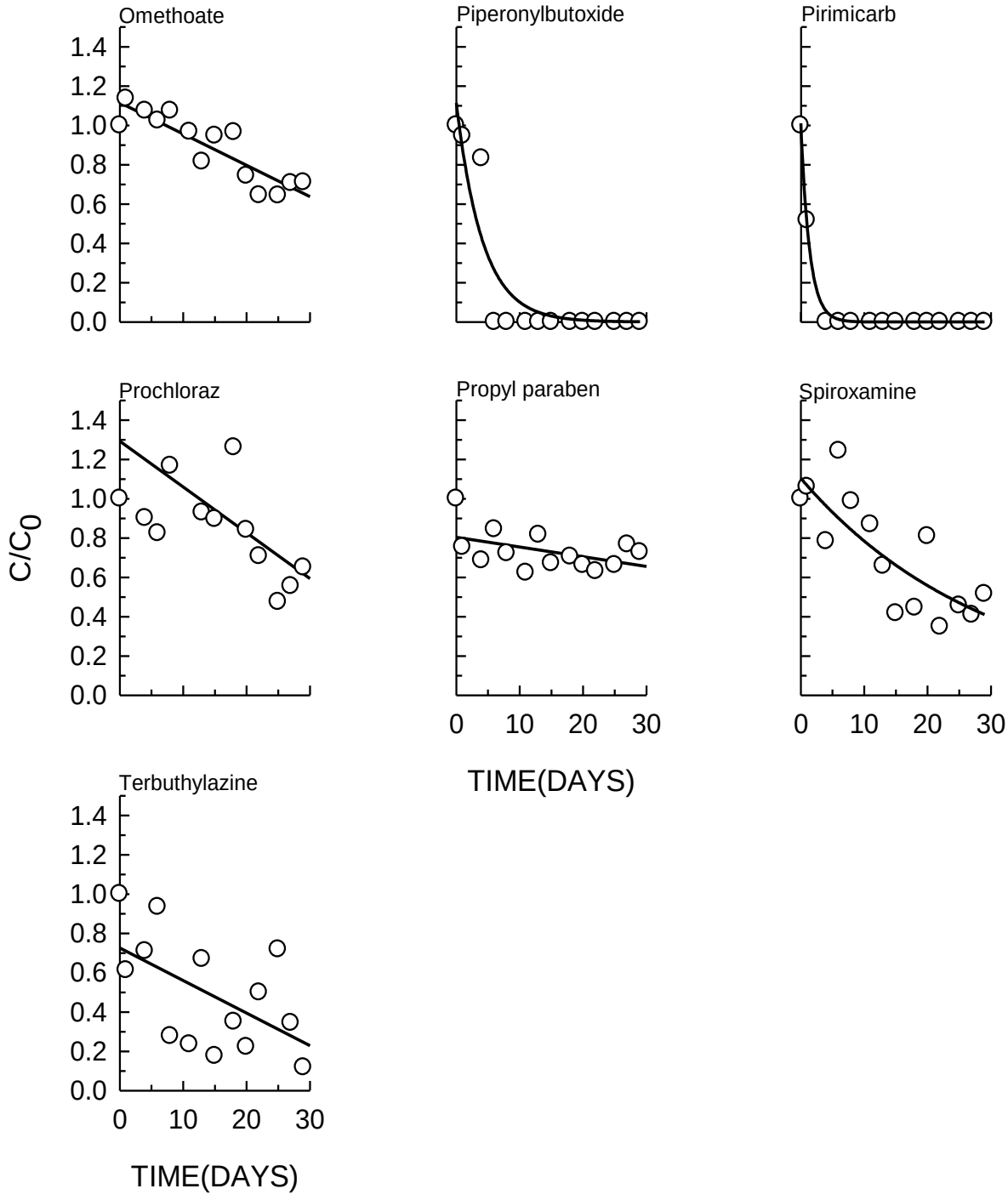


Figure B.7. Biodegradation profile of chemicals at sampling point 10.

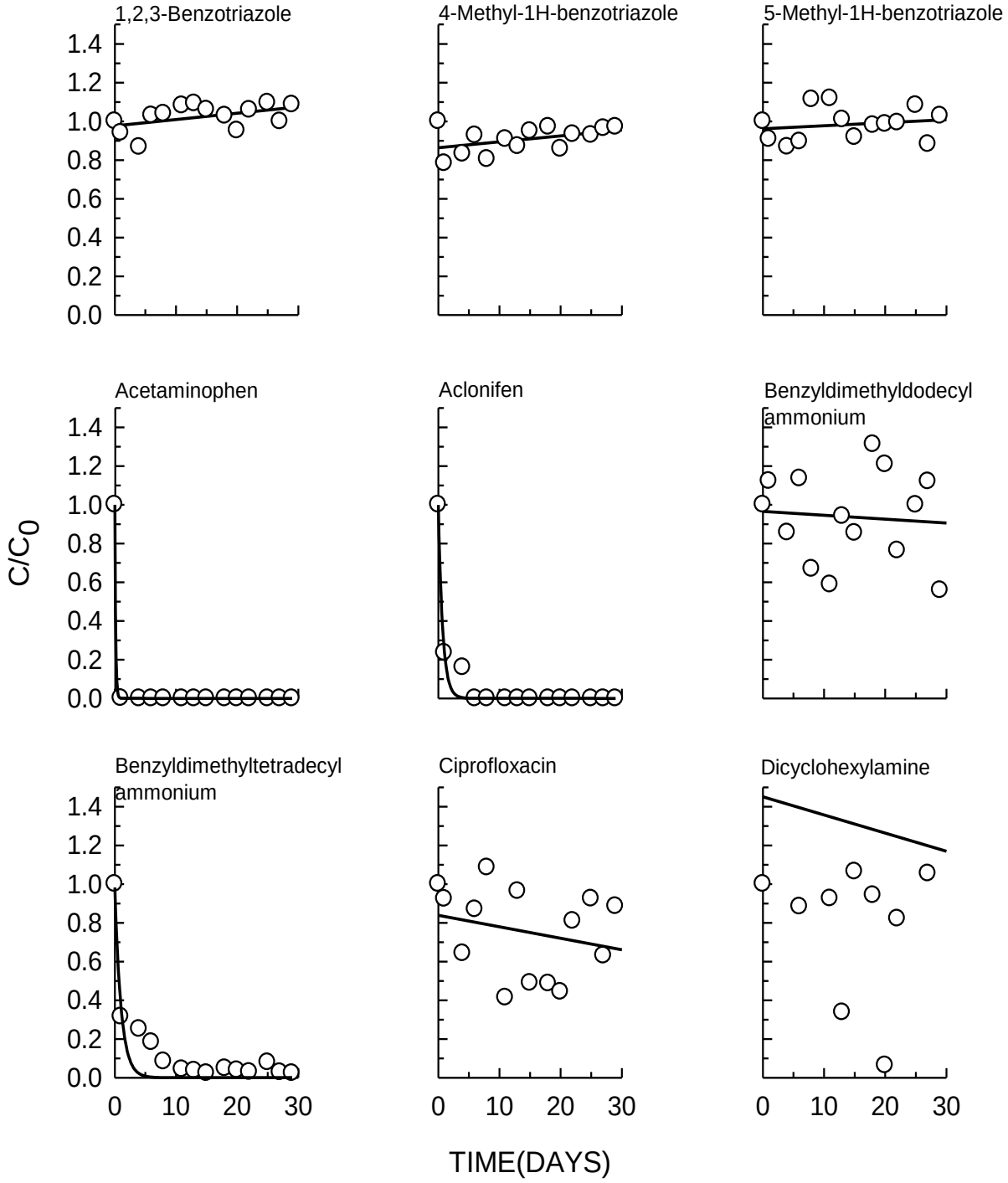


Figure B.7. Biodegradation profile of chemicals at sampling point 10 – Cont'd.

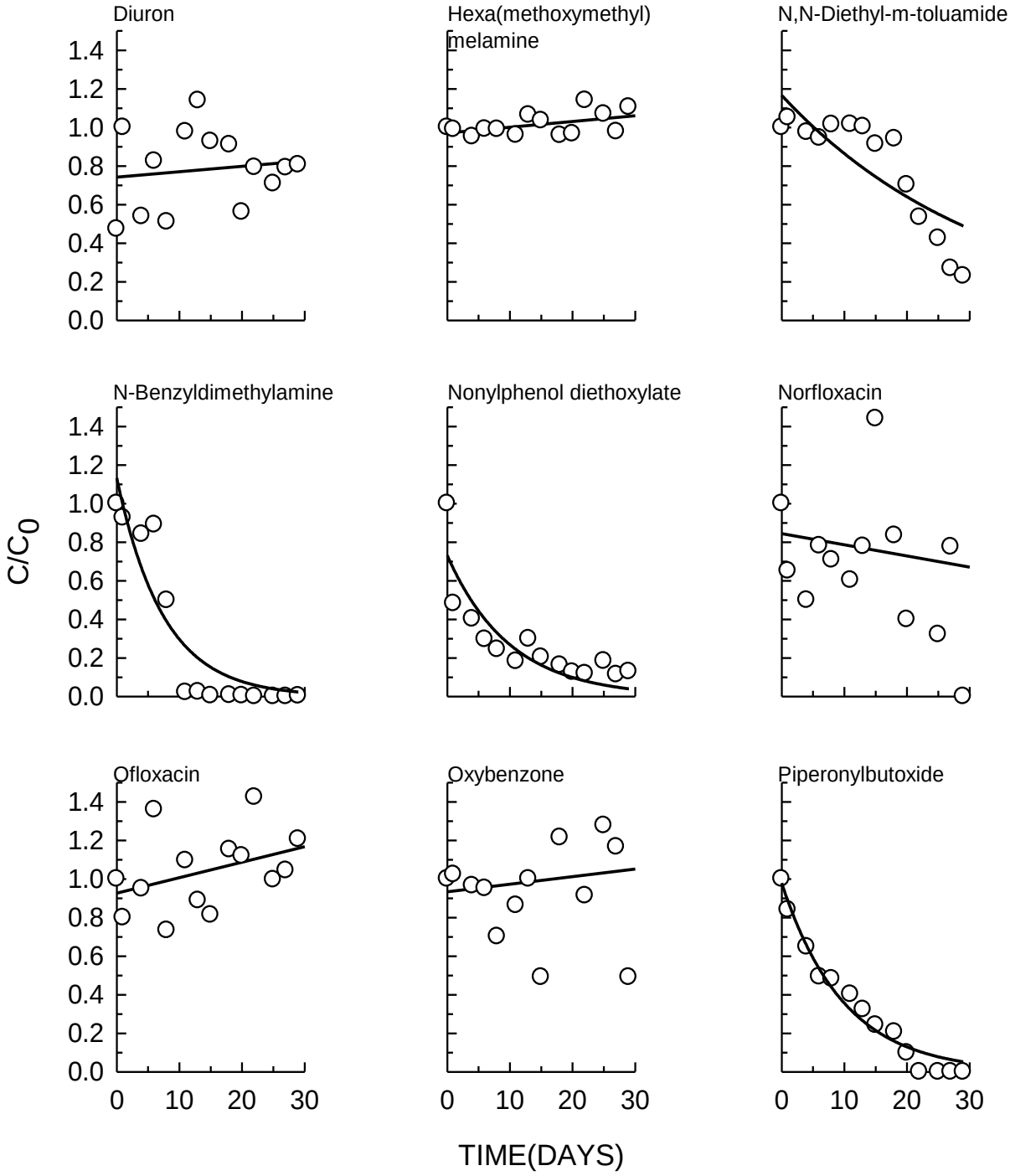


Figure B.7. Biodegradation profile of chemicals at sampling point 10 – Cont'd.

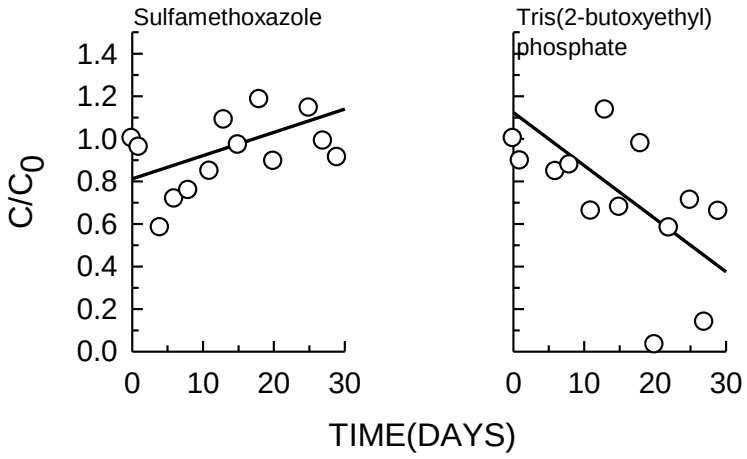


Figure B.8. Biodegradation profile of chemicals at sampling point 11.

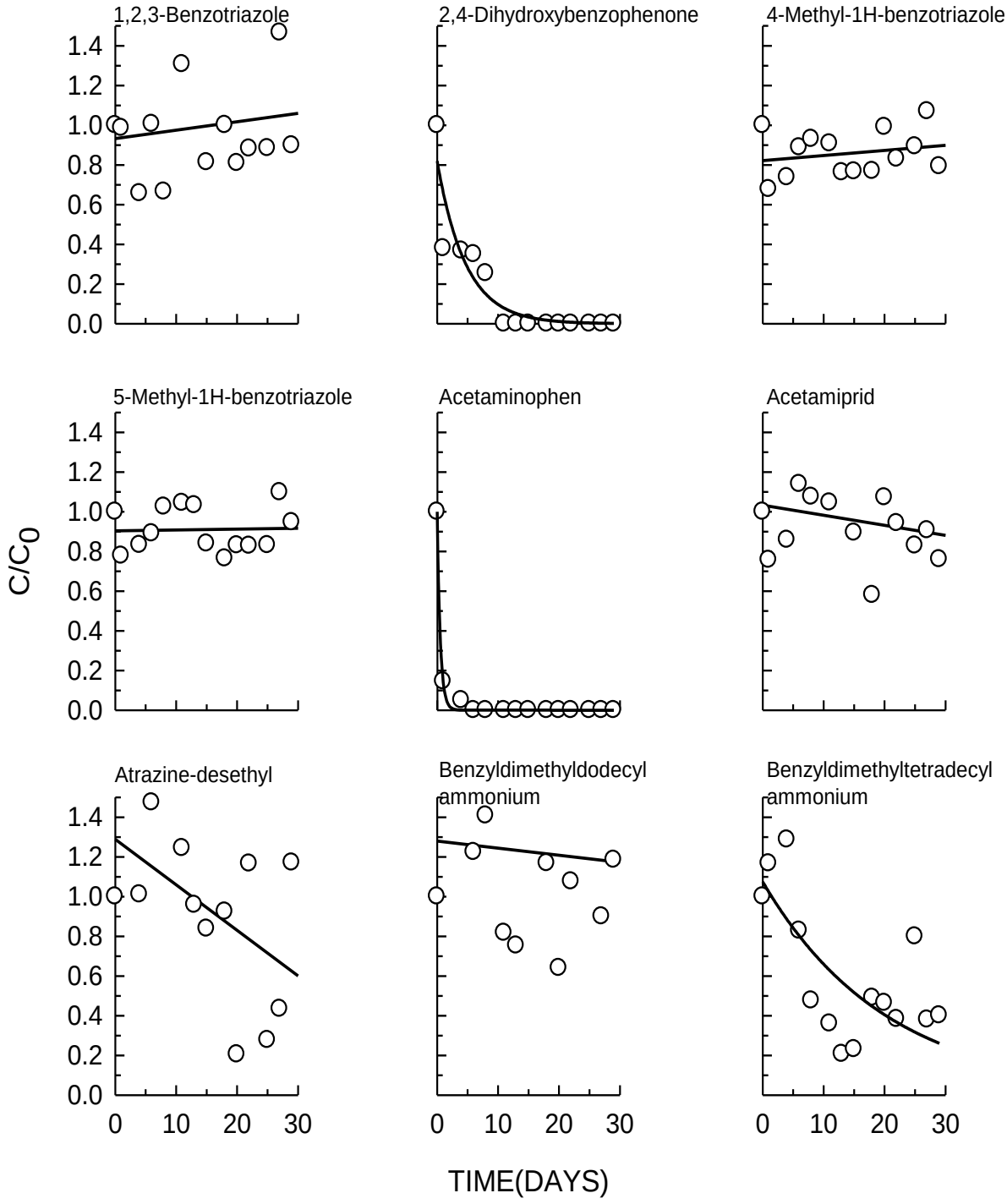
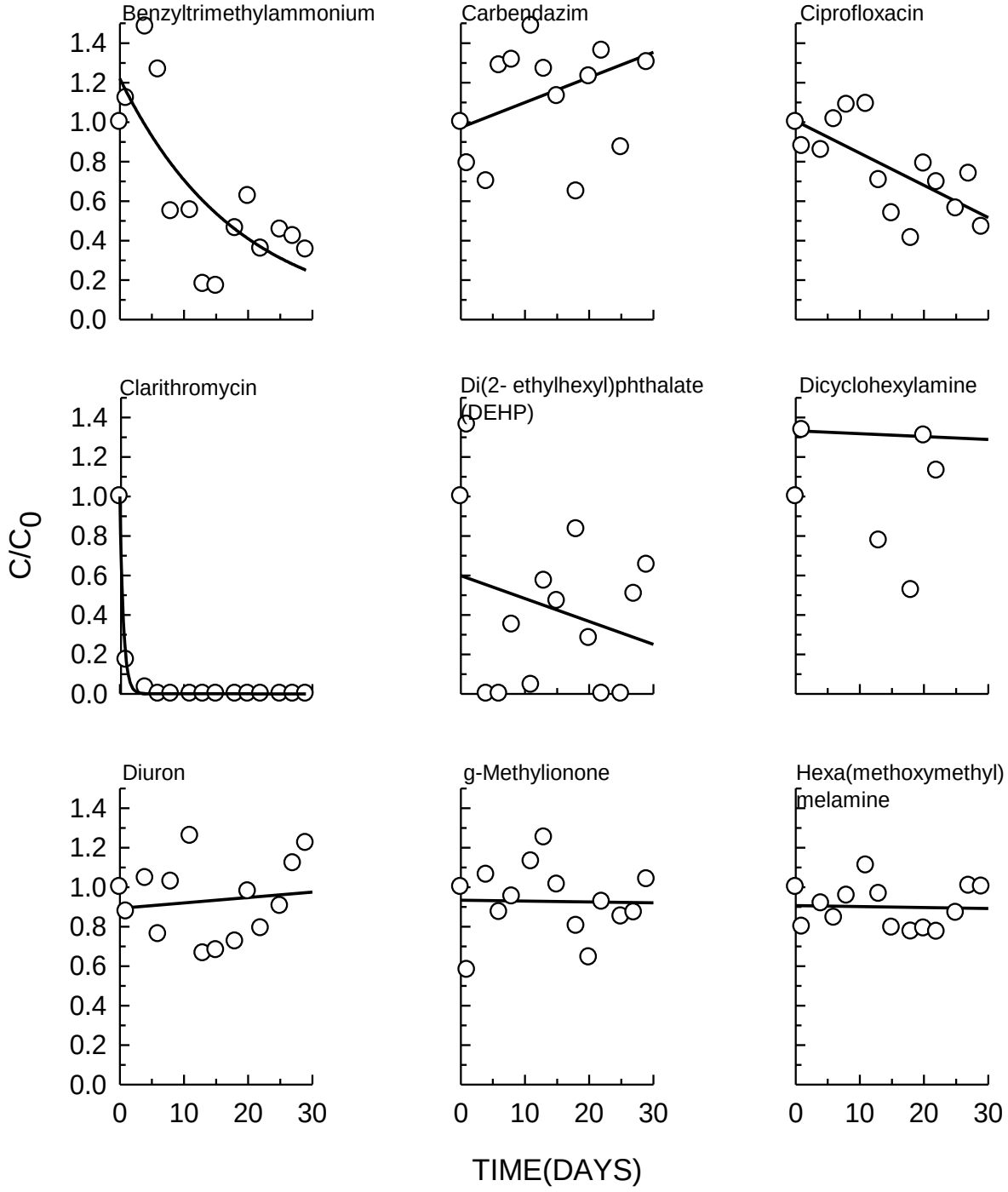


Figure B.8. Biodegradation profile of chemicals at sampling point 11 – Cont'd.



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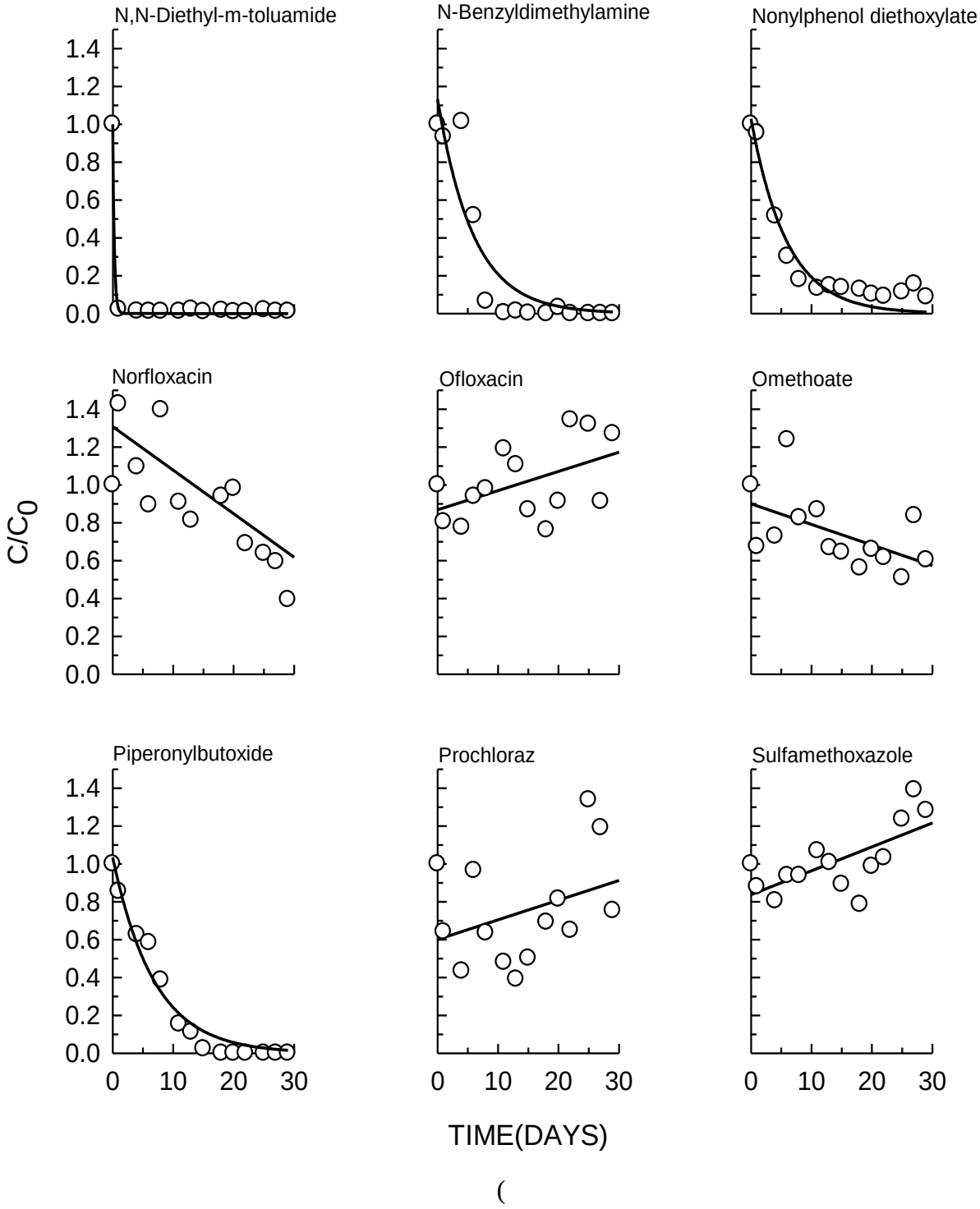

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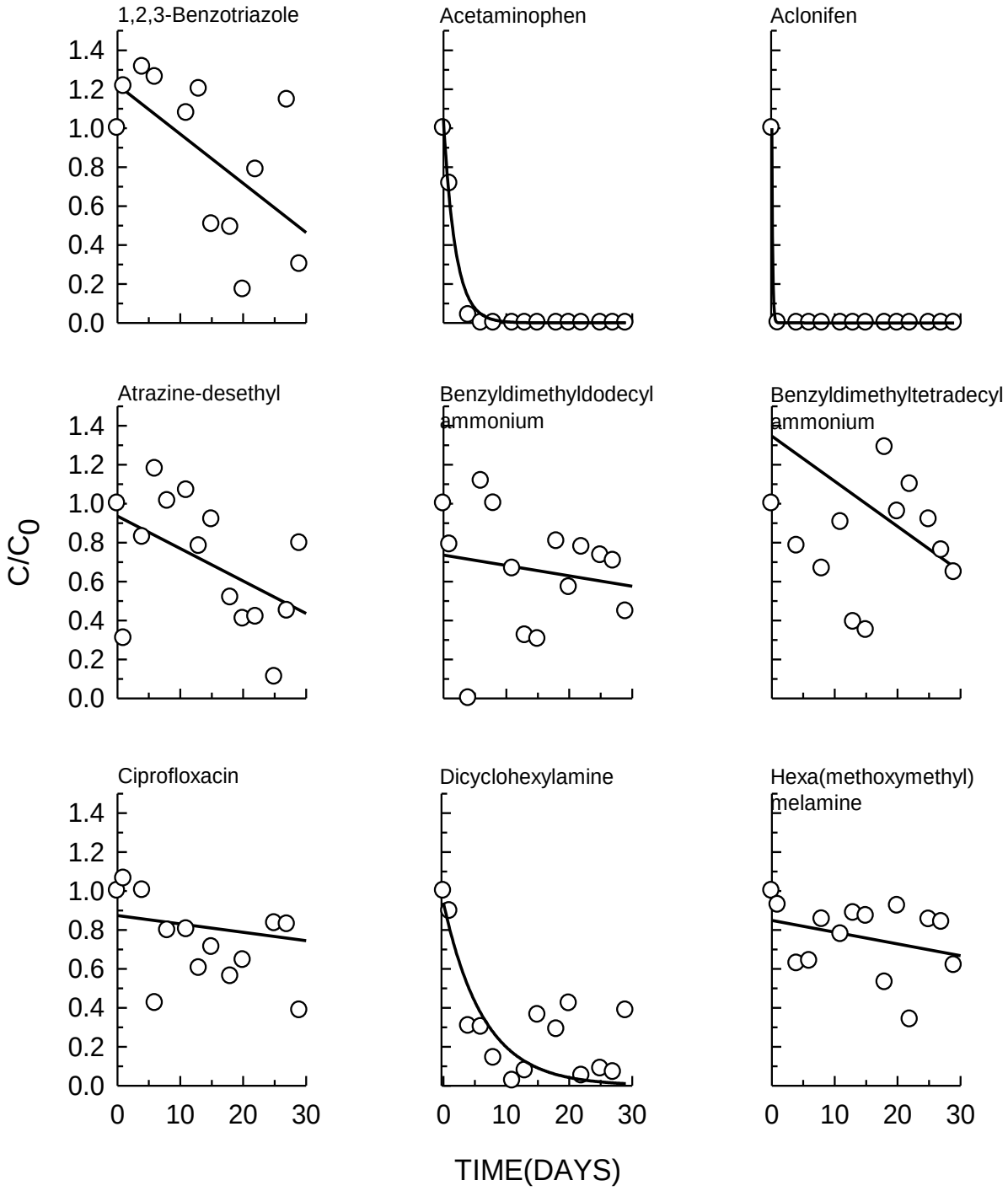
Figure B.9. Biodegradation profile of chemicals at sampling point 12.



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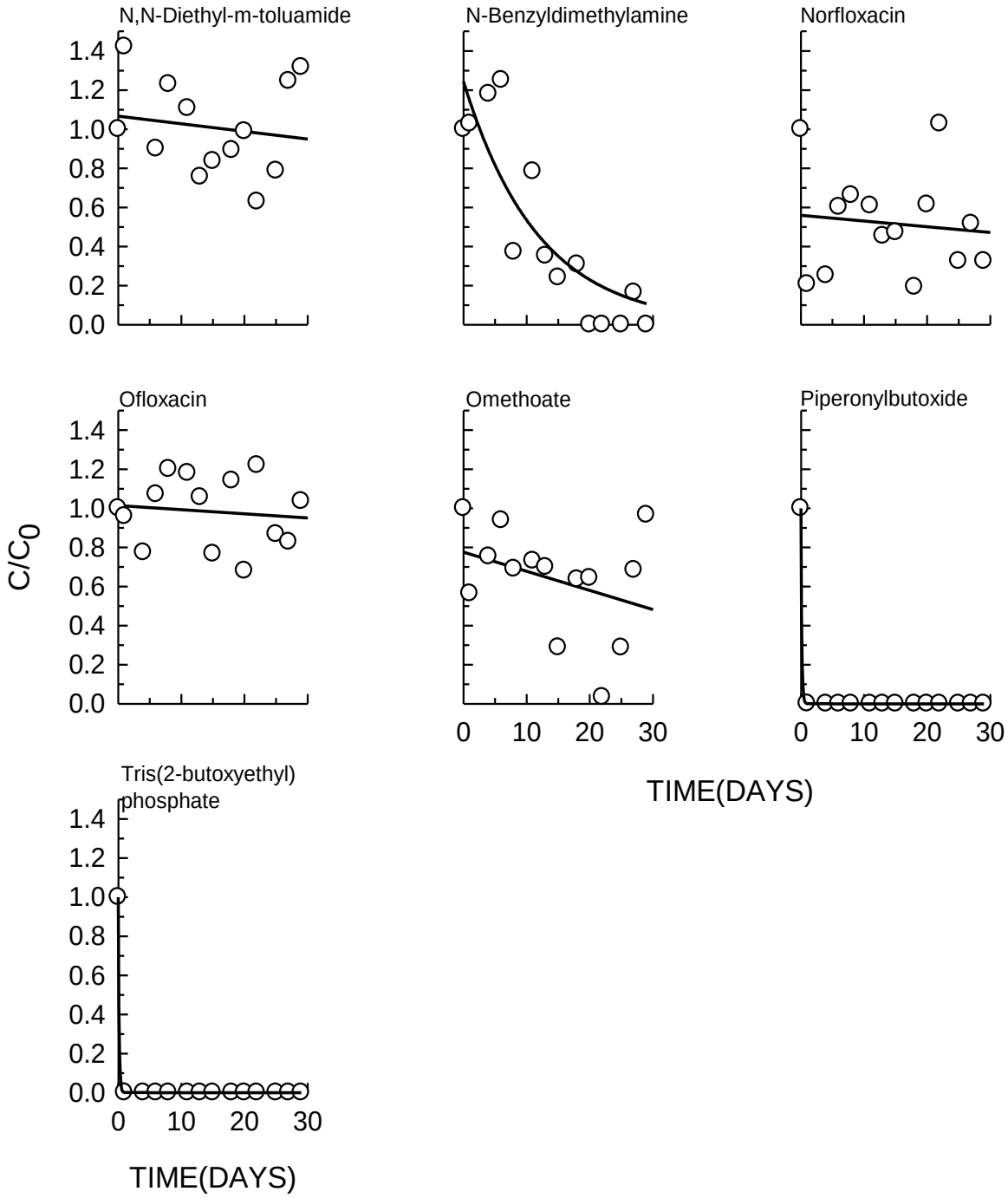
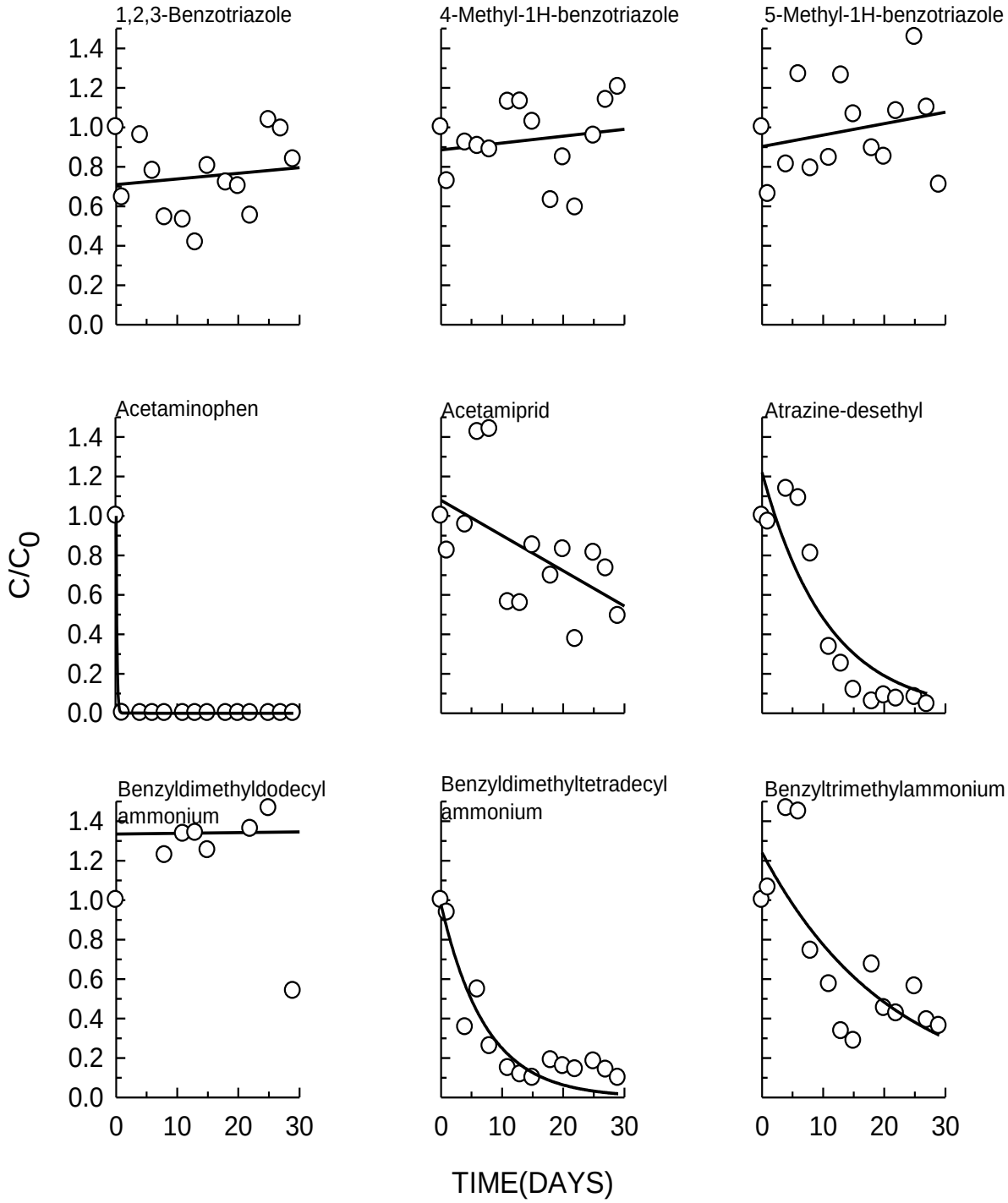


Figure B.10. Biodegradation profile of chemicals at sampling point 13.



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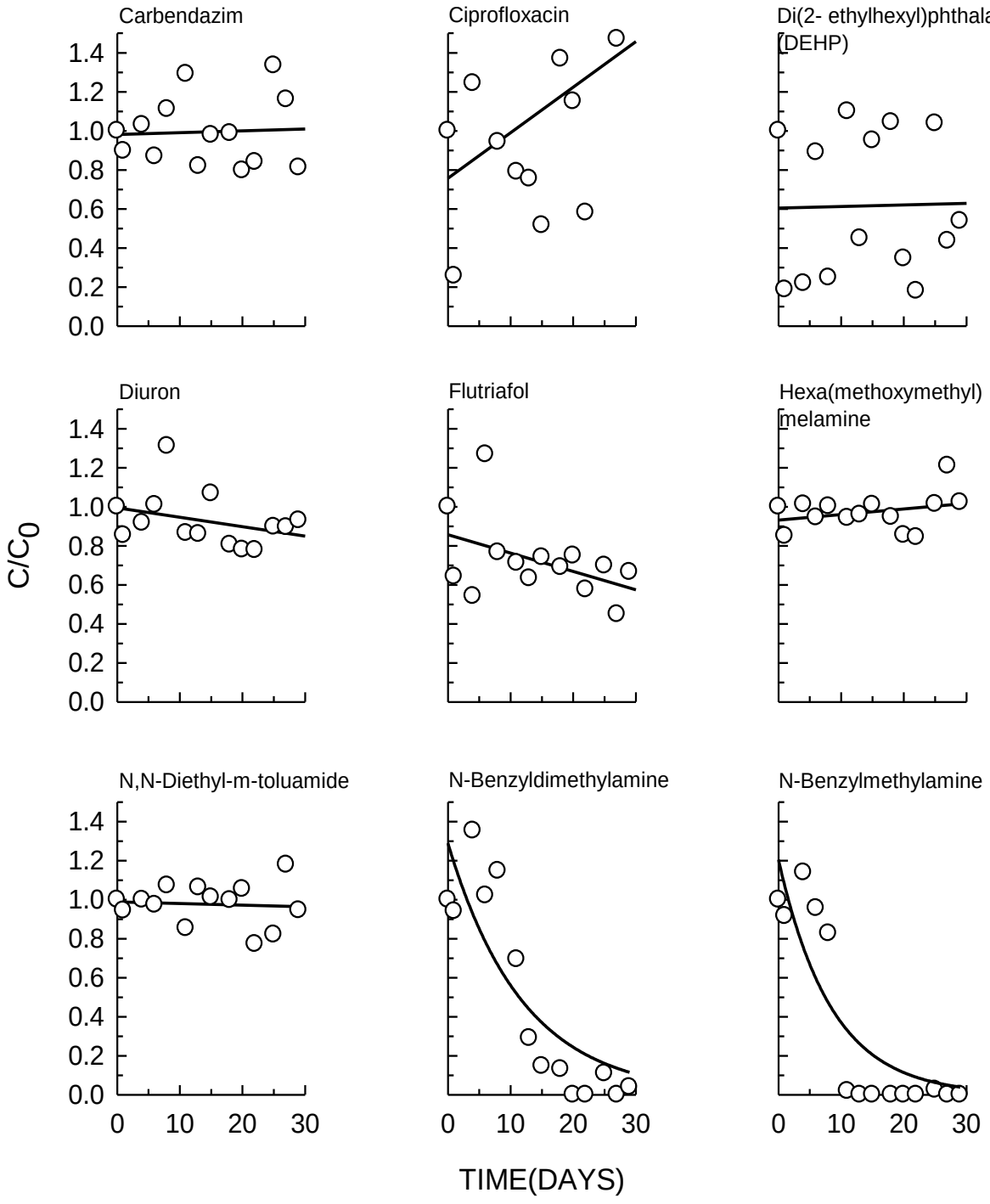

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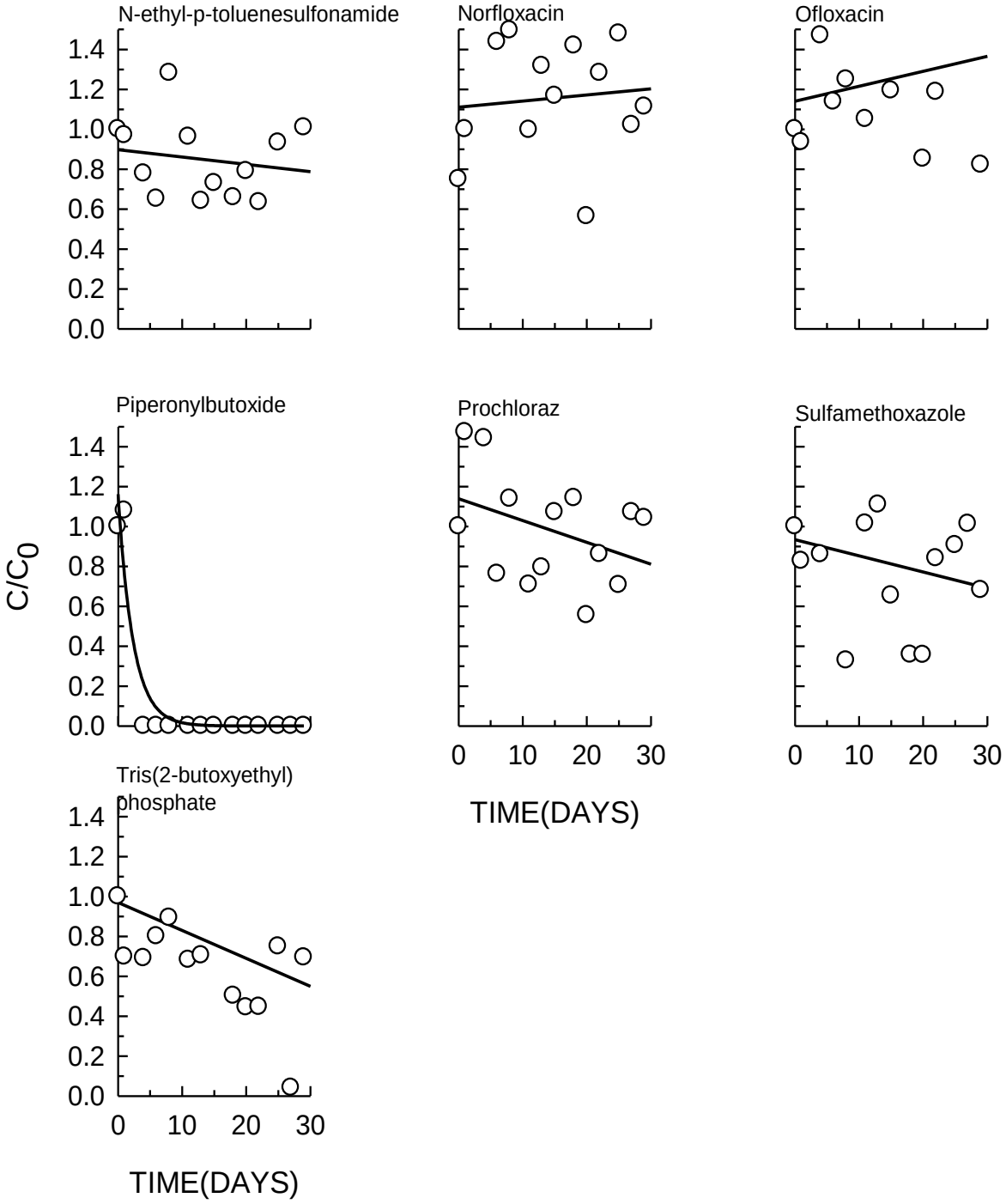
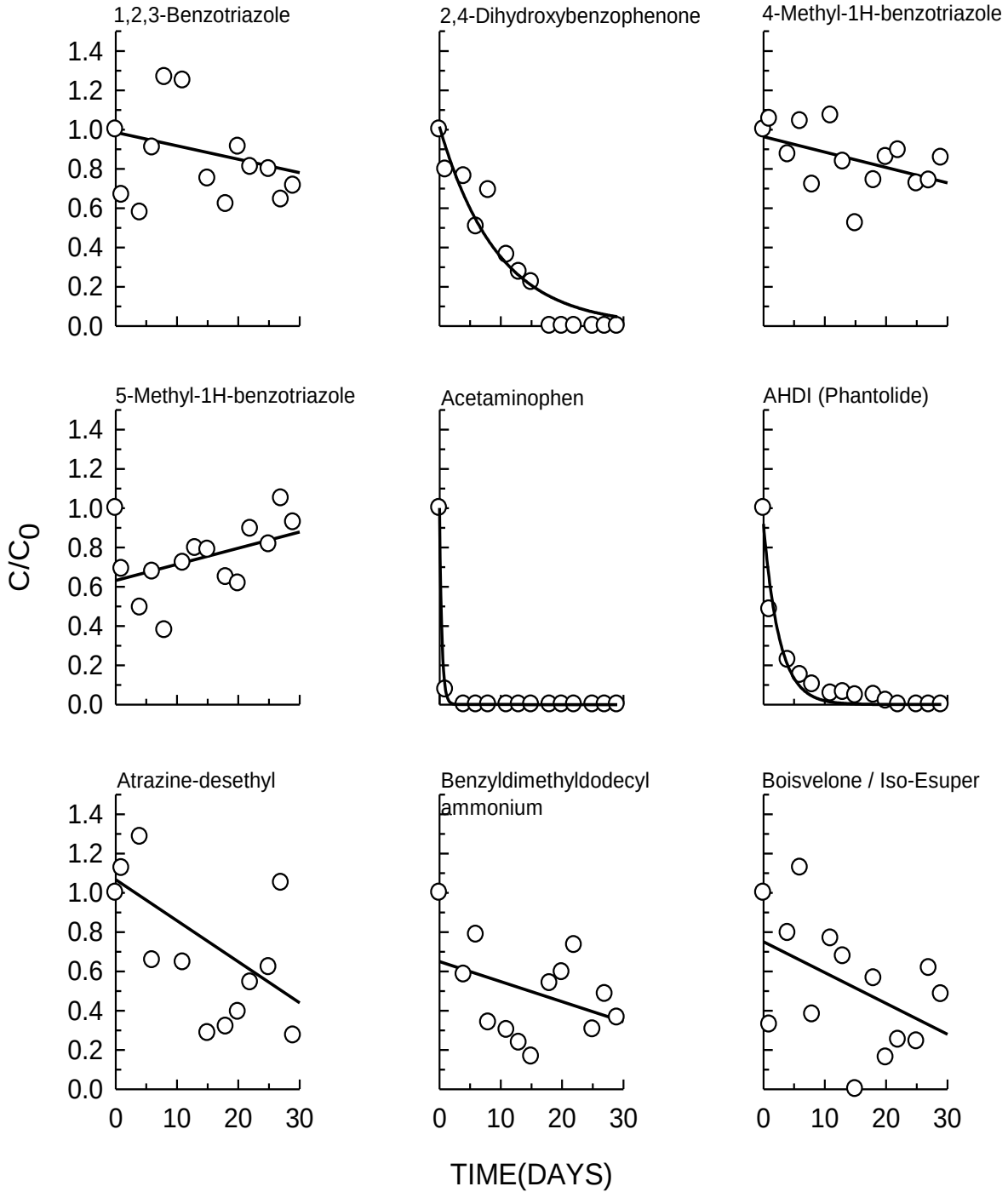


Figure B.11. Biodegradation profile of chemicals at sampling point 14.



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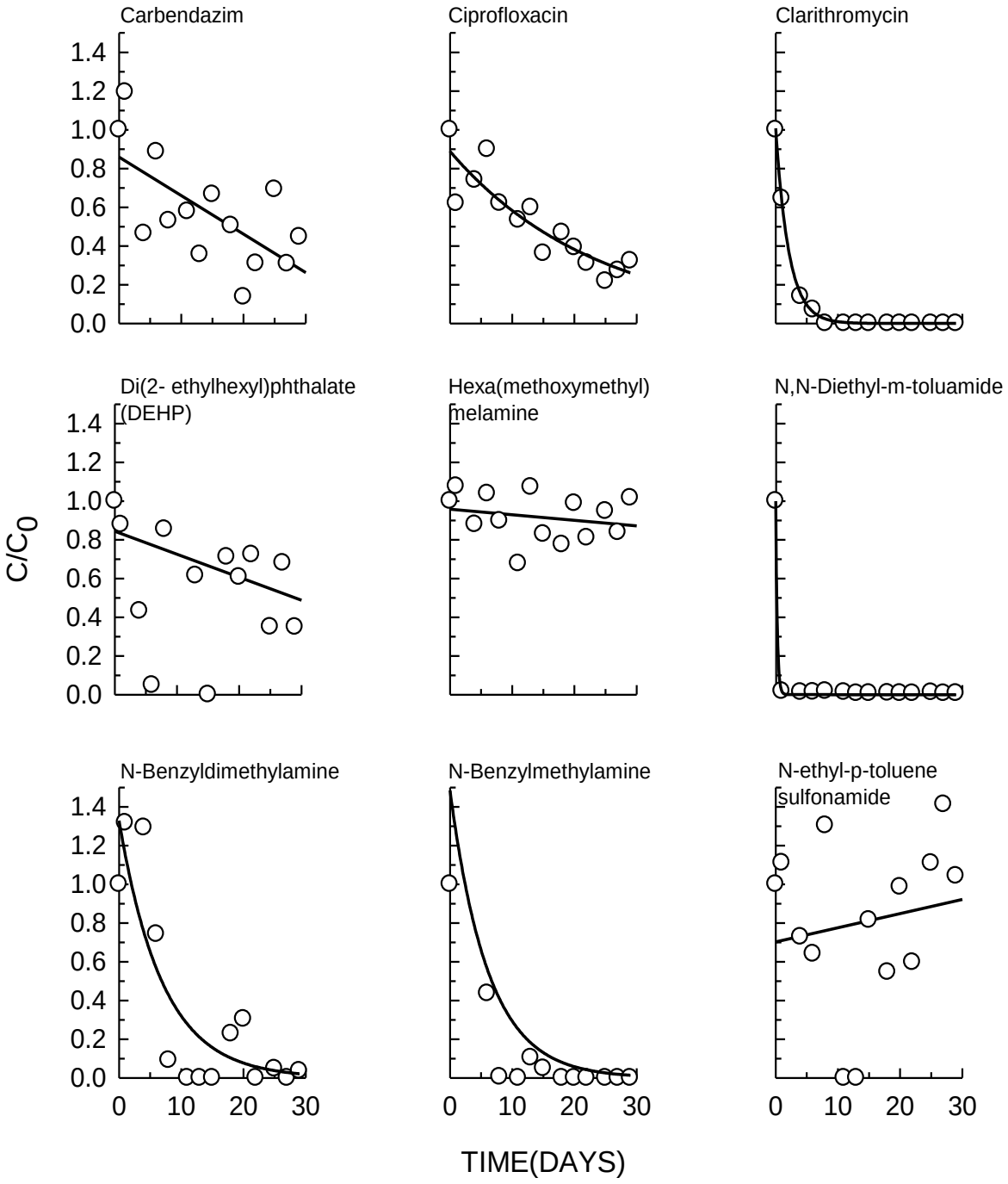

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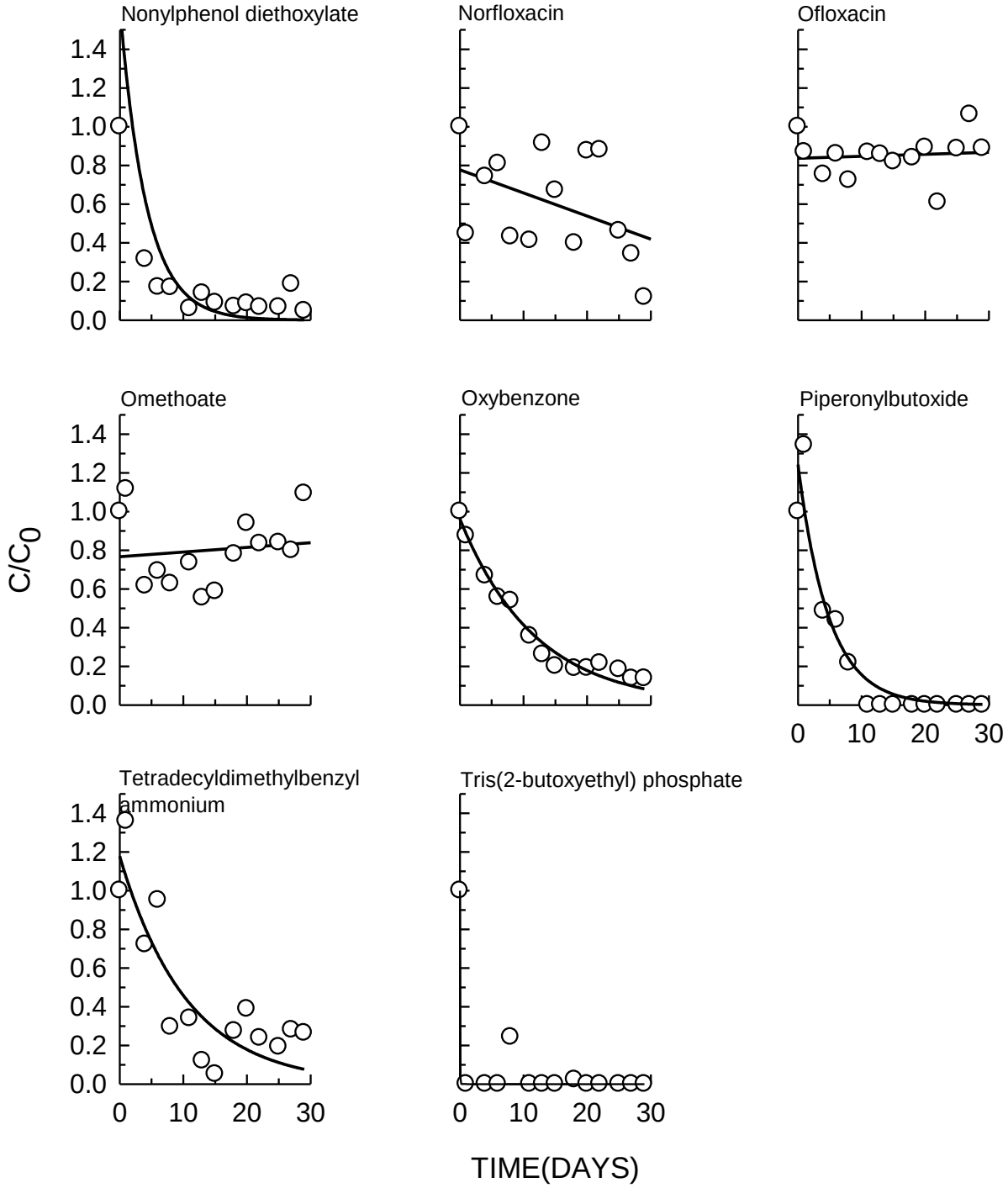
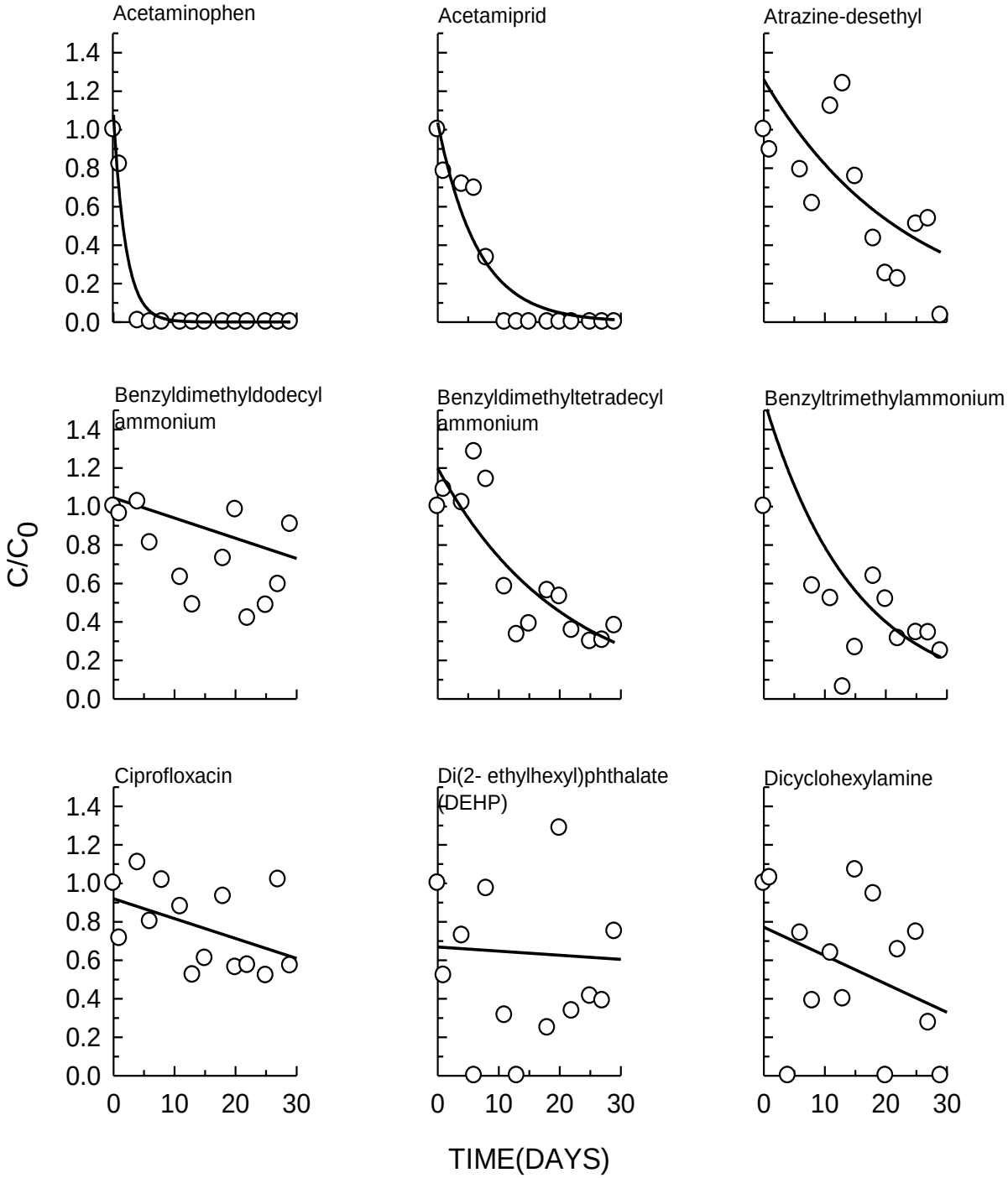


Figure B.12. Biodegradation profile of chemicals at sampling point 15.



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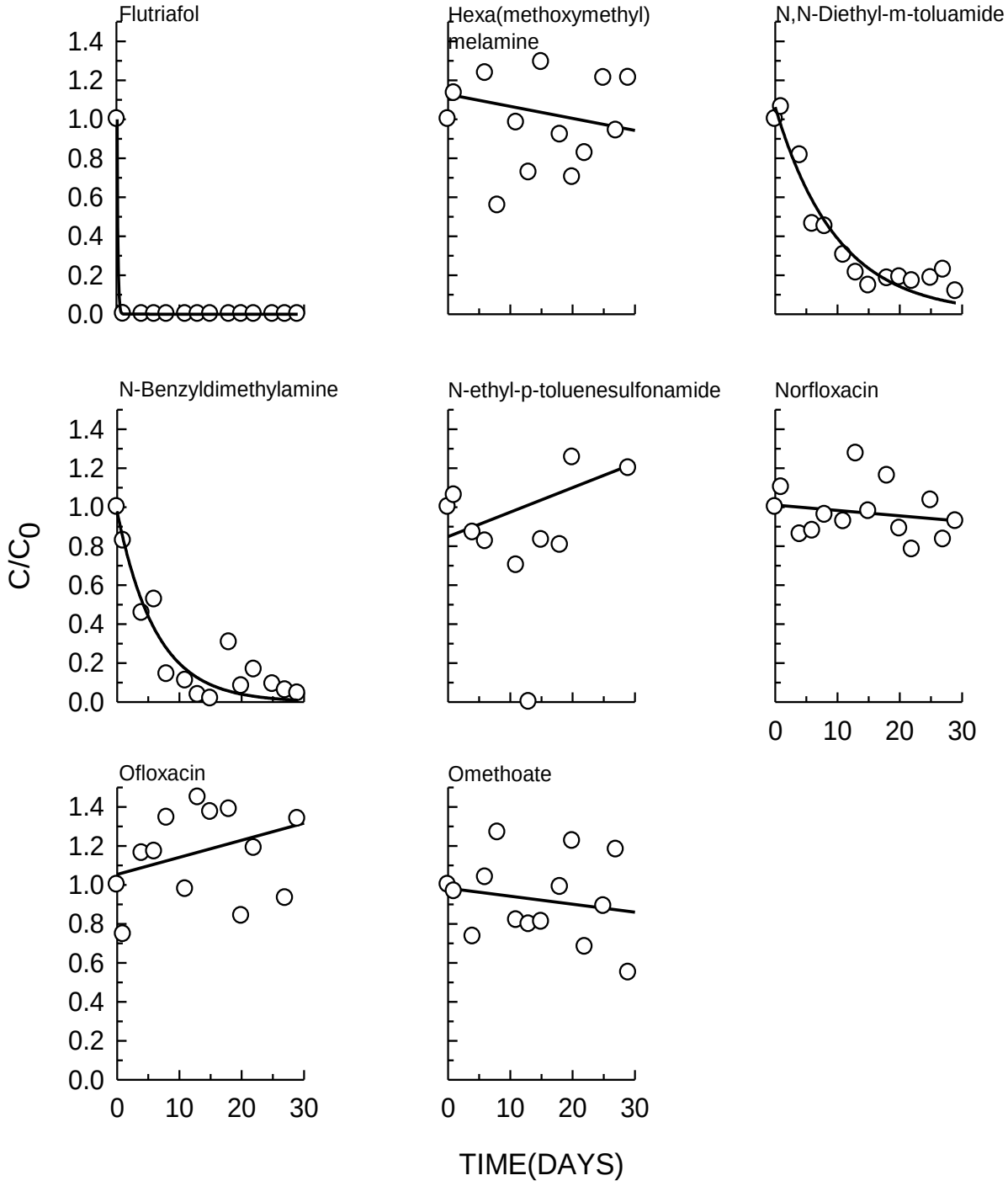

Figure B.13. Biodegradation profile of chemicals at sampling point 16.

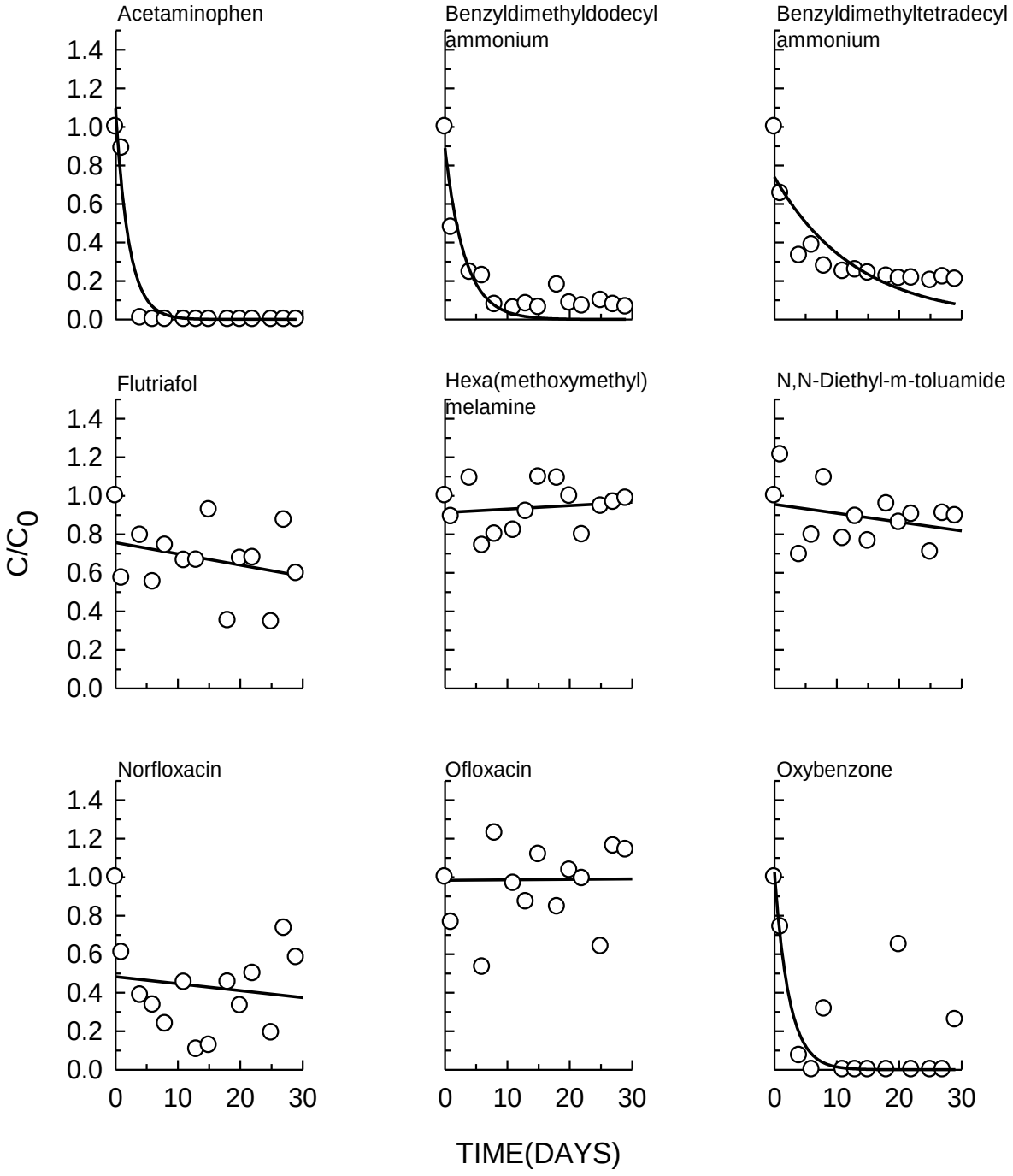

Figure B.13. Biodegradation profile of chemicals at sampling point 16 – Cont'd.

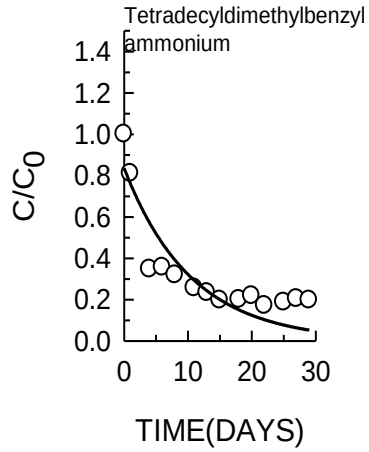

Figure B.14. Biodegradation profile of chemicals at sampling point 17.

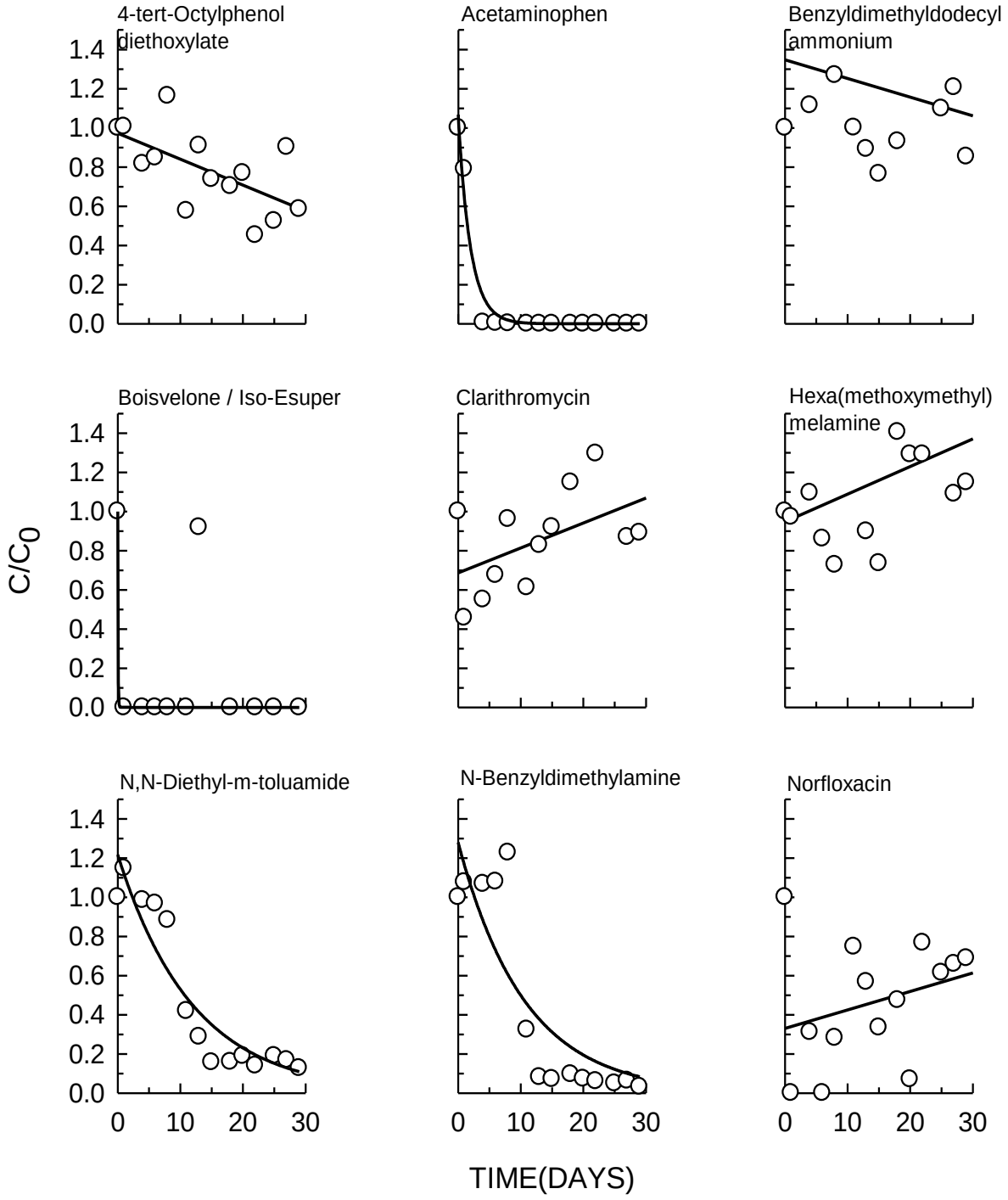

Figure B.14. Biodegradation profile of chemicals at sampling point 17 – Cont'd.

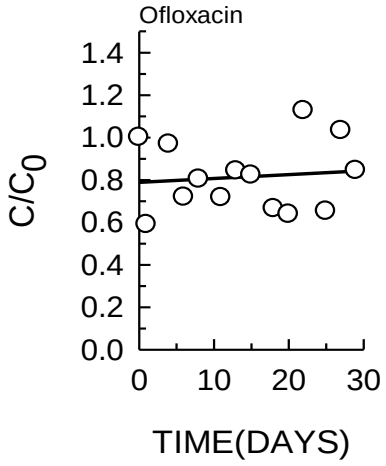

Figure B.15. Biodegradation profile of chemicals at sampling point 18.

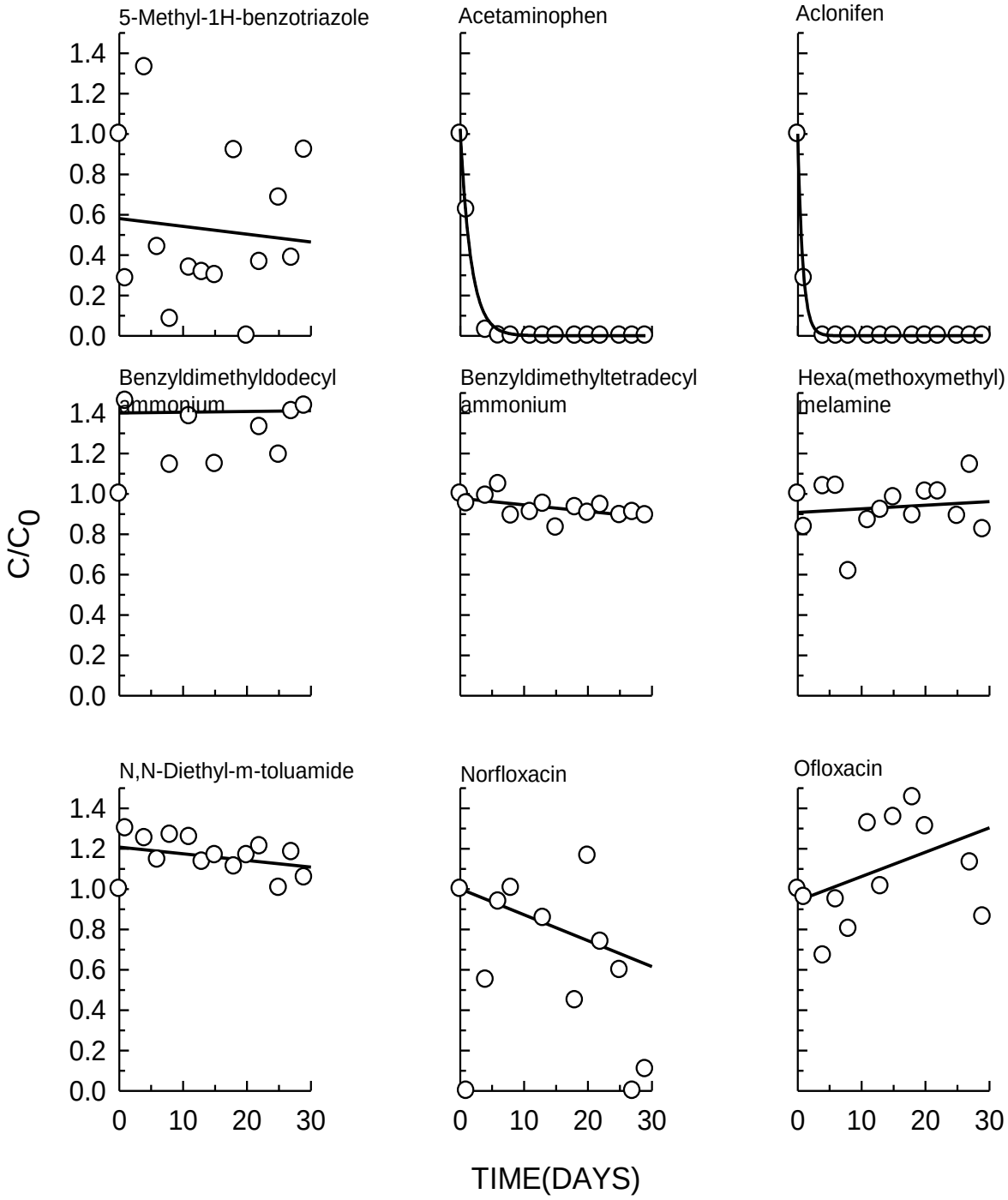

Figure B.15. Biodegradation profile of chemicals at sampling point 18 – Cont'd.

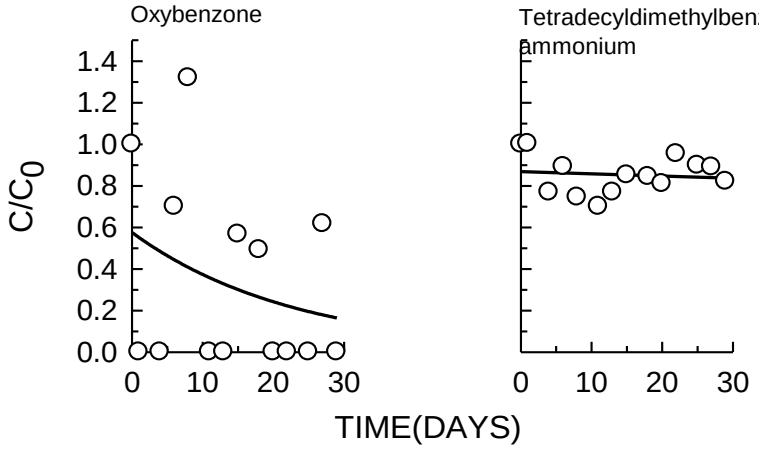

Figure B.16. Biodegradation profile of chemicals at sampling point 19.

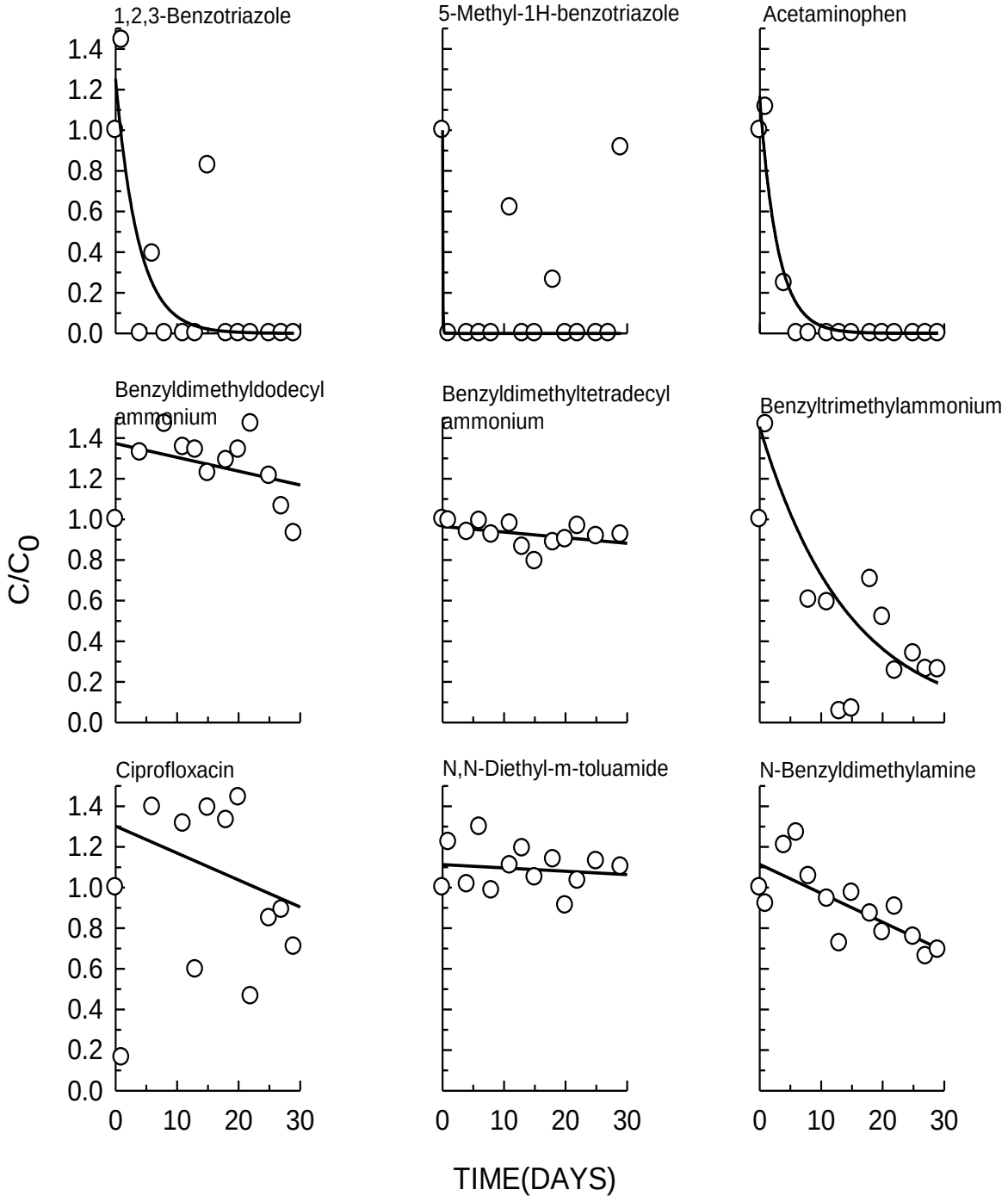

Figure B.16. Biodegradation profile of chemicals at sampling point 19 – Cont'd.

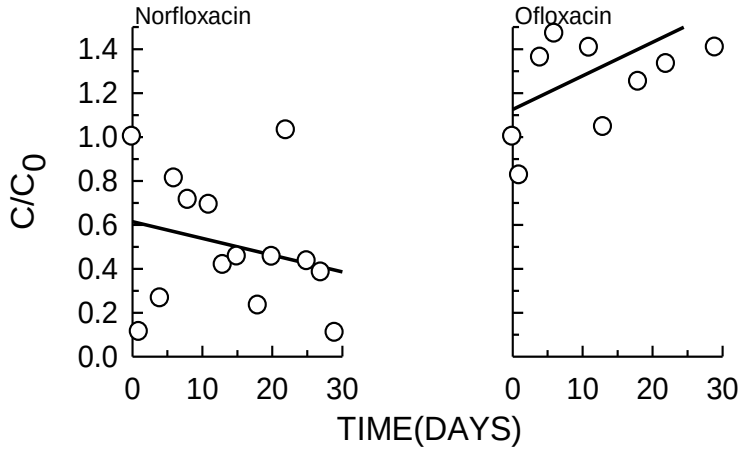

Figure B.17. Biodegradation profile of chemicals at sampling point 20.

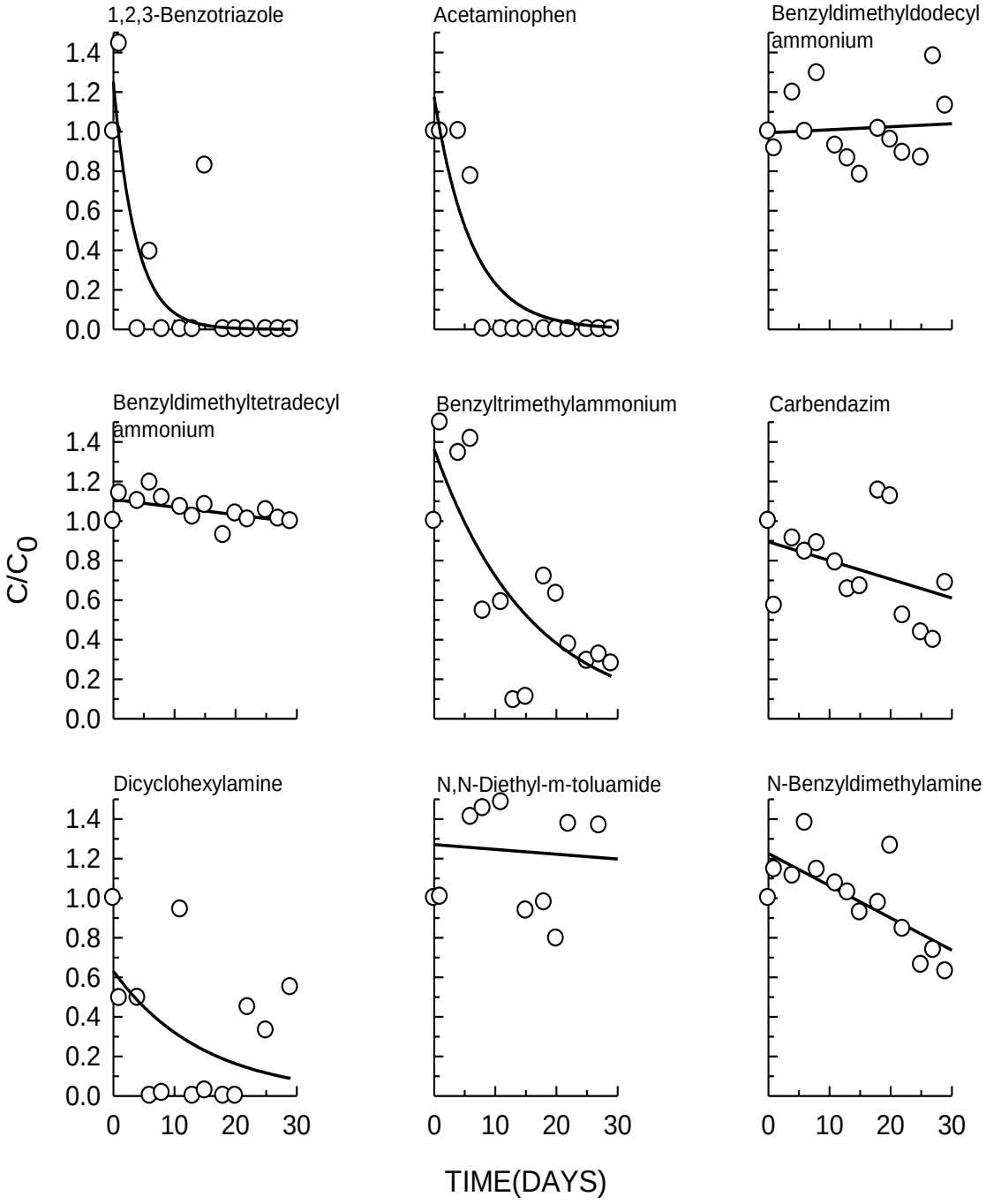

Figure B.17. Biodegradation profile of chemicals at sampling point 20 – Cont'd.

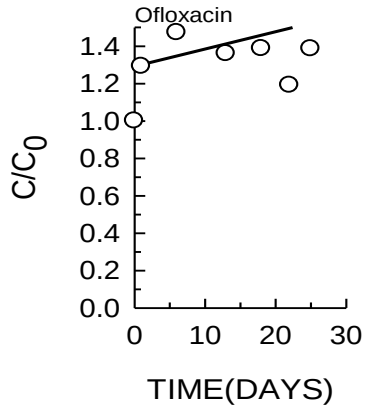

Figure B.18. Biodegradation profile of chemicals at sampling point 21.

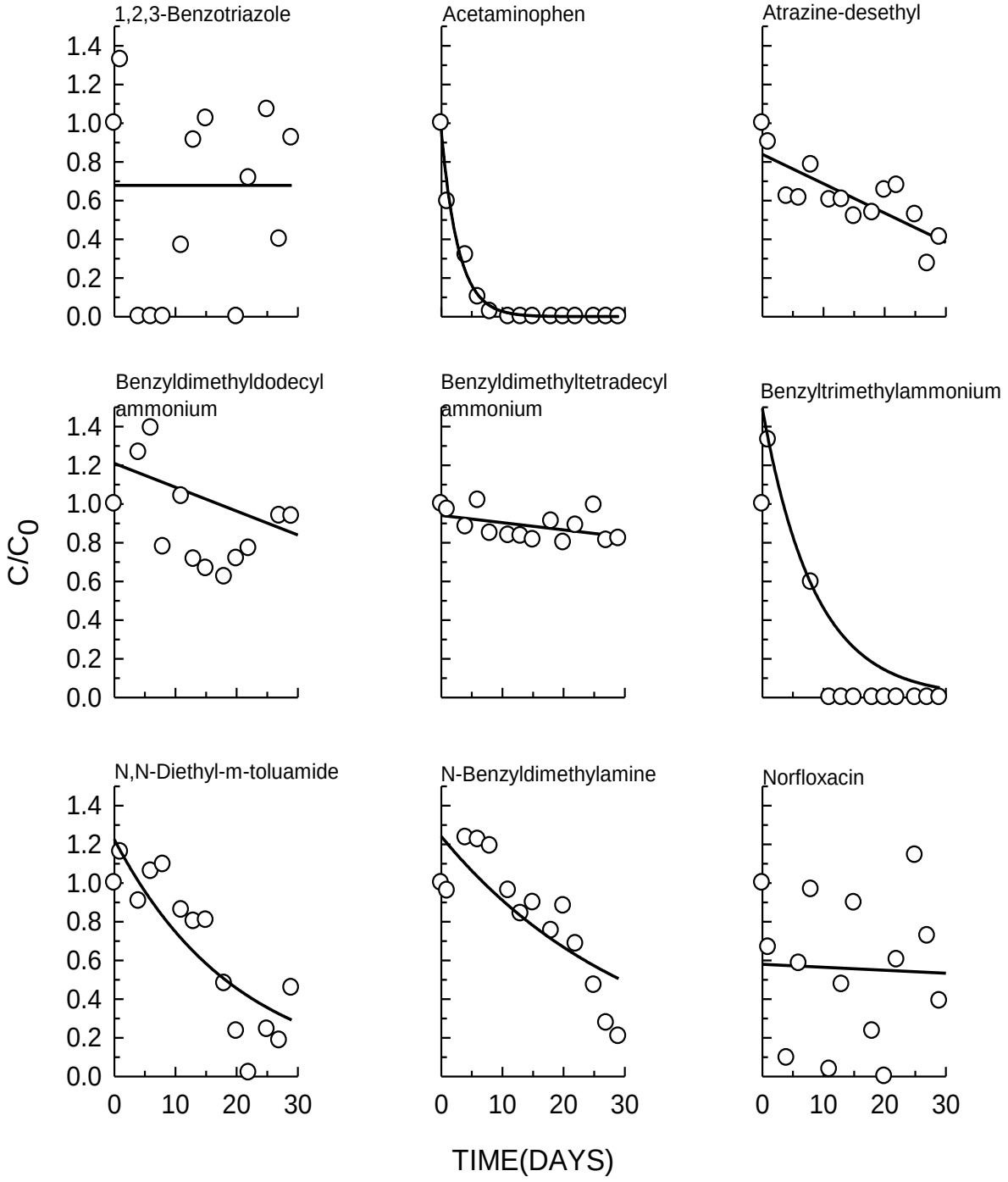

Figure B.18. Biodegradation profile of chemicals at sampling point 21 – Cont'd.

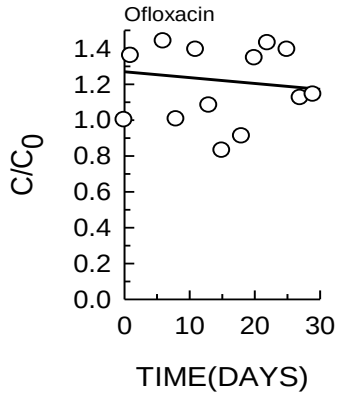

Figure B.19. Biodegradation profile of chemicals at sampling point 22.

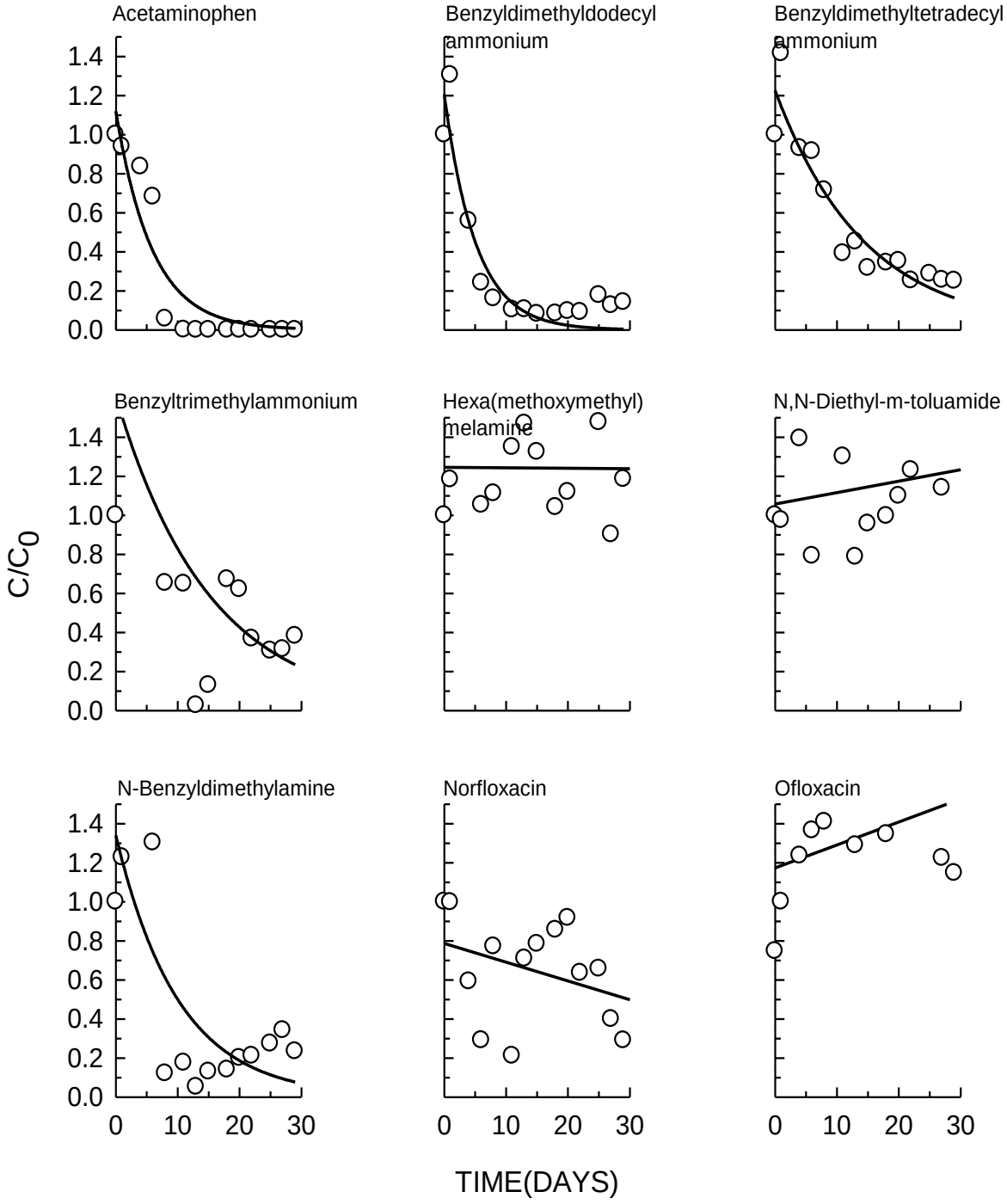

Figure B.20. Biodegradation profile of chemicals at sampling point 23.

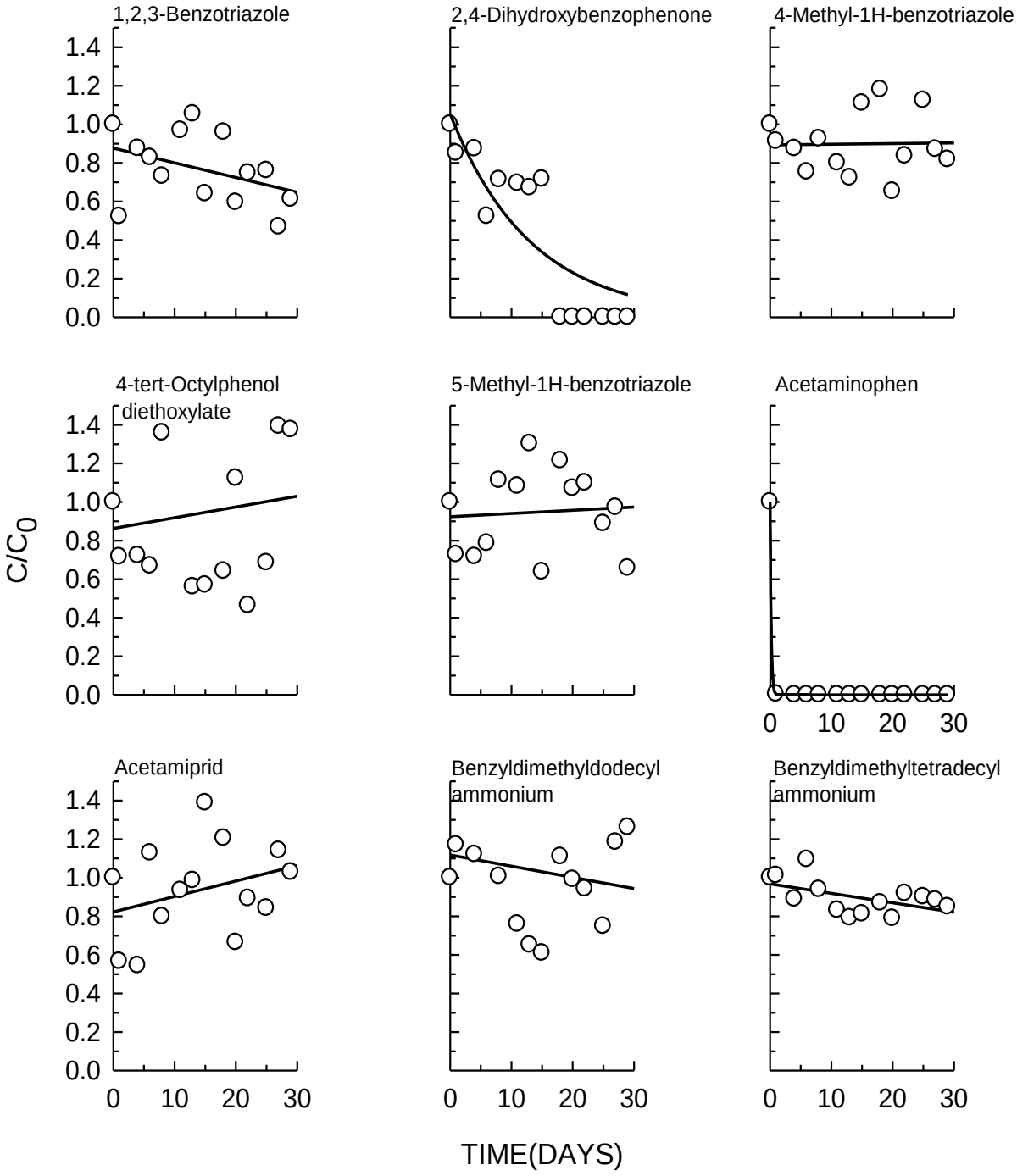

Figure B.20. Biodegradation profile of chemicals at sampling point 23 – Cont'd.

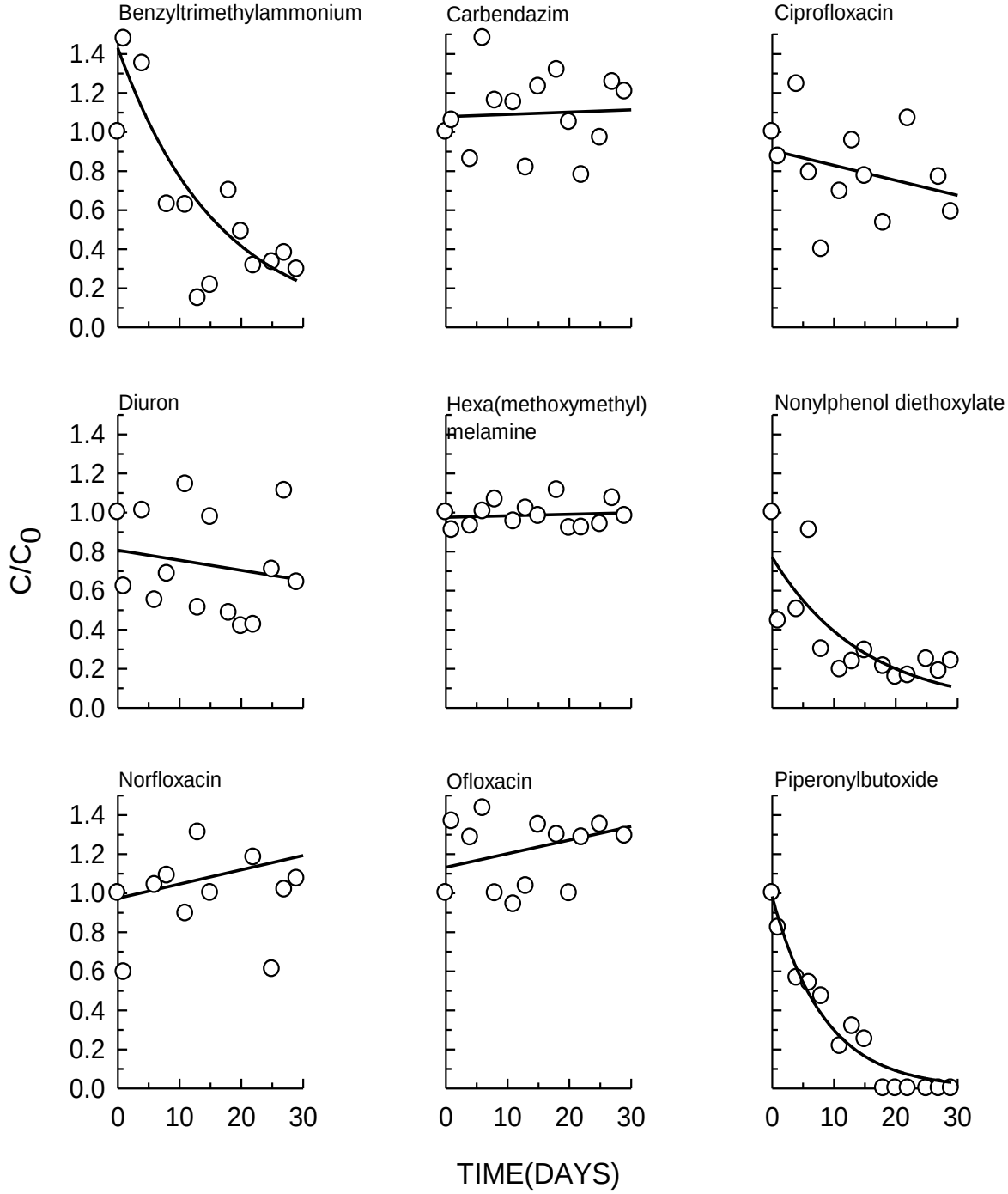

Figure B.20. Biodegradation profile of chemicals at sampling point 23 – Cont'd.

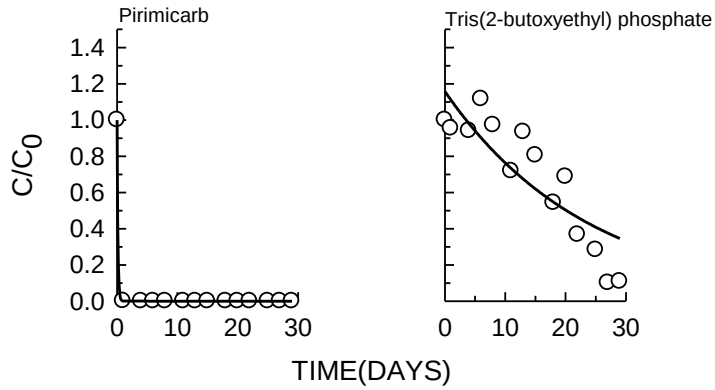

Figure B.21. Biodegradation profile of chemicals at sampling point 24.

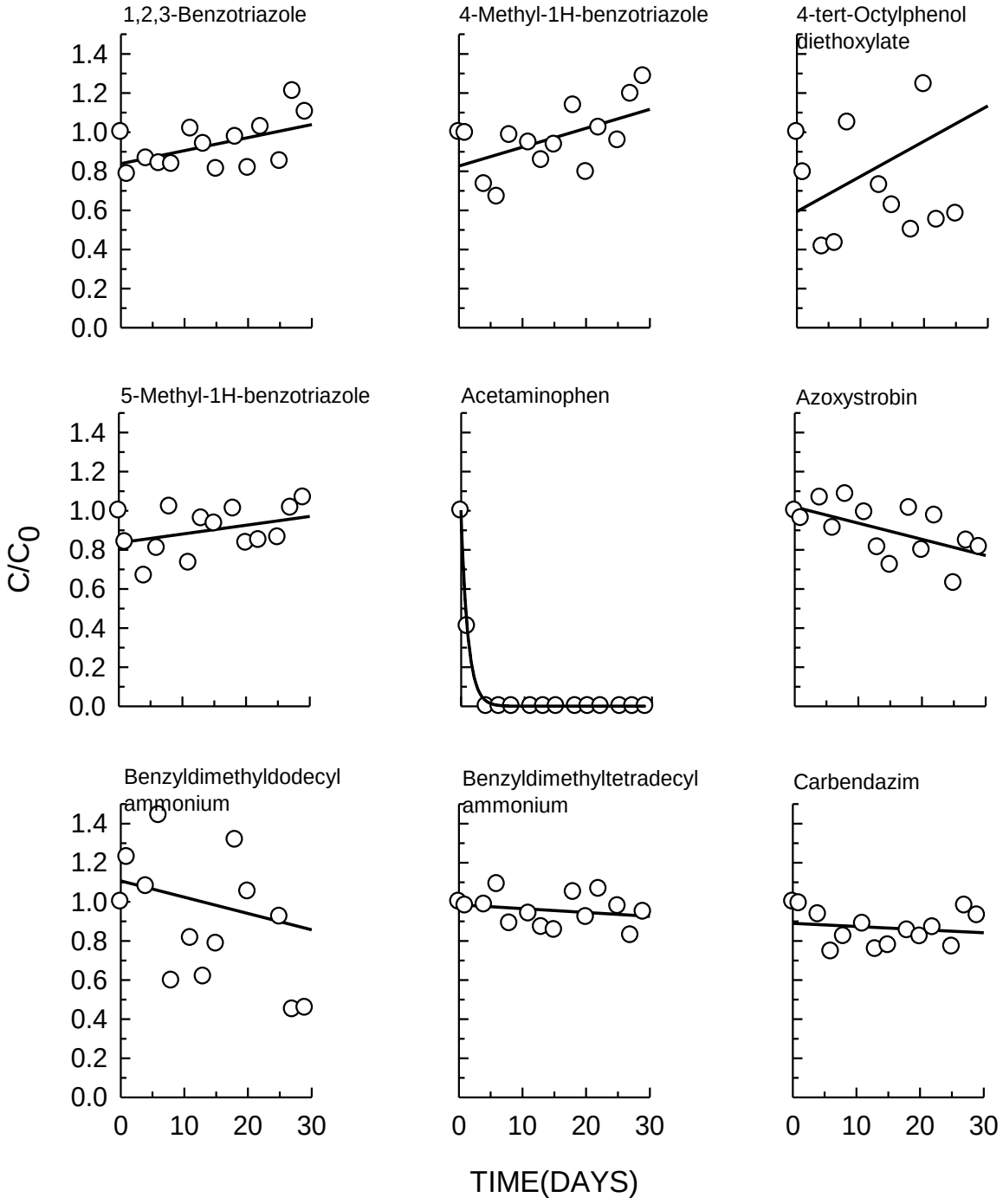

Figure B.21. Biodegradation profile of chemicals at sampling point 24 – Cont'd.

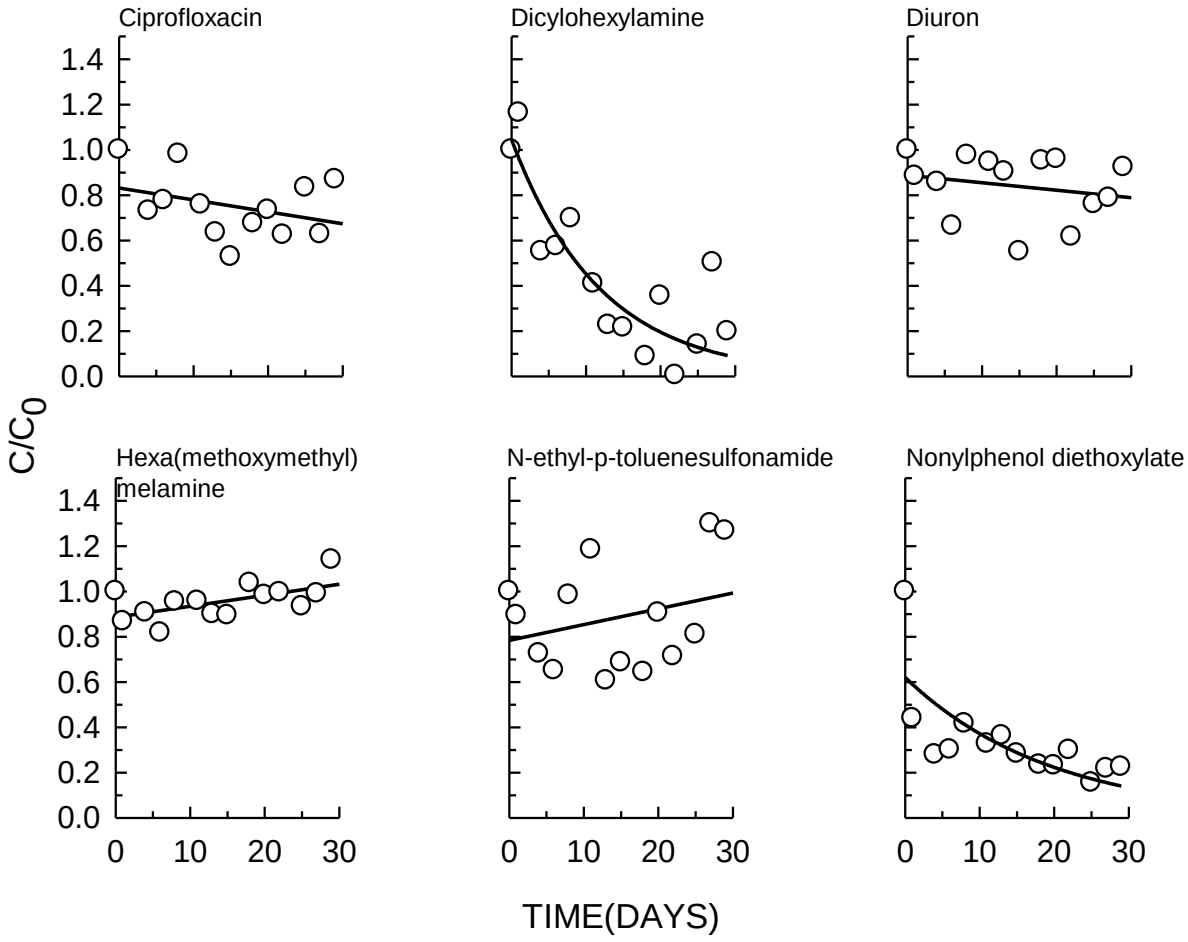

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Figure B.22. Biodegradation profile of chemicals at sampling point 25.

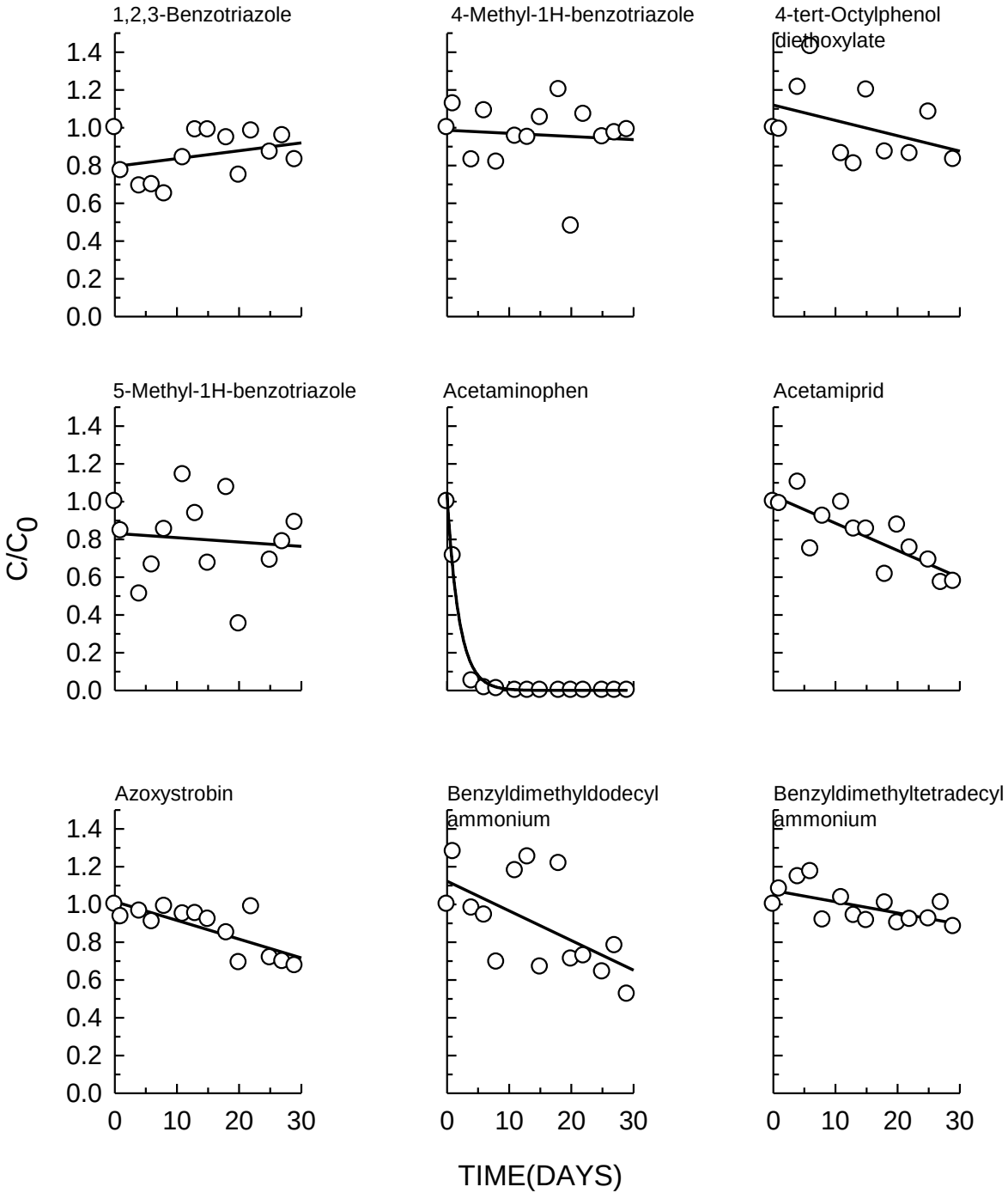

Figure B.22. Biodegradation profile of chemicals at sampling point 25 – Cont'd.

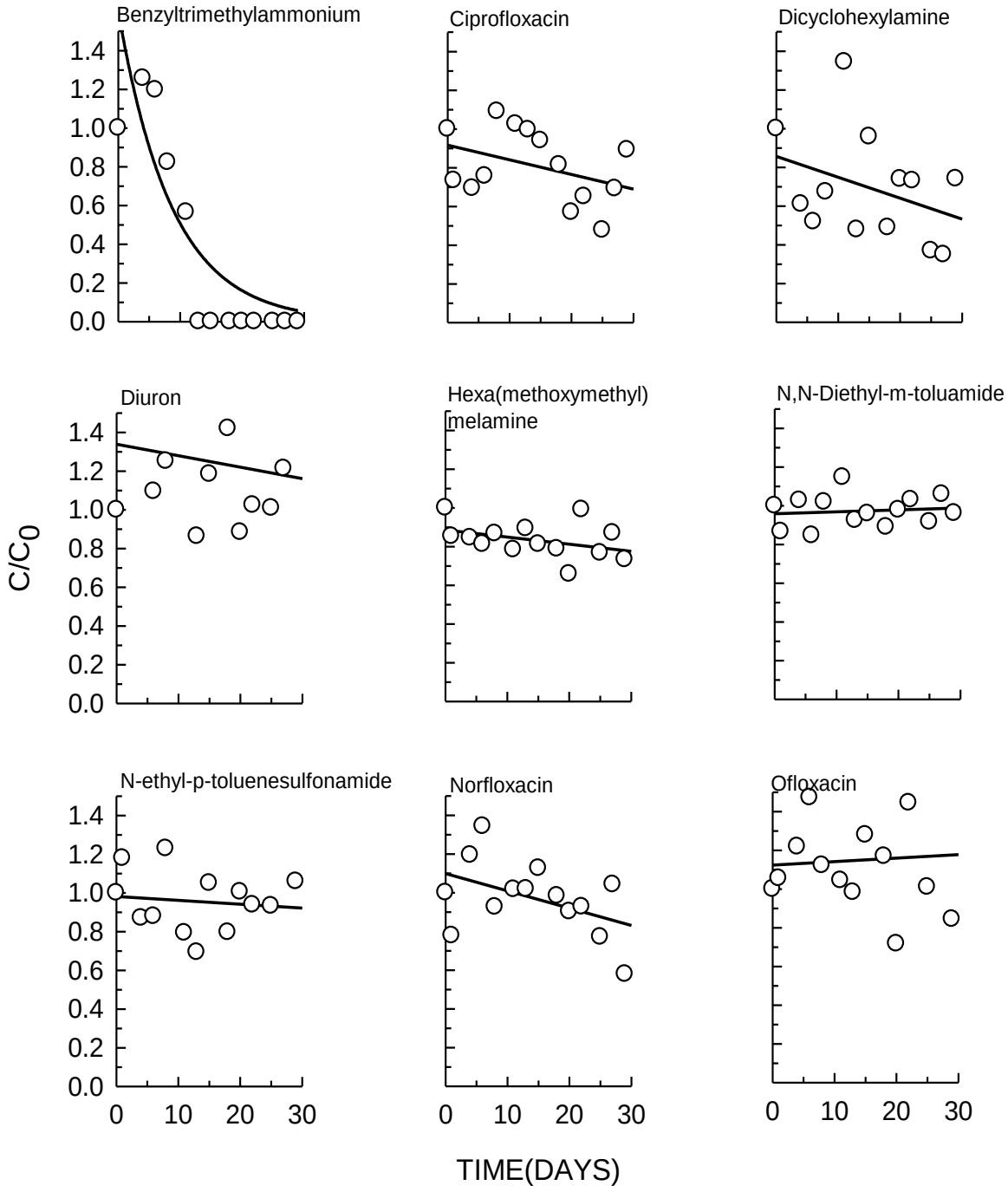

Figure B.22. Biodegradation profile of chemicals at sampling point 25 – Cont'd.

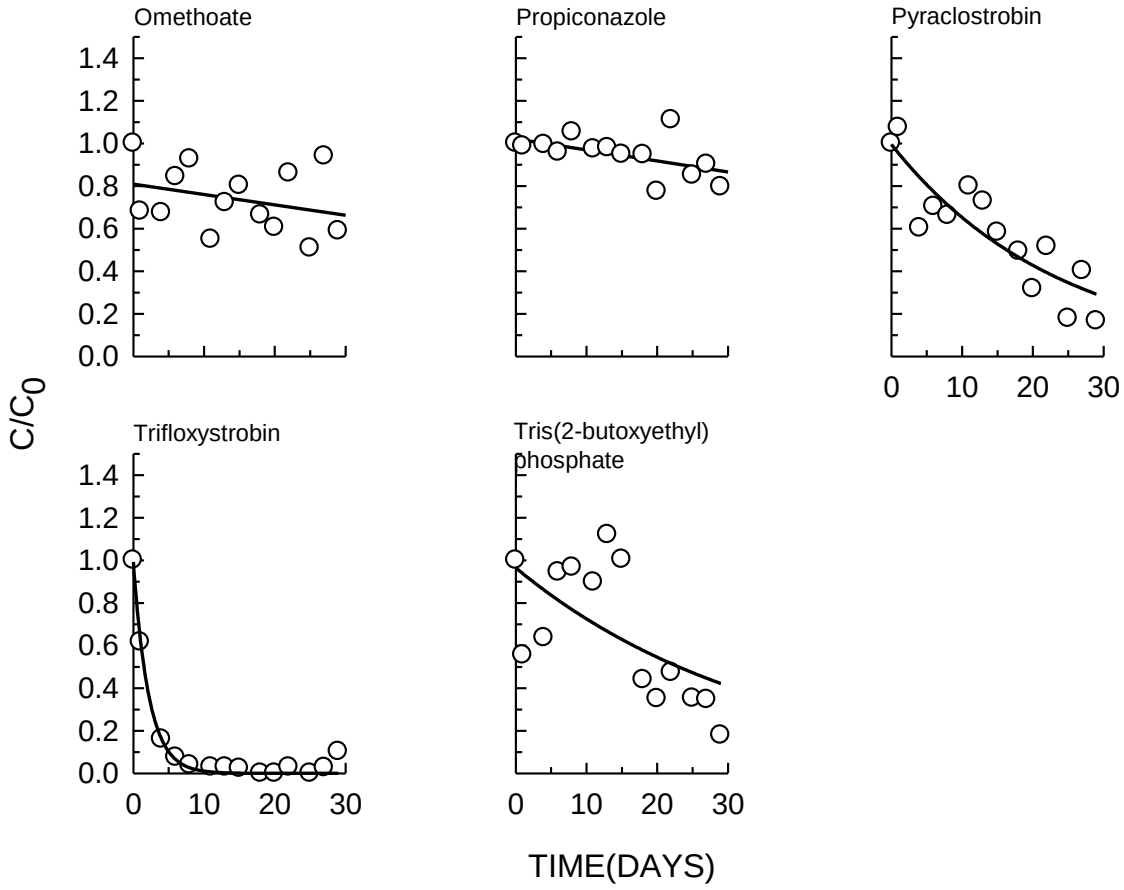

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Figure B.23. Biodegradation profile of chemicals at sampling point 26.

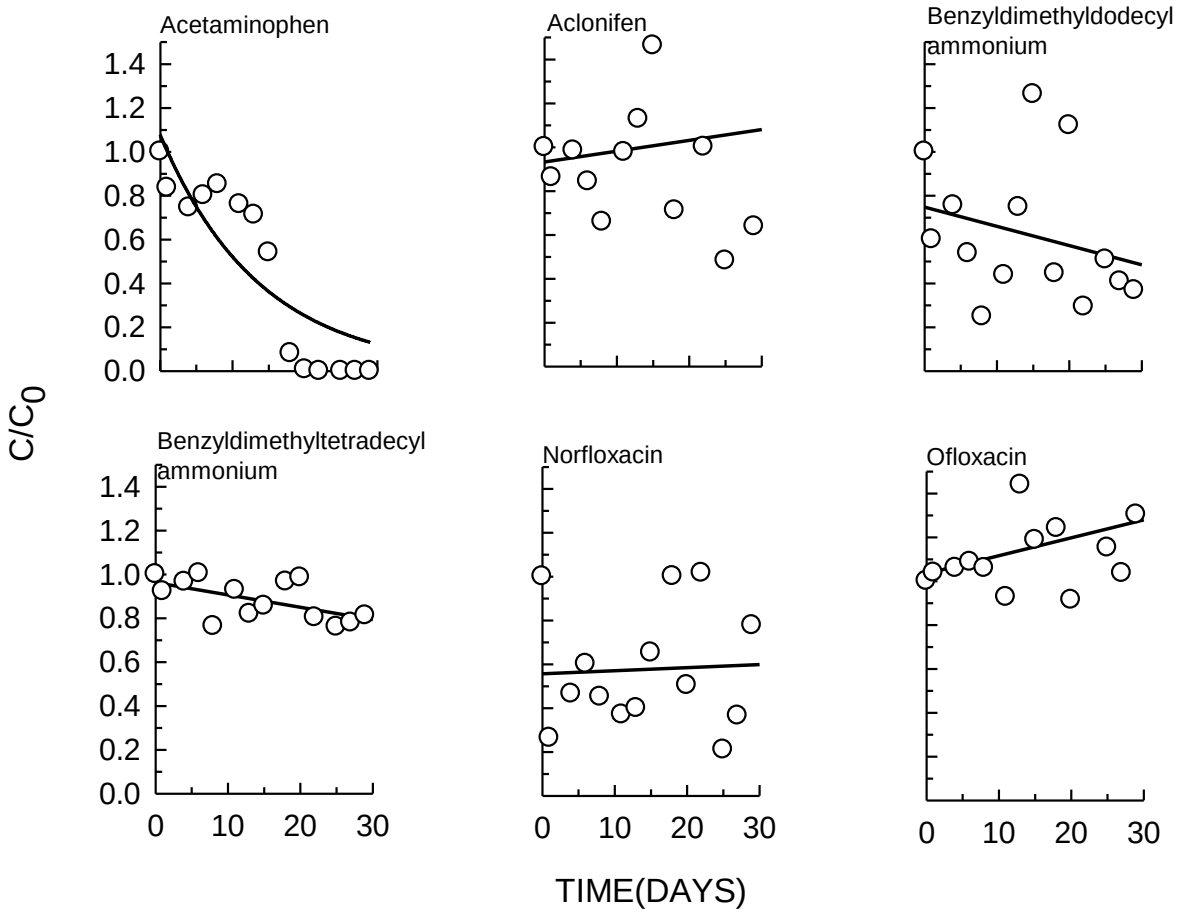

Figure B.24. Biodegradation profile of chemicals at sampling point 28.

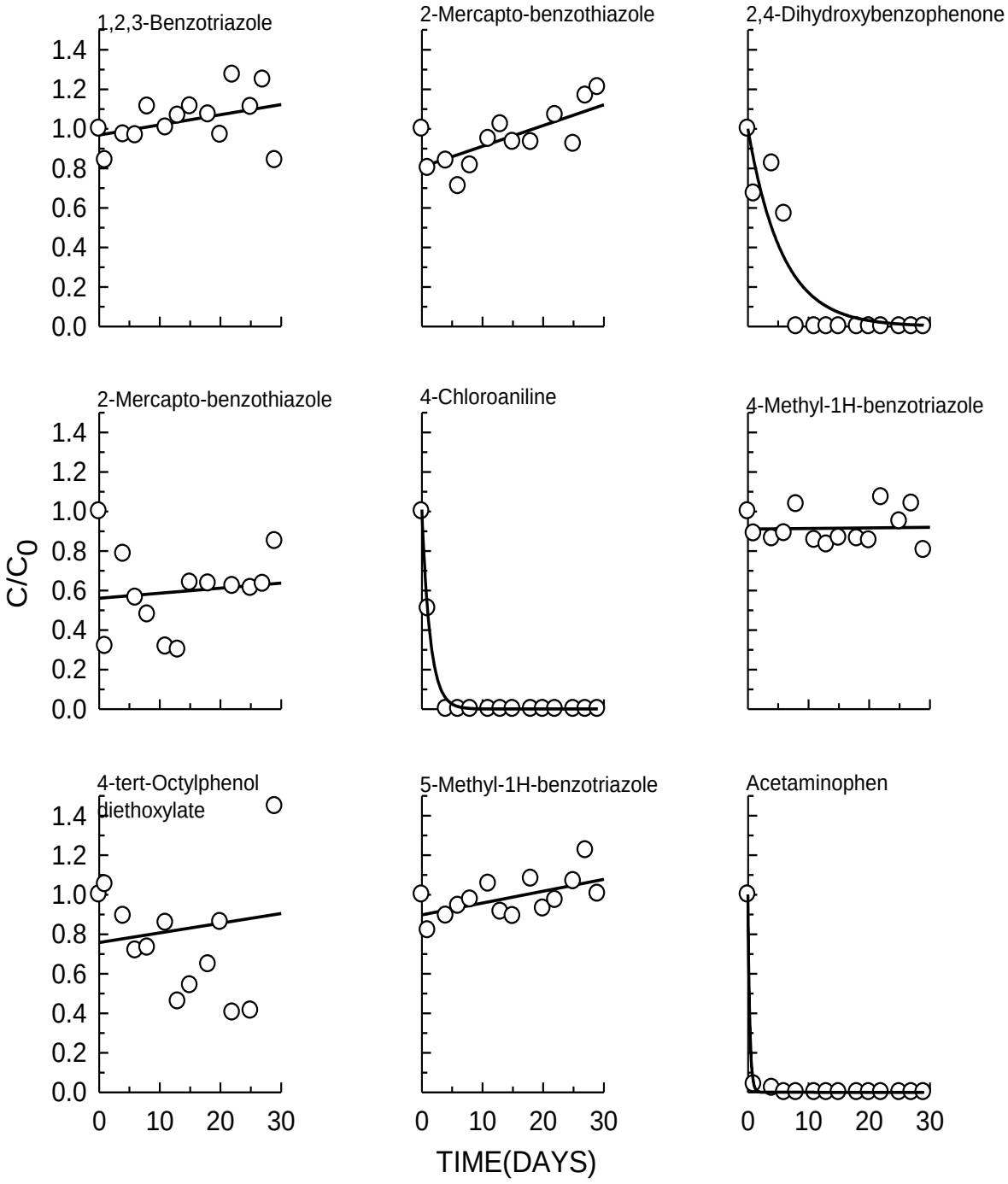

Figure B.24. Biodegradation profile of chemicals at sampling point 28 – Cont'd.

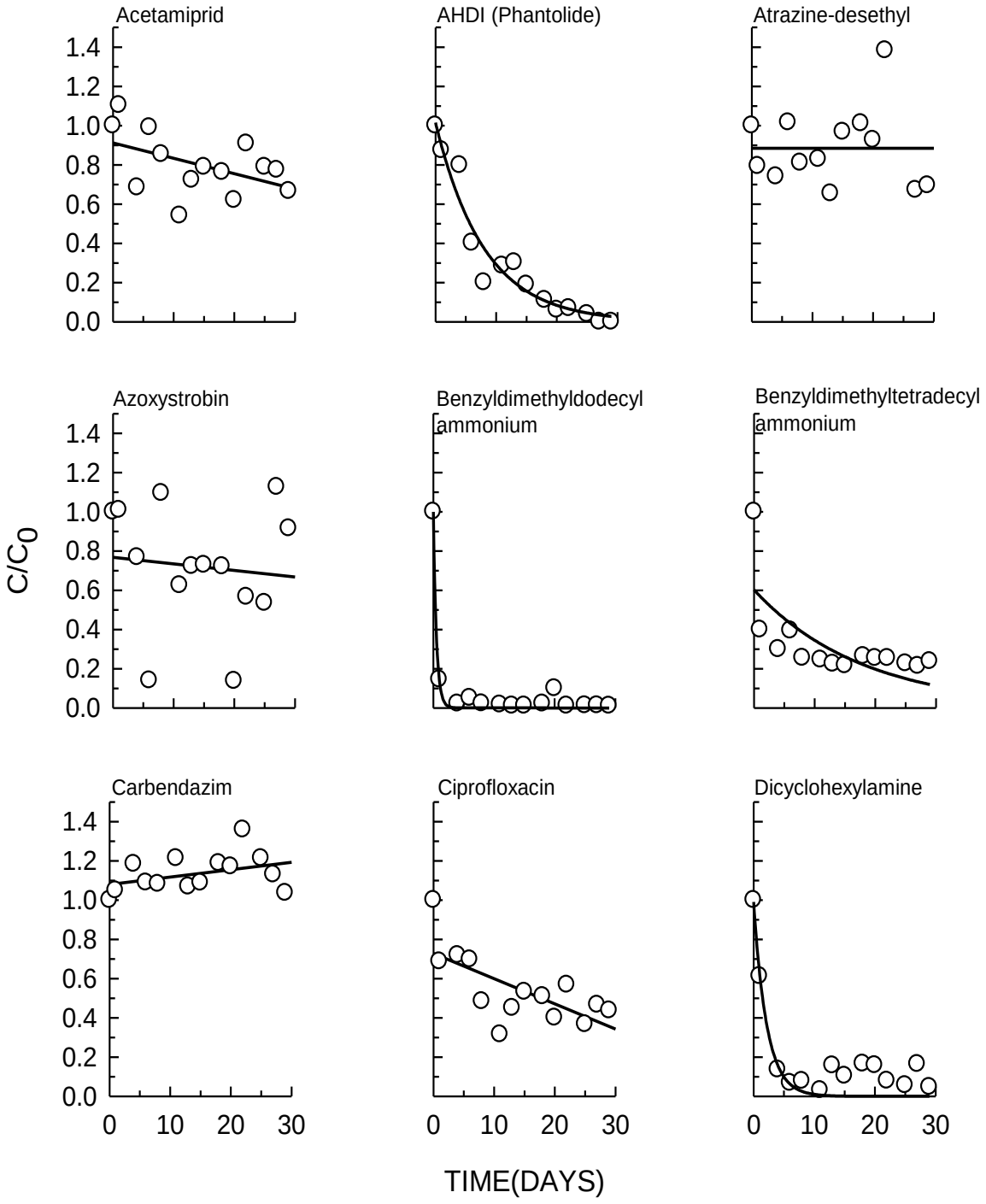

Figure B.24. Biodegradation profile of chemicals at sampling point 28 – Cont'd.

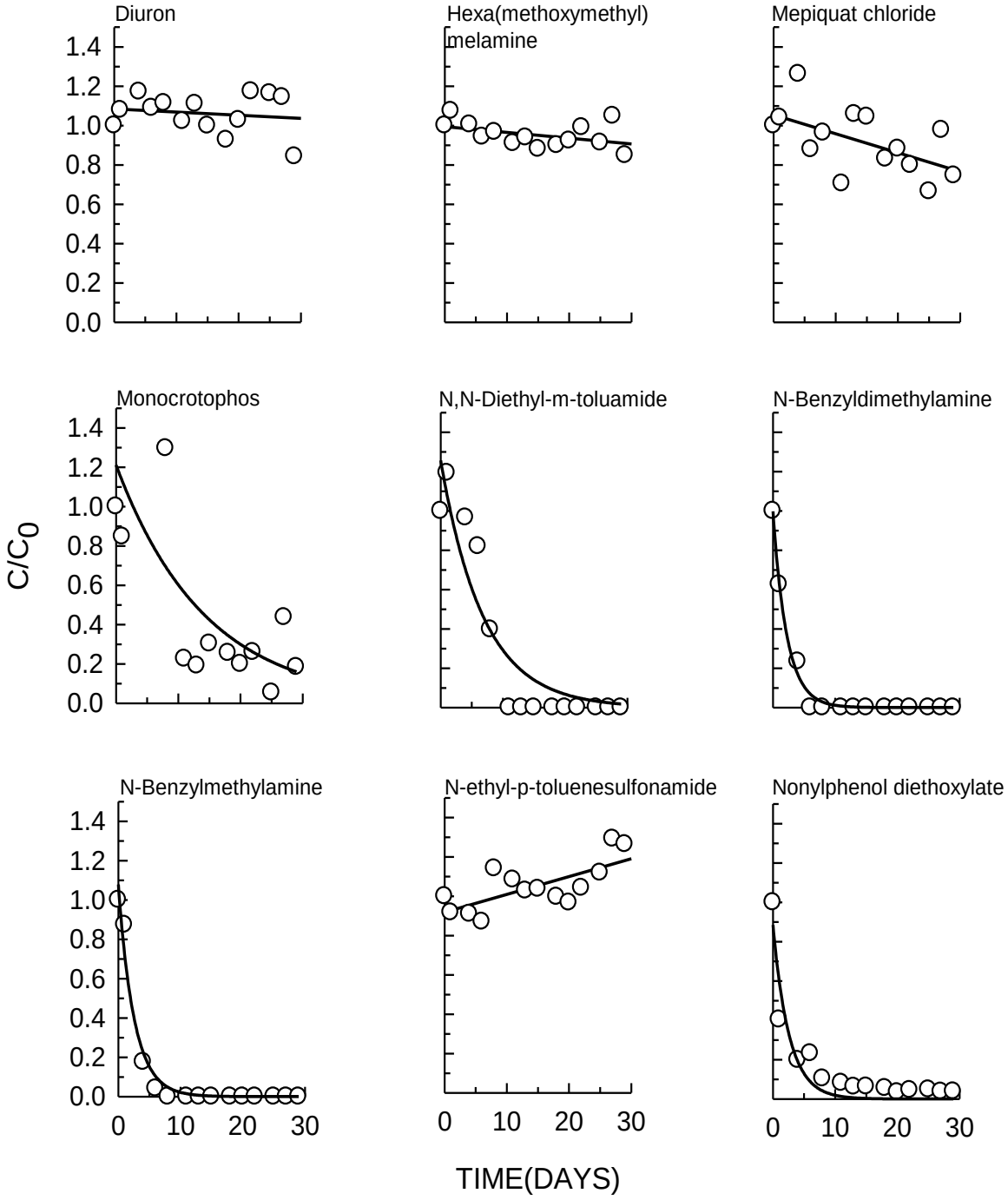

Figure B.24. Biodegradation profile of chemicals at sampling point 28 – Cont'd.

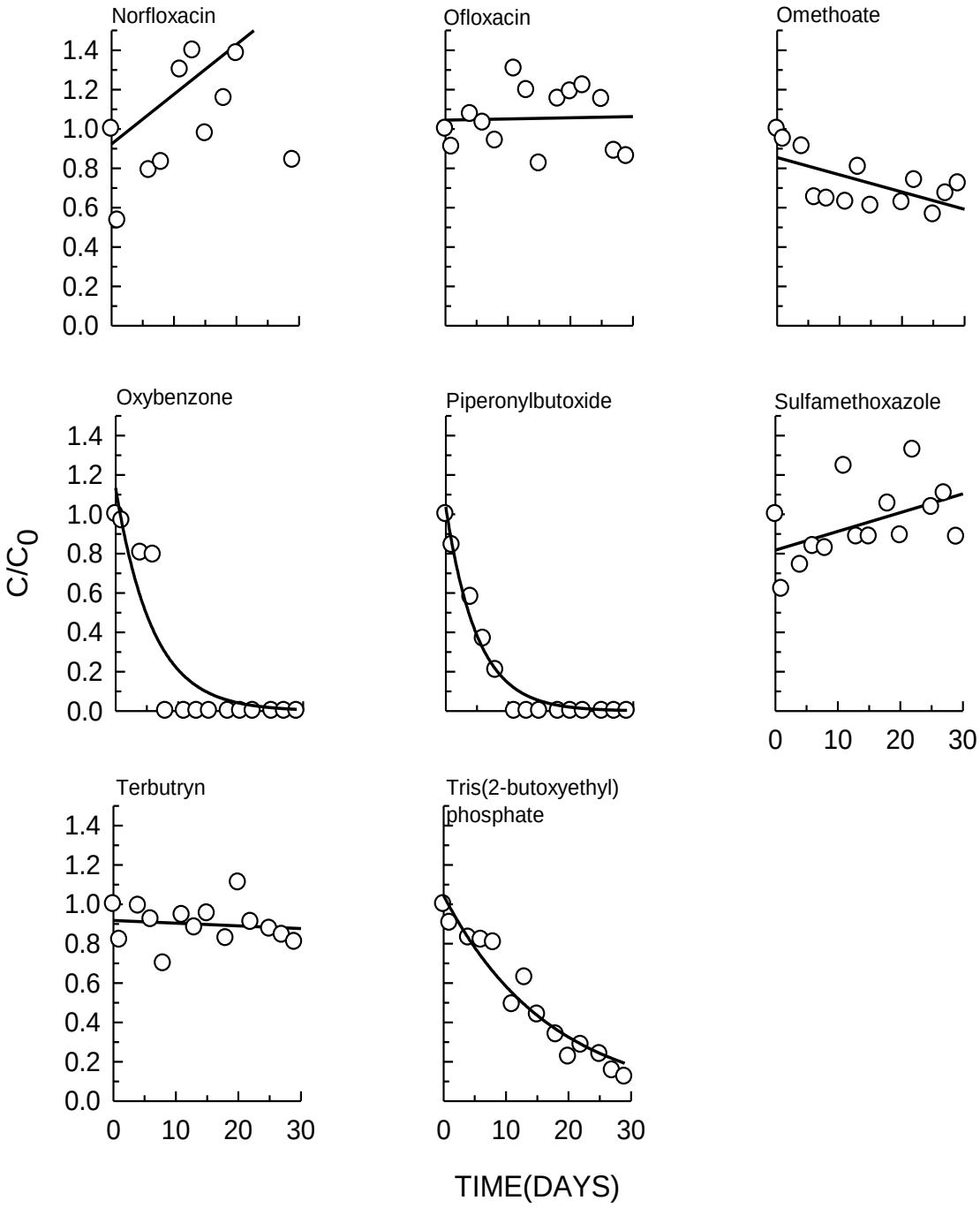

Figure B.25. Biodegradation profile of chemicals at sampling point 48.

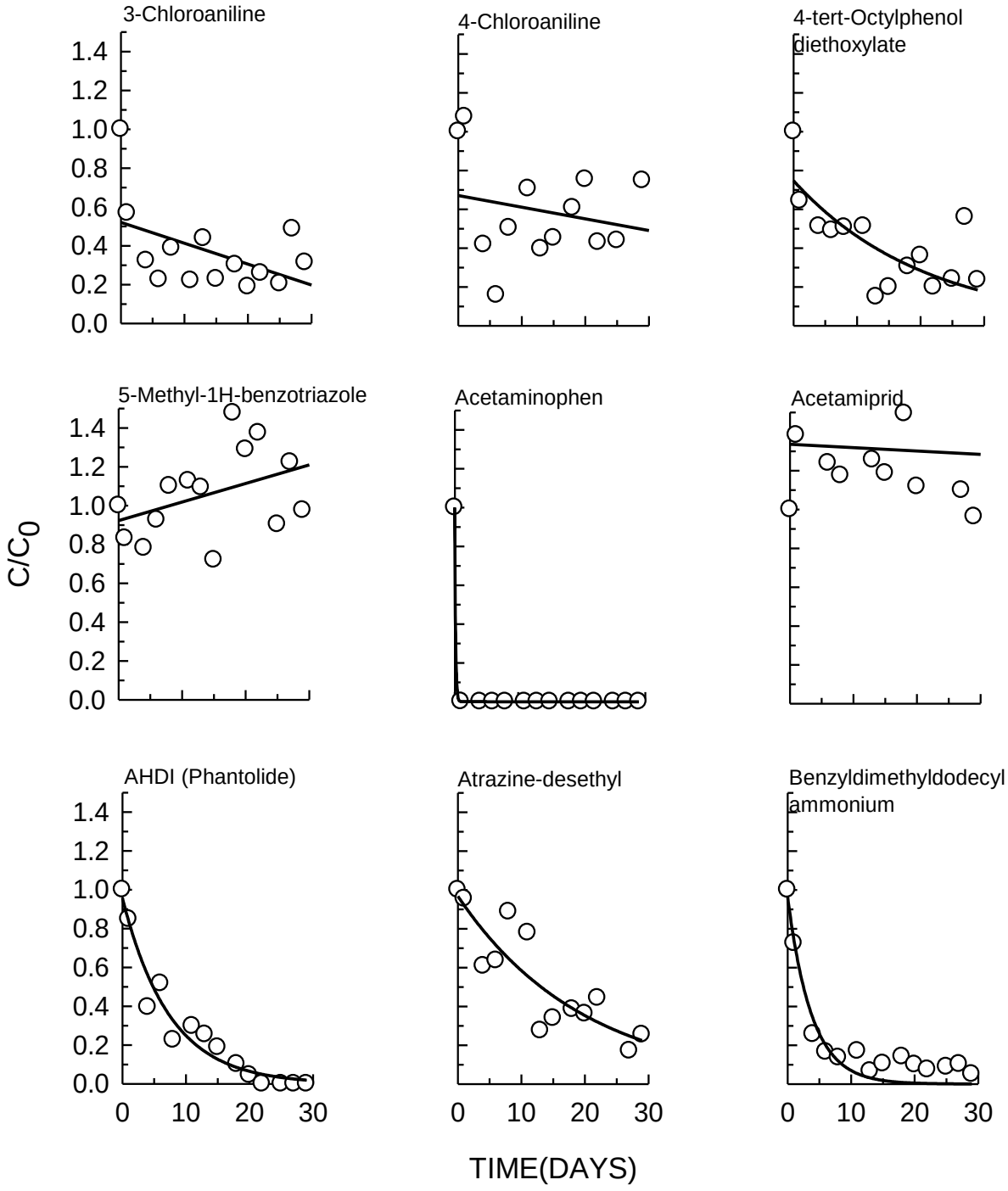

Figure B.25. Biodegradation profile of chemicals at sampling point 48 – Cont'd.

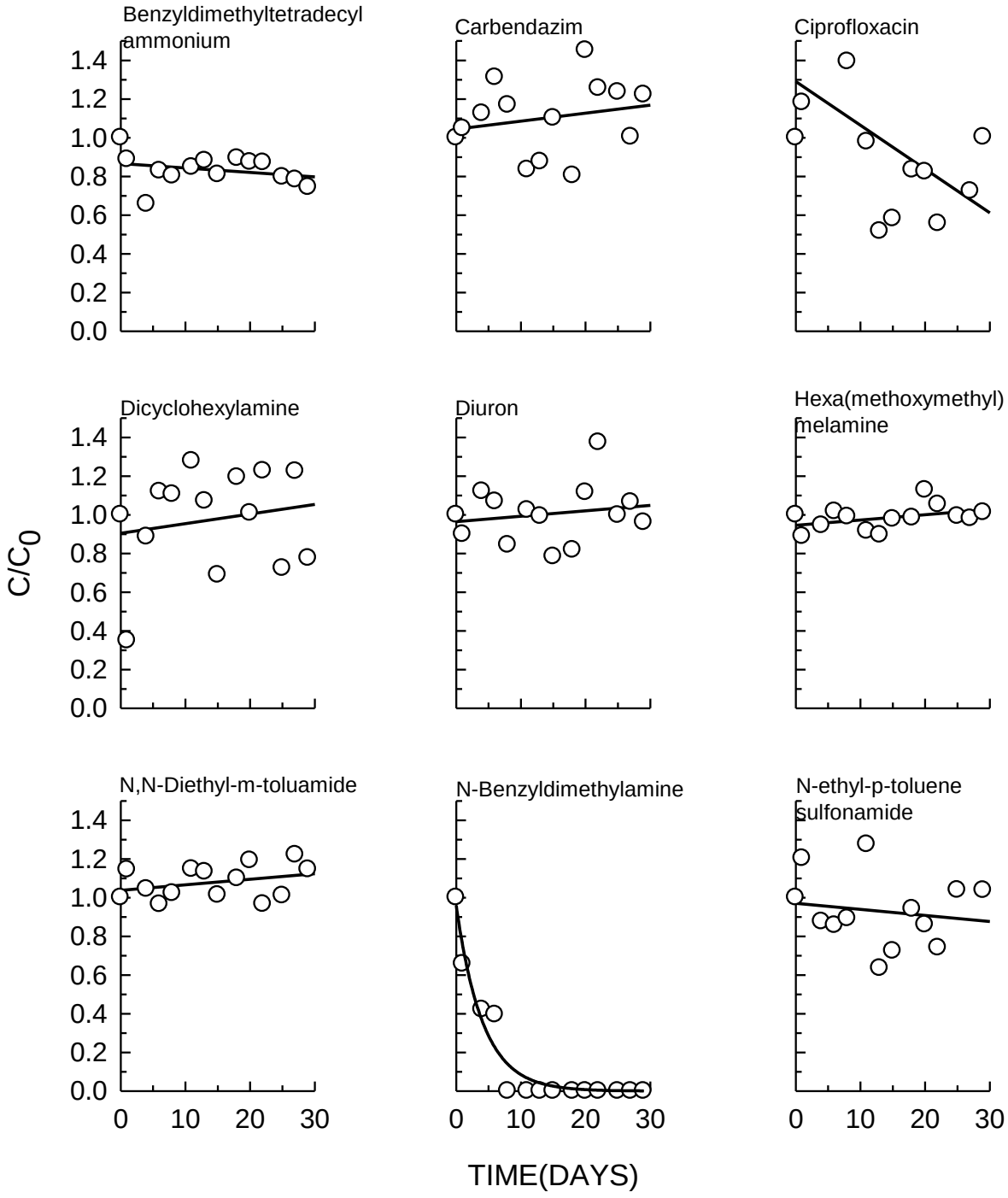

Figure B.25. Biodegradation profile of chemicals at sampling point 48 – Cont'd.

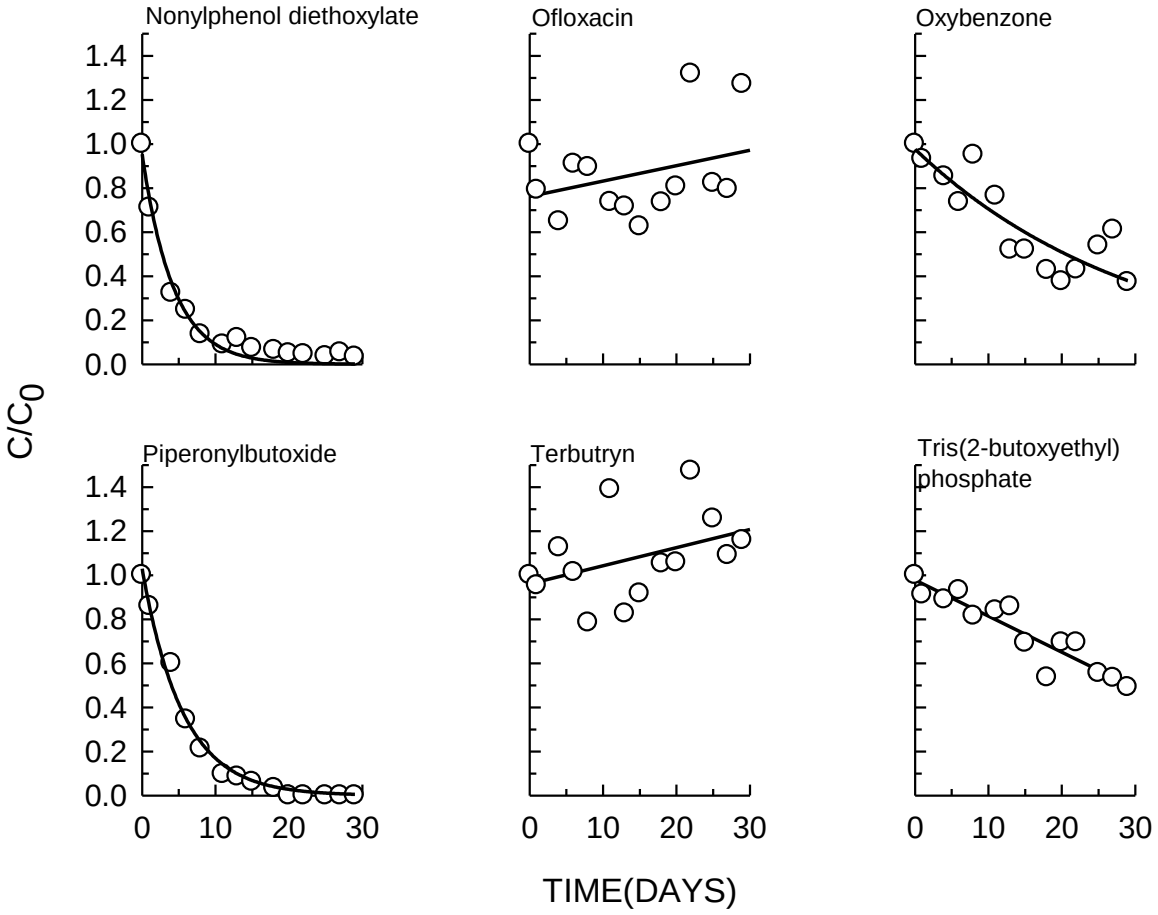

Figure B.26. Biodegradation profile of chemicals at sampling point 50.

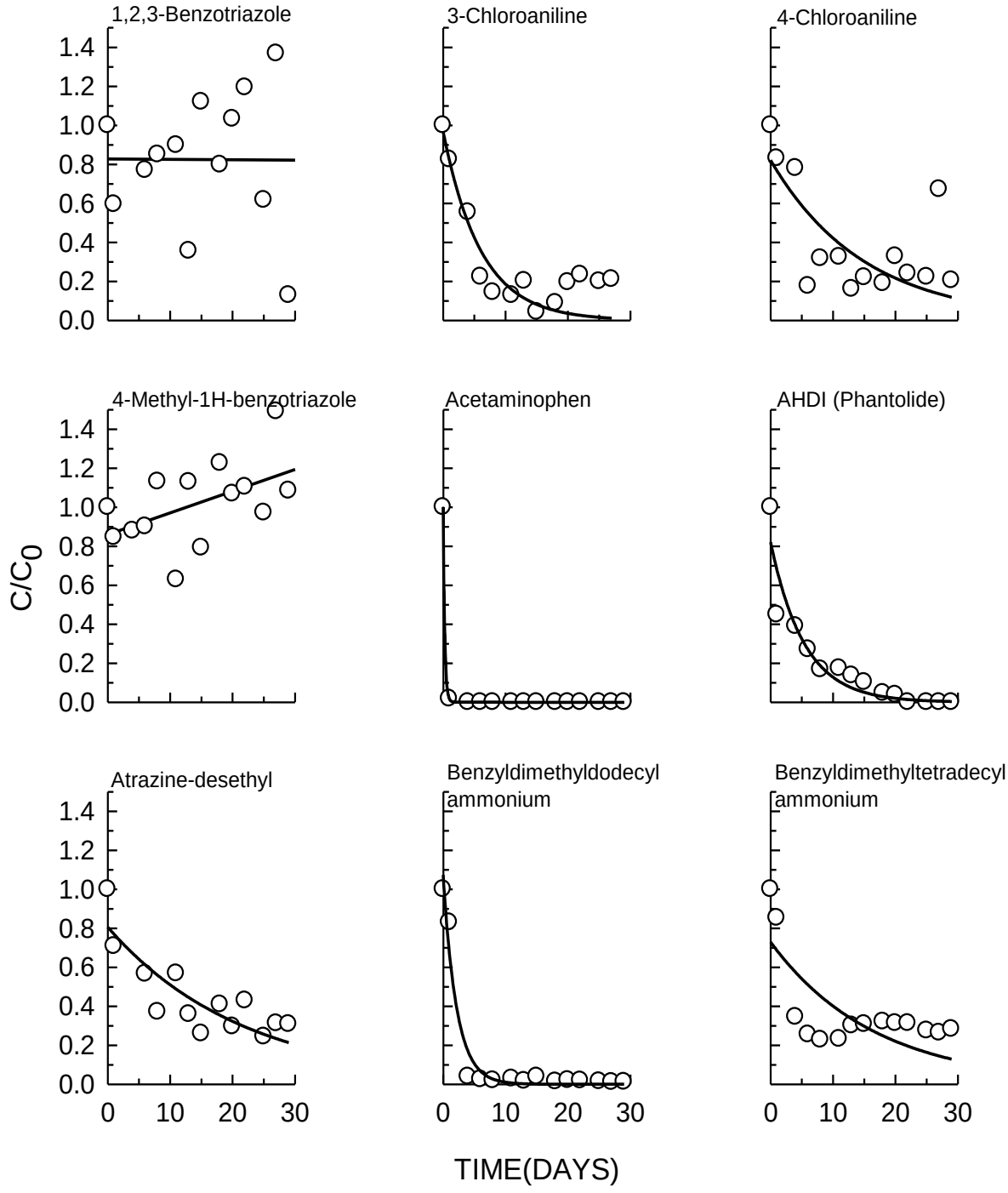

Figure B.26. Biodegradation profile of chemicals at sampling point 50 – Cont'd.

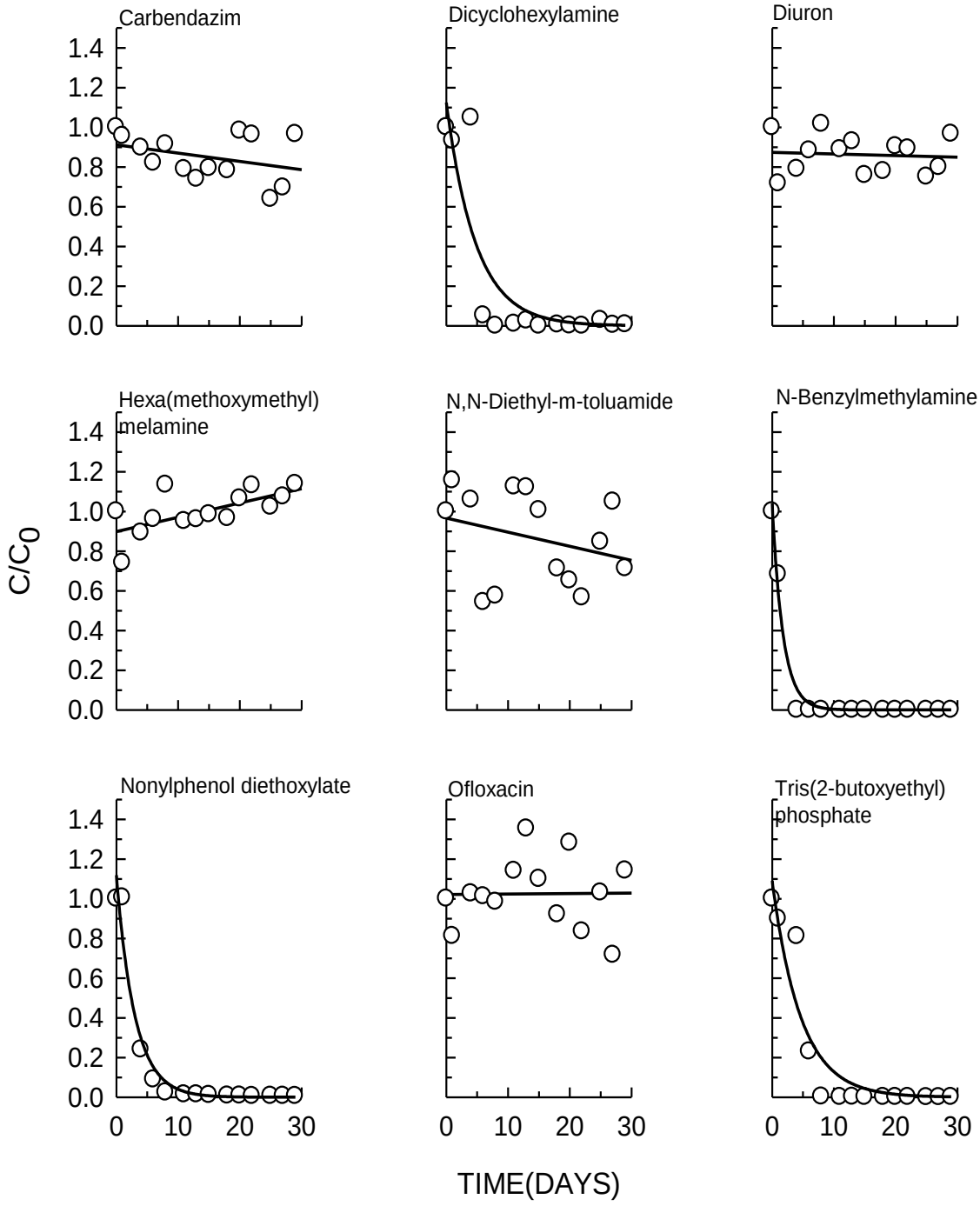

Figure B.27. Biodegradation profile of chemicals at sampling point 54.

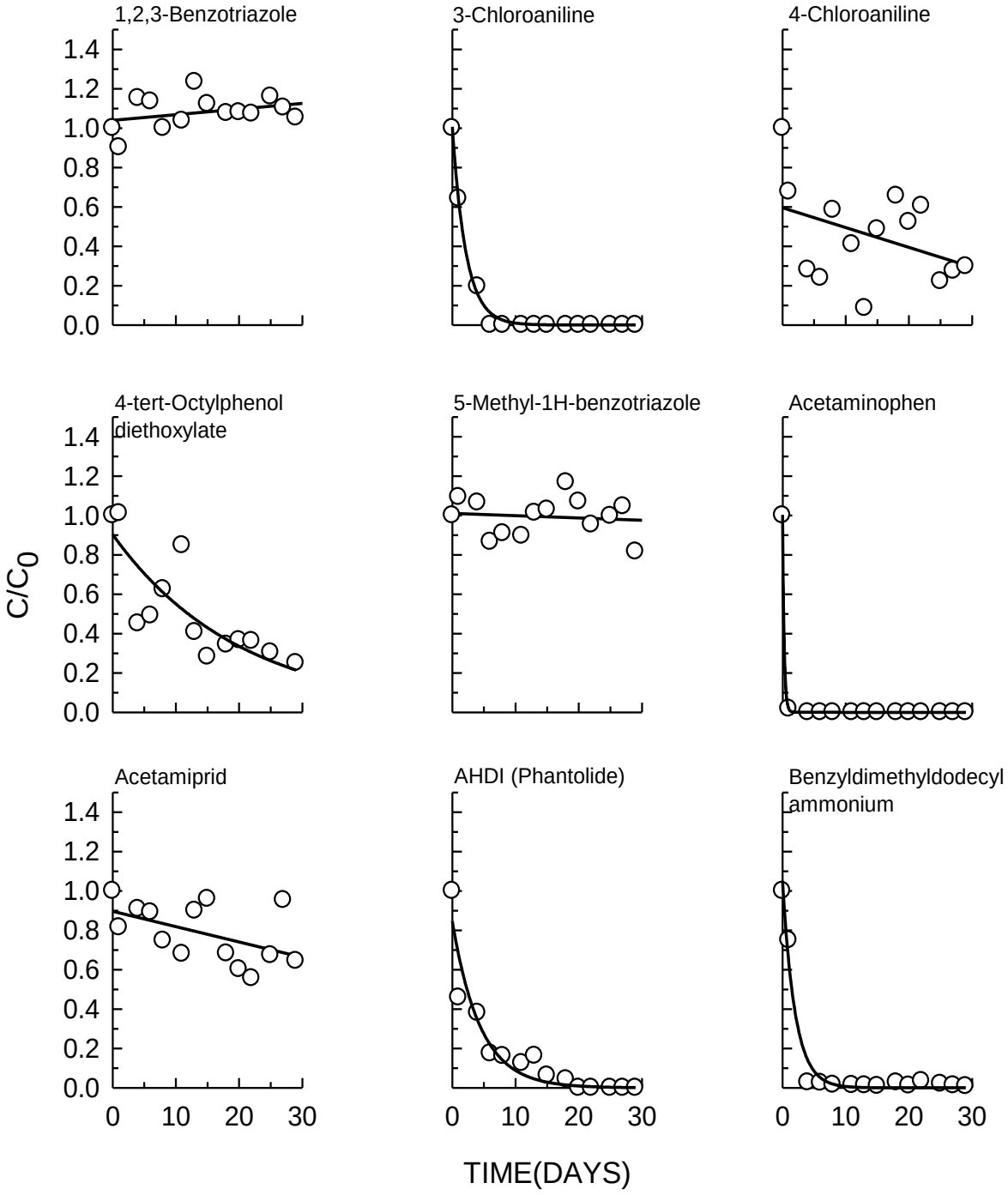

Figure B.27. Biodegradation profile of chemicals at sampling point 54 – Cont'd.

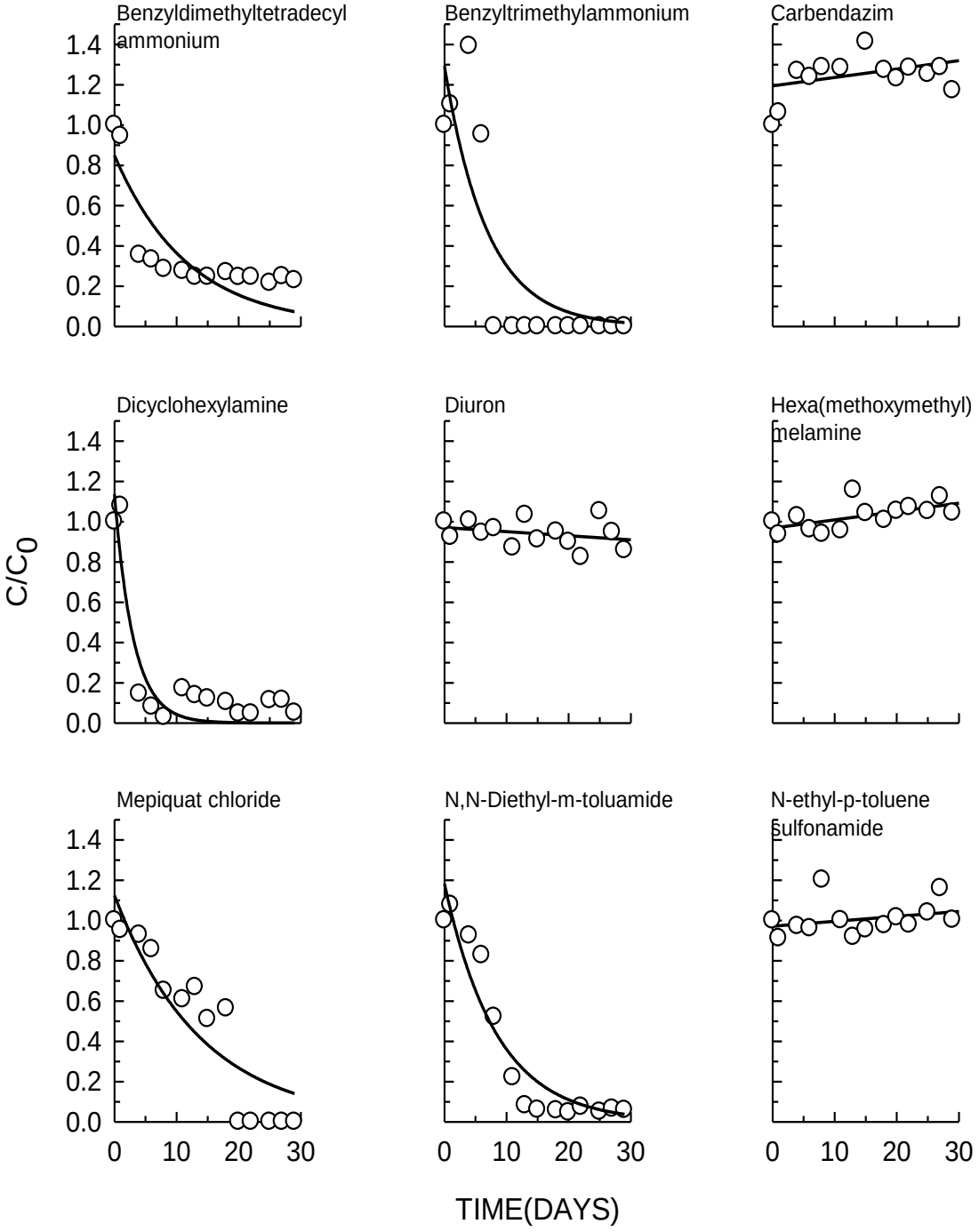

Figure B.27. Biodegradation profile of chemicals at sampling point 54 – Cont'd.

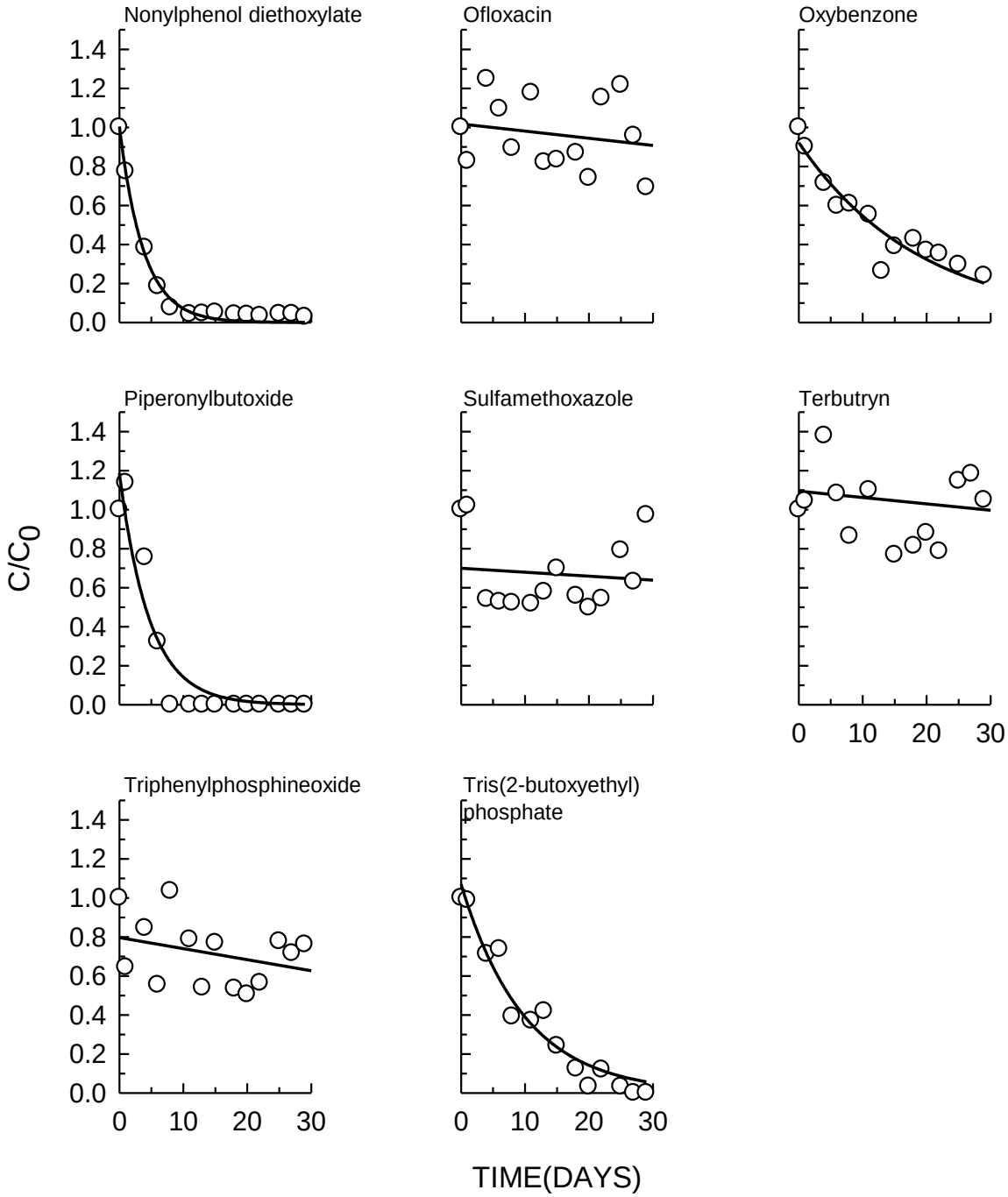

Figure B.28. Biodegradation profile of chemicals at sampling point 55.

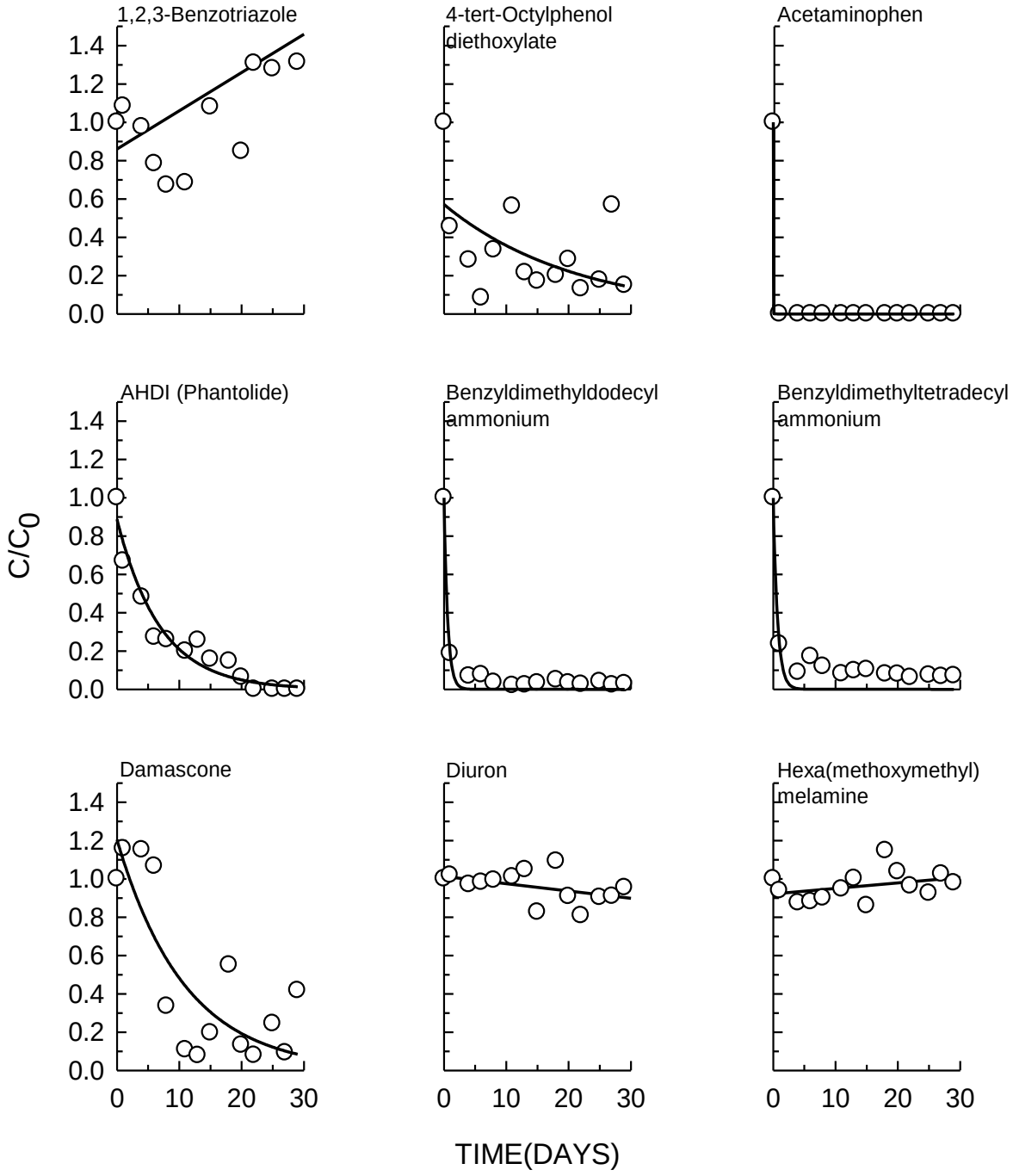

Figure B.28. Biodegradation profile of chemicals at sampling point 55 – Cont'd.

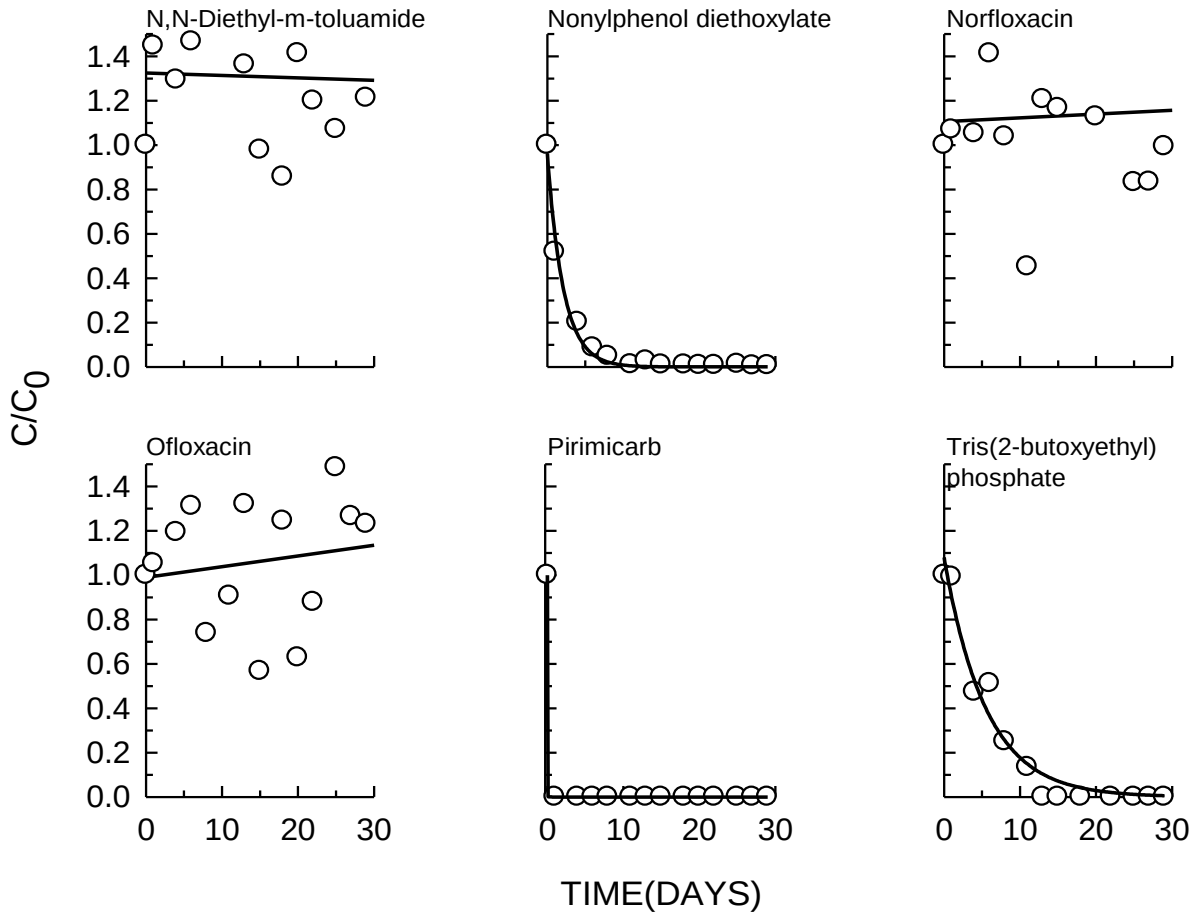

Figure B.29. Biodegradation profile of chemicals at sampling point 65.