Review Study on Fate and Degradation of Organic Micropollutants

Master Thesis

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Abstract

After the wide use and application of many organic chemicals the last 50 years, they have been detected in trace amounts in water and soil samples. Chemicals can be released accidentally or after their application in the environment and later can reach drinking water wells, surface water or groundwater. The chemical properties of the compound is a major factor for its distribution in the environment but also physical, chemical and biological process in the close environment are also determinant factors for chemical's transport and degradation. The soil properties and the hydrogeology of the contaminated site affect the transport of the contaminant. In addition, chemical and biological processes can transform the chemical into harmless molecules. Different redox reactions lead to distribution of microorganism populations according to oxygen presence or nutrients. Many water disinfection techniques are used to treat the contaminants and produce safe water. One popular and economical technique, which used in many European countries, is the river bank filtration, where pumping wells near riparian areas collect water from river. It was considered as a safe water treatment process, because chemical and biological reactions during subsurface passage could reduce the amount of contaminants. However these processes are affected by climate, soil properties, geological characteristics of the aquifer, redox conditions and microbial activity, so in some cases the filtration is not efficient. Many chemicals have been found below or above the health threshold in water samples or in drinking water wells. The evaluation of the environmental fate of most chemicals and their transport and degradation under different redox conditions should be investigated, so better water treatment techniques could be developed. This review study focuses on the environmental transport and degradation studies of selected chemicals that have been widely used in the last decades. These chemicals are the methyl tert-butyl ether (MTBE), bisphenol-a (BPA), metformin, metolachlor and mecoprop. Results from this study showed that the most of them are persistent in the water and have low degradation rates in the deeper aquifers and under anaerobic conditions. Metformin was found to be fully degraded to its metabolite, Guanylurea and further studies for this chemical should be conducted. Bisphenol-a can be completely eliminated during conventional treatment techniques but not under anaerobic conditions. Some degradation of MTBE, metolachlor and mecoprop occurs under aerobic conditions.

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Introduction

Due to the human activities and needs of the current life many organic chemical compounds have been developed. These could be pharmaceuticals, pesticides, food additives, plasticizers, detergents, flame retardants, benzene derivatives etc.. Recently many of these compounds, that were not previously detected, have been found in trace amounts in groundwater and surface water, and even in drinking water. The term micropollutans or emerging contaminants is referring to those substances that may induce adverse effects to humans and to biota even at low concentration (ng/L) (1). The major sources of the soil and water contamination, is the wide usage of chemicals in agriculture, the municipal and industrial effluents and the leaking of underground disposal tanks. According to WHO (2011) (2), about the 20% of the humanity has no access to safe water and the contamination of water causes more than 2 million deaths every year. In Europe safety thresholds have been set for the most frequently detected compounds to protect consumers (EC,1998) (3).

The fate of a chemical in the environment depends on chemical, biological and physical processes. These processes can affect or not the chemical structure and distributed later in the environment. Physical processes depend on the soil properties, as organic carbon content, porosity, and geological conditions (4). These do not affect the chemical structure but affect its sorption in soil matrix, mobility and transport between the environmental compartments. In addition, major factor on physical processes have the chemical properties of the compound. The vapour pressure determines if the chemical prefers to be in the air phase or not. The hydrophobicity of a compound is determined by the solubility of the chemical in water or by the octanol-water partition coefficient. Moreover, the organic molecules could be neutral or polar, which indicates the dissolution of the compound in water phase. The charged compounds react with the soil surface and their environmental fate is pH-dependent (19,20).

On the other hand, chemical and biological reactions can affect the chemical structure of the compound (degradation). This process may yield harmless products or can lead to mineralization of the chemical and produce CO_2 and H_2O with other mineral products (Cl^- ,NO_3^-, etc.). The mineralization depends on the bacterial and microbial activity (biodegradation). Many environmental factors affect the degradation process, as the redox potential, pH, temperature, moisture etc.. The redox conditions is referring mostly to aerobic (presence of oxygen) and anaerobic conditions (without oxygen). During the turn-over of organic compounds as an electron donors, the sequential use of O_2, NO_3^-, NO_2^- , SO_4^{2-}, Mn(IV), Fe(III) as electron acceptors, create a redox zonation (5). The microorganisms use the energy gained from the oxidation and degradation of the organic carbon for growth and reproduction. The concentration of oxygen, nitrate and sulphate decreases in an anaerobic aquifer, while the concentration of ammonia and sulphide increases. The energy released under aerobic conditions is higher than under anaerobic conditions. Microbial activity under anaerobic conditions leads to methanogenesis. Due to the variability of the redox environment in the subsurface and groundwater surface, the degradation of the contaminant varies equally (6). Although some compounds degraded better under aerobic environment, there are also some chemicals that need anaerobic conditions to mineralised, as many halogenated molecules (7).

Usually the water from rivers, lakes and aquifers close to residential areas is used for drinking water consumption. Unfortunately, this water is the most contaminated from chemical pollutants and needs to be carefully and completely disinfected. There are conventional techniques already which remove the major contaminants and produce drinking water with chemical's concentration below the health threshold. Some common techniques for water treatment are: sand-filtration, ultra-filtration, ozonation, active carbon filtration, chlorination, reversed osmosis, etc. In addition to above, some more affordable water extraction techniques

are the river bank filtration (RFB) and the artificial recharge or managed aquifer recharge (MAR) (8,9,18).
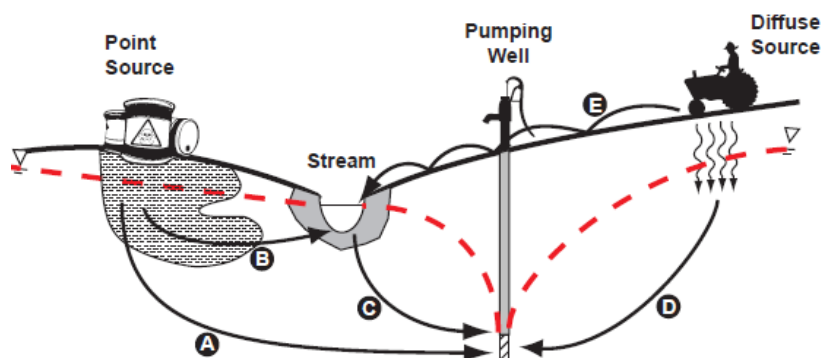

Figure 1 Pathways of contaminant to reach a drinking water well, Malaguerra 2011 (16)

These extraction techniques use pumping wells to collect the water from rivers and streams. However, the pumping could reverse the water flow from the groundwater to stream and a possible contamination of the drinking water well can occur (10). Figure 1 demonstrates the possible pathways of a contaminant to reach a drinking water well. Many countries in Europe (Netherlands, German, France, etc.) use the water filtration to produce drinking water for the citizens. For example, the seventy percentage of the drinking water source in Berlin comes from the bank filtrate (11,12). Riverbank filtration to produce safe drinking water has wide application for drinking water production. The sorption of the contaminants in the soil matrix, the presence of oxygen and the microbial activity can reduce the concentration of these compounds which reach to the drinking water well (11,13). However, many times the bank filtration cannot remove efficiently the contaminants because several factors affect the underground passage of water (11,14). These include the water travel time, water quality, redox potential, temperature, pH, moisture, microbial presence, porosity of the soil, geological conditions etc. In addition to the above, contaminants' infiltration depends strongly on the climate, which can easily affect the water recharge (15). Figure 2 depicts the reactions for water filtration during a river bank filtration.
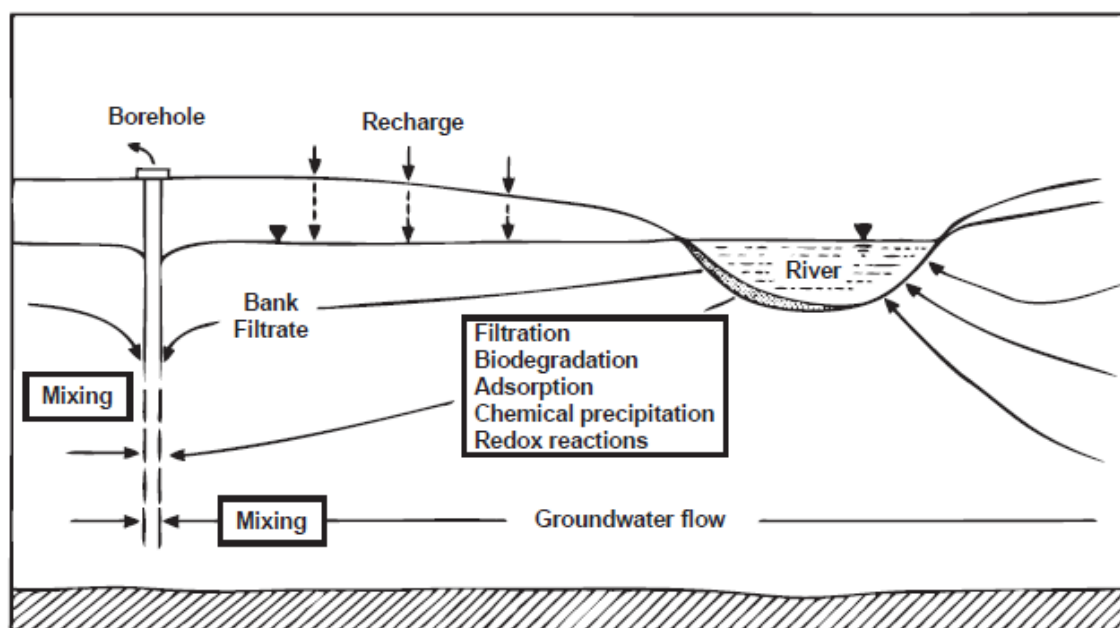

Figure 2 Processes of contaminant elimination during river bank filtration, adapted from Malaguerra, 2011 (16)

Changes in surface water quality can occur during the years, which may affect the characteristics of the environmental redox potential. Bank filtration from Rhine river is a good example to show how the water quality can influence the redox potential of the aquifer (17). As it is observed in the figure 3 below, in 1973 the high presence of ammonia and almost the absence of oxygen determine anaerobic redox conditions of the aquifer. That happened because of highly polluted river's water over this period. The biodegradation processes during the water filtration reduced the oxygen present and the manganese. Later, in 1980, the water quality improved because of the improved municipal and industrial management and wastewater treatment, so the oxygen increased and the aquifer get into aerobic redox status.
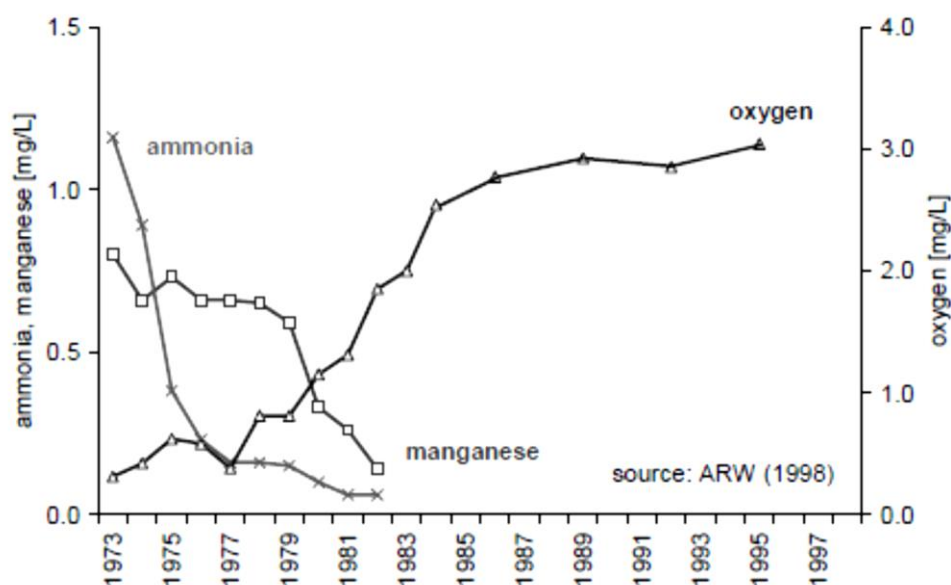

Figure 3 Demonstration of aquifer conditions under river bank filtration and river's water quality, adapted by Schmidt et al. (4).

Based on the contamination of drinking water sources by man-made substances, this study reviews the environmental fate and the degradation of five different organic contaminants, which recently detected in water samples at trace amounts, under different redox conditions. These compounds are

- a benzene oxygenate, methyl tert-bulty ether (MTBE),
- a plasticiser, bisphenol-A (BPA),
- a diabetic drug, metformin
- and two herbicides, metolachlor and mecoprop

By the results of this study, the presence and distribution of these compounds in water and soil compartments can be predicted. In addition, the monitoring of their metabolites should be further assessed, because in some cases metabolites are in more potential risk for human lives than the parent compound.

Methods

The literature review conducted from extracted studies of the database of Scopus, Pubmed and Science direct. In addition, searching on manuscripts and books for the theoretical parts of this study was potential factor for understanding on the physical, chemical and biological processes which are referred into the introduction part. Moreover, knowledge from Environmental hydrogeology course was necessary for contaminant transport in shallow and deep aquifers and groundwater.

References

1. M. E. Stuart, K. Manamsa, J.C. Talbot, E.J. Crane, Emerging Contaminants in groundwater, British Geological Survey, Open report, OR/11/013, 2011
2. WHO, Facts and figures: water, sanitation and hygiene links to health, 2011
3. EC, Counsil directive 98/83/ec of 3 November 1998 on the quality of water intended for human consumption, Official Journal of European Communities,L330/32-54,1998
4. C.K. Schmidt, F. T. Lange, and H.J. Brauch, Assesing the impact of different redox conditions and residence times on the fate of organic micropollutants during riverbank filtration, DVGW/Technologiezentrum Wasser (TZW), Germany, Unpublished report
5. C.N. Dahm, N.B. Grimm, P. Marmonier, H.M. Valett, Nutrient dynamics at the interface between surface waters and groundwaters, Freshwater Biol., 40,427-451, 1998
6. B. Conant, J.A Cherry, R.W. Gillham, A pce groundwater plume discharging to a river: influence of the streamed and near-river zone on contaminant distributions, J.Contam. Hydrol. 73, 249-279, 2004
7. S. Fetzner, Bacterial dehalogenation, Appl. Microb. And Biotechnol., 50, 633-657, 1998
8. R.W. Masters, I.M. Verstraeten, T. Heberer, Fate and transport of pharmaceuticals and endocrine disrupting compounds during ground water recharge, Ground Water Monit. and Remed, 24, 54-57, 2004
9. P. Eckert, R.Irmscher, Over 130 years of experience with riverbank filtration in Dusseldorf, Germany, Journ. Of Water Supply: Resear. And Techn. AQUA, 55, 283-291,2006
10. T.C. Winter, J.W, Harvey, O.L. Franke, W.M. Alley, Ground water and surface water: a single resource, Techn. Report, U.A. Geological Survey, 1998
11. N. Tufenkij, J. Ryan, M. Elimelech, The promise of bank filtration, Environ Sci Techn., 36, 422A-428A, 2002
12. T. Heberer, A. Mechlinski, B. Franck, A. Knappe, G. Massmann, A. Pekdeger, B. Fritz, Filed studies on the fate and transport of pharmaceutical residues in bank filtration, Ground Water Monit. And Remed., 24,70-77,2004
13. C. Kohfahl, G. Massmann, A. Pekdeger, Sources of oxygen flux in groundwater during induced bank filtration at a site in Berlin, Germany, Hydrogeol. Jour., 17, 571-578, 2009
14. R.P. Schwarzenbach, W. Giger, E. Hoehn, J.K. Schneider, Behavior of organic compounds during infiltration of river water to groundwater, Environ. Sci. Technol. 17, 472-479, 1983
15. T. Giambelluca, K. Loague, R. Green, M. Nullet, Uncertainty in recharge estimation: impact on groundwater vulnerability assessments for the Pearl Harbor Basin, Oáhu, Hawaii, Usa. Journ. Contm. Hydrol., 23, 85-112, 1996
16. F. Malaguerra, Models and statistical analysis of organic micropollutants in groundwater-based drinking water resources, PhD Thesis, 2011
17. C.K. Schmidt, F.T. Lange, H-J. Brauch, W. Kuhn, Experiences with riverbank filtration and infiltration in Germany: Proceedings International Symposium on artificial recharge of groundwater, 14.11.2003, Daejon, Korea, 115-141, 2003
18. M. Kuster,S. Diaz-Cruz, M. Rosell, M.L. de Alda, D. Barcelo, Fate of selected pesticides, estrogens, progesogens and volatile organic compounds during artificial aquifer recharge using surface wáter, Chemosphere, 79, 880-886, 2010
19. R.P., Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, John Wiley and Sons, New York, 1993
20. M.B. McBride, Environmental Chemistry of soils, Oxford University Press, New York, 1994

Review Discussion

> *Methyl tertiary-butyl ether (MTBE)*

In order to minimize CO_2 emissions and to improve the combustion efficiency, fuel oxygenates have been added to gasoline. MTBE is the most important fuel oxygenate, which is used more than 20 years. About 20 million tons of MTBE (60% America and 15% Europe) are consumed each year around the world. Over 78000 tons are emitted annually in Europe, where the 92.4% is emitted into the atmosphere, and the rest in water and soil phase (1). In table 1 below, some chemical properties of MTBE are shown.
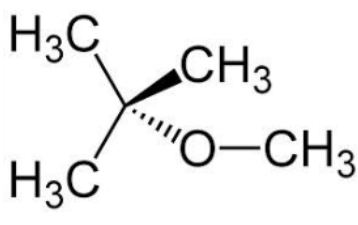
IUPAC name	2-Methoxy-2-methylpropane	
CAS number	1634-04-4	
Molecular formula	$C_5H_{12}O$	
Molar mass	88.15 g mol^{-1}	
Vapour Pressure	250 mmHg (25 °C)	
Solubility in water	26 g/L (20 °C)	

Table 1 Chemical properties of MTBE

MTBE's widespread use was intended to reduce air pollution (Pb) but MTBE itself has been found in trace concentrations in water resources such as rain water, surface water, groundwater and drinking water (2). MTBE concentrations in German surface waters were estimated in the range of 0.2-0.3 ug/L (3). By accidental leaking of underground gasoline tanks or by air MTBE diffusion in soil, MTBE can contaminate soil sites. Mobile gasoline moves continually downward until the gasoline comes into contact with groundwater. MTBE can persist to groundwater and dissolve to it due to its high water solubility and low biodegradability. Figure 4 demonstrates the movement of MTBE through the environmental compartments.

In Europe there is no health effect threshold for MTBE for drinking water consumption, but there are taste (25-60 ug/L) and odour (40-70ug/L) thresholds for this compound at very low concentrations (4). LC_{50} for tested mice was reported to be 1.6 mmole/L (5). In addition, a Maximum Contaminant Level-Goal (MGLG) was set at 0.03 mg/L/day (5). Under the possible MTBE presence in drinking water, USEPA classified MTBE as a possible human carcinogen (6).
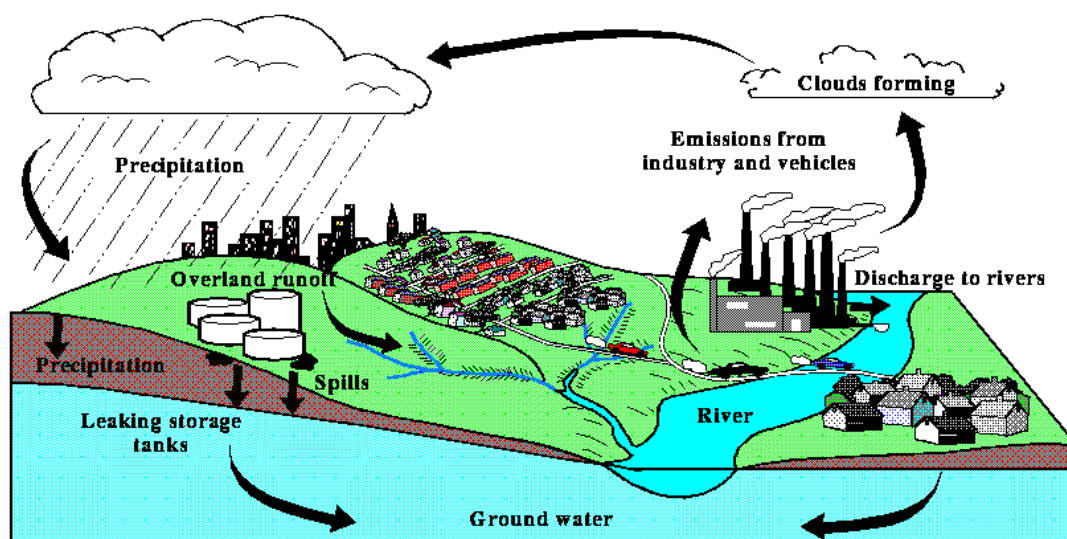
Figure 4 The movement of MTBE in the environment (extracted by South Dakota water science centre website)

Effective treatment techniques have not yet been applied to remove MTBE from wastewater and groundwater. Recently the riverbank filtration (RBF) has been found ineffective at removing MTBE concentrations from water (2,). For soil and groundwater remediation the full scale implementation is based on expensive treatment techniques (pump-and-treat, biostimulation, bioaugmentation) so the reduction of MTBE concentration depends on natural remediation as biodegradation and physical processes including dispersion, sorption, dilution and volatilization. The biodegradation process depends on the hydrochemical, biological and hydraulic boundary conditions of the aquifer. In addition, the organic carbon content and oxygen presence affect the redox reactions of the chemical degradation (7,15).

Many studies to examine the degradation of MTBE and its by-products have already been conducted. The main products from degradation of MTBE are tert-butyl alcohol (TBA) and tert-butyl formate (TBF). Secondary metabolites of MTBE degradation are acetone and methyl acetate (8). However, the general degradation products should be different due to different degradation pathways and systems. According to Arp et al. (2004) (2), TBA is difficult to measure at trace concentrations and TBF is rarely measured in environmental samples because it transformed directly to TBA (8). Henry's constant, K_{iH}, is highly temperature dependent and expresses the contaminant distribution in air-water phase. As it is described in Arp et al. (2004), TBA has lower K_{iH} than MTBE, so it has more affinity for the water phase. The water contamination with TBA should be also taken into consideration because TBA can be equally widespread as MTBE. Hong et al. (2006) (9), have investigated the degradation of MTBE by anodic Fenton treatment (AFT). The results showed that MTBE and its degradation products were fully degraded in 32 min via AFT ($Fe^{2+}:H_2O = 1:5$). This outcome can offer an efficient remediation technique for MTBE contaminated wastewater.

In addition to the above, anaerobic degradation of MTBE has been studied under methanogenic, sulfate-reducing and denitrifying conditions (10). A study of Somsamak et al. (2005) (10), tested the carbon isotope fractionation during anaerobic degradation of MTBE under sulfate-reducing and methanogenic conditions. This study demonstrated significant enrichment of C^{13} in MTBE fractions under both conditions and suggests that carbon isotope fractionation can be used as a tool for *in situ* anaerobic MTBE degradation. Yeh and Novak (1993) (5) demonstrated that MTBE was not degraded in any of the contaminated soil microcosms in the period of 250 days of incubation time. Nevertheless, MTBE degradation took place only in olitrophic soils with low organic matter (pH=5-6).

Several studies demonstrate the degradation of MTBE under aerobic conditions (11). Mo et al. (1996) (11) have studied the biodegradation of MTBE by pure bacterial cultures under aerobic conditions. Pure bacterial cultures of *Methylobacterium, Phodococcus* and *Arthrobacter* genus completely mineralized MTBE as shown by the appearance of C^{14} CO_2. The addition of easily degradable organic compounds in soil with low organic carbon reduced the MTBE degradation by pure microbial cultures, as in the study of Yeh and Novak mentioned above (1993). A later study of Steffan et al. (1997) (12), evaluated MTBE metabolism by propane-oxidizing bacteria. Mineralization of C^{14} MTBE to CO_2 can occur by P-450 enzyme with the presence of molecular oxygen. However, not all P-450 enzymes can degrade MTBE. Some proposed pathways for MTBE degradation by propane-oxidizing bacteria are shown on figure 5. These bacteria could be sinks for MTBE contaminated soils and groundwater.

Kolhatkar et al. (2000) (13) conducted a literature survey evaluating the natural biodegradation of MTBE in sites with underground storage tanks. Table 2 below shows the biodegradation rates extracted from field studies. In addition, in the same review, many laboratory studies exist but demonstrate higher degradation rates than the field studies.
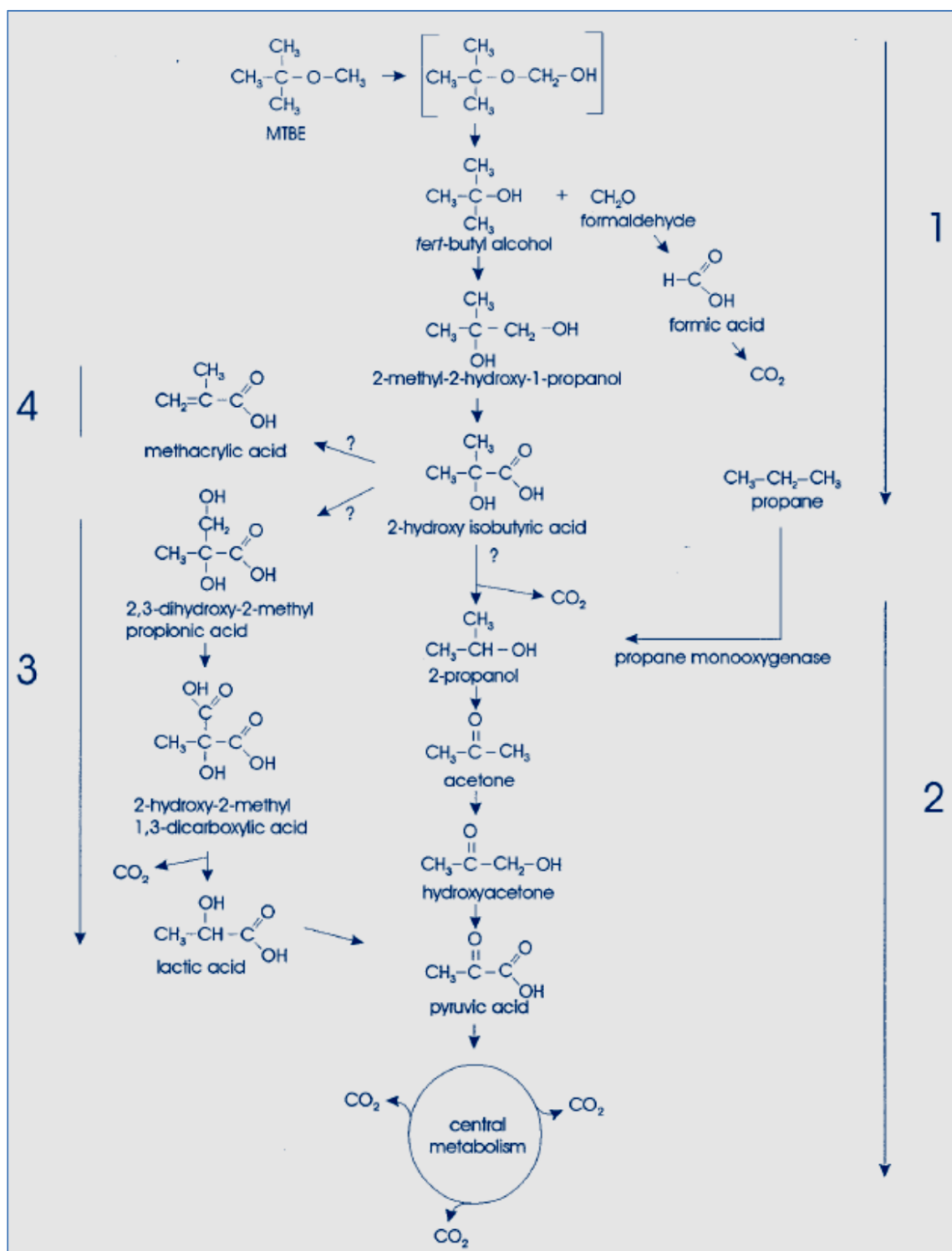
Figure 5 Proposed pathways for the degradation of MTBE by propane-oxidizing bacteria. Steffan et al. 1997

Aquifer Conditions	1st Order Attenuation Rate (1/yr)	Half/Life (days)
Aerobic and Nitrate Reducing	0-0,37	Infinite - 684
Sulfate Reducing	0-0,3	Infinite – 843
Methanogenic	0,3-10,9	843 – 23

Table 2 MTBE Biodegradation rates from field studies. Kolhatkar et al. 2000

References

1. EUR 20417 EN- European Union risk assessment report tert-butyl methyl ether, B.G. Hansen, S.J. Munn, S. Pakalin, C. Mussete, M. Luotamo, J. de Bruijn, F. Berthault, S. Vegro, G. Pellegrini, R. Allanou, S. Scheer, Office for official pupblications of the European Communities, Luxembourg, 19, 2002
2. H.P. H. Arp and T.C. Schmidt, Air-Water of MTBE, its degradation products, and alternative fuel oxygenates: The role of temperature, Environ. Sci. Technol., 38, 5405-5412, 2004
3. C. Achten, A. Kolb, W. Puttmann, Methyl tert-bytyl ether (MTBE) in river and wastewater in Germany, Environ. Sci Techn. 36,3652-3661,2002
4. M. Rosell, S. Lacorte, C. Forner, H-P Rohns, R. Irmscher D. Barcelo, Fate of gasoline oxygenets in conventional and multilevel wells of a contaminated groundwater table in Dusseldorf, Germany, Environ. Toxic. and Chem. , 24,11,2785-2795,2005
5. C.K. Yeh and J.T. Novak, Anaerobic biodegradation of gasoline oxygenates in soils, Water Environ. Research, 66, 744-752, 1994
6. P.J. Squillace, J.F. Pankow, N.E. Korte, J.S. Zogorski, Review of the environmental behaviour and fate of methyl tert-butyl ether, Environ. Toxic. And Chem.,16,1836,1997
7. C.K. Schmidt, F. T. Lange, and H.J. Brauch, Assesing the impact of different redox conditions and residence times on the fate of organic micropollutants during riverbank filtration, DVGW/Technologiezentrum Wasser (TZW), Germany, Unpublished report
8. T. C. Schmidt, Analysis of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) in ground and surface water, Trends Anal. Chem., 22, 776-784, 2003
9. S. Hong, H. Zhang, C.M. Duttweiler, A.T. Lemley, Degradation of methyl tert-butyl ether (MTBE) by anodic fenton treatment, Journ. of Hazrd. Materials, 144, 29-40, 2007
10. P. Somsamak, H.H. Richonow and M.M. Haggblom, Carbon isotope fracionation during anaerobic degradation of methyl tert-butyl ether under sulfate/reducing and methenogenic conditions, Appl. And Environ. Microbiol.,72, 2, 1157-1163, 2005
11. K. Mo, C.O. Lora, A.E. Wanken. M. Javanmardian, X. Yang and C.F. Kulpa, Biodegradation of methyl tert-butyl ether by pure bacterial cultures, Appl. Microbiol. Biotecnol., 47, 69-72, 1997
12. R.J. Steffan, K McClay, S. Vainberg, C.W. Condee and D. Zhang, Biodegradation of the gasoline oxygenates MTBE, ETBE and TAME by propane/oxidizing bacteria, Appl. And Environ. Microbiol, 63, 4216-4222, 1997
13. R. Kolhatkar, J. Wilson, L.E Dunlap, Evaluating natural biodegradation of MTBE at multiple UST sites. Proceedings, Petreleum Hydrogarbons anf organic chemicals in groundwater: prevention, detection and remediation, Anaheim, California, 2000
14. R.K. Juhler and G. Felding, Monitoring methyl tert-butyl Ether (MTBE) and other organic micropollutans in groundwater: results from the Danish National monitoring program, Water, Air and Pollution, 149, 145-161, 2003
15. Tim Douthit, The Environmental Characteristic of MTBE: Fate, Transport, Remediation & Comparison w/Ethanol, In Aqua Veritas, Technical Report, 2003

> ### *Bisphenol – A (BPA)*

Polycarbonate (PC) is a polymeric chain product made by the monomer bisphenol- A (BPA). In 1953, Dr. H. Schnell discovered that commercial product at Bayer Germany. It has worldwide consumption due to its multilateral properties and applications in industry. Some of the most important properties which made this product so widely used are flame retardance, electrical insulation, transparency, thermal stability and lightweight. Industrial applications of this thermoplastic material are phones, compact discs, lenses and food contact products. The total amount of BPA produced during the period 1997-1999 in Europe was 700.000 tons per year. In 2005, the worldwide production exceeded 2.000.000 tons. BPA is produced by the chemical reaction of acetone and phenol catalysed by acid. Table 3 below shows some chemical properties of BPA (1).
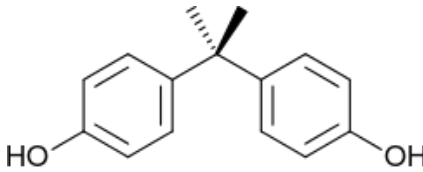
IUPAC name	4,4'-(propane-2,2-diyl)diphenol	
CAS number	80-05-7	
Molecular formula	$C_{15}H_{16}O_2$	
Molar mass	228.29 g mol^{-1}	
Vapour Pressure	7.25 e-007 mmHg (25 °C)	
Solubility in water	120–300 ppm (21.5 °C)	

Table 3 Chemical Properties of BPA

Models that predict the distribution of BPA in the environmental compartments have been developed. Equilibrium Criterion (EQC) is a model which uses chemical properties to investigate the fate of a compound. (2). The vapour pressure of BPA is very small which indicates that only small amount of BPA will be transferred to the air phase. In addition, as K_{ow}=103.4, it is considered to have moderate hydrophobicity. The fugacity capacity of this compound in soil is much larger than the water, as it is described from the fugacity capacity constant of soil Z_s=1.23*107 mol/m^3 Pa and water Z_w=2.48*105 mol/m^3 Pa. This determines that BPA is mostly to soil phase when it enters the environment. Figure 6 demonstrates the distribution of BPA by EQC model when thermodynamic equilibrium has been achieved (Level 1).
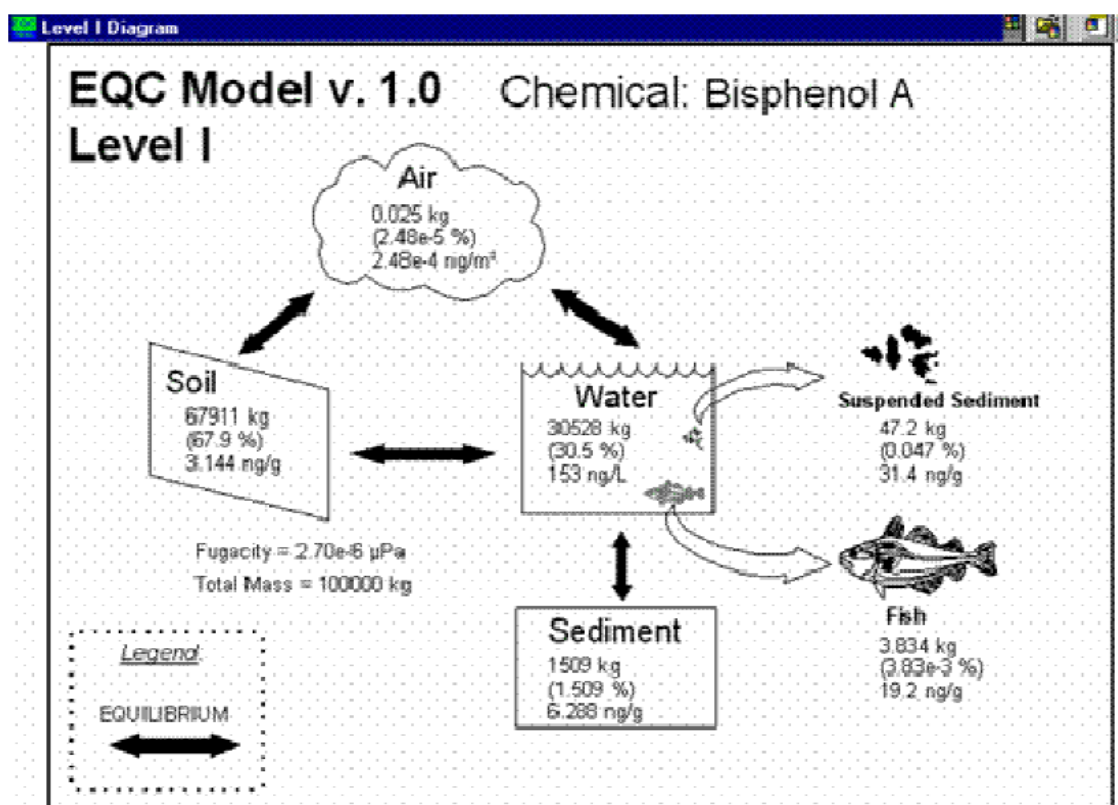

Figure 6 Level I, Equilibrium Criterion (EQC) modiling diagram, Cousins et al. 2002

It is assumed that very low concentrations of BPA are released into the environment during the production, usage and disposal of polycarbonate. Water, high extraction temperatures and use of additives can cause and promote the degradation of polycarbonate. BPA has been found in wastewater at very low concentrations, not shown to have any environmentally adverse effect. BPA concentrations in The Netherlands are reported in the range of 0.004 ug/L - 0.065 ug/L (3). Monitoring programs for BPA in German surface waters and wastewater have reported low concentrations about 0.125 ug/L. In a study of Sajiki and Yonekubo (2003) (4), the leaching of BPA from polycarbonate tubes to water was investigated. They used control water, seawater and river water at two different temperatures (T=20 ˚C, T=37˚C) as a function of time. The leached concentration of BPA to water increases with the passage of time. In addition, the velocity of this procedure is pH-dependent. The entry of BPA (ng/mL) to water samples as a function of time (days) at T=20˚C is demonstrated in figure 7. As it is observed BPA concentration in seawater increases faster than river water, which is due to larger amount of sodium ions in seawater.
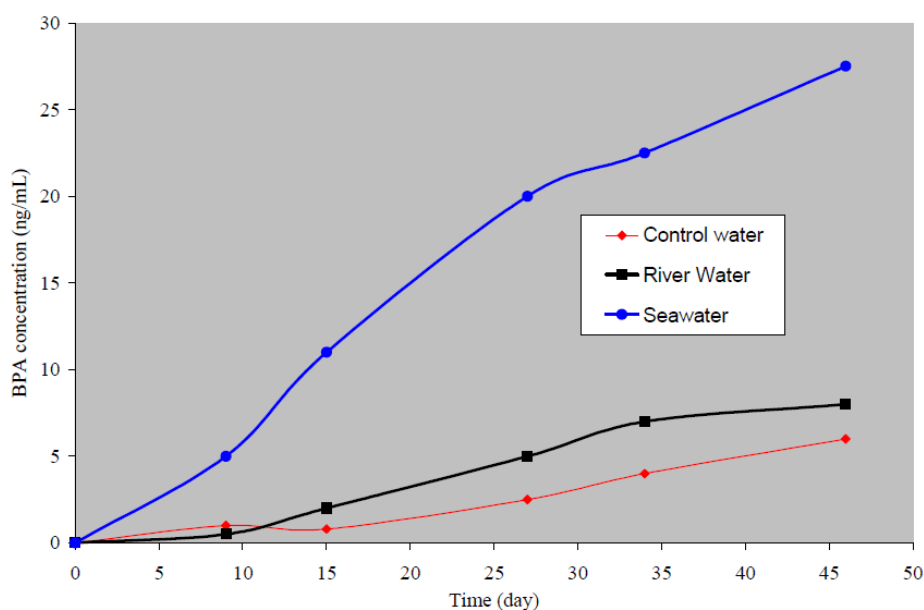

Figure 7 Change of BPA concentration leached from polycarbonate tubes to water samples at 20˚C as a function of time, Saijki and Yonekubo, 2003

The removal rate of BPA from wastewater of chemical manufacturing plants is very high. The mechanism of removal probably is adsorption to sludge or biodegradation. Many studies have already been conducted to test the degradation of BPA under different conditions. According to the manometric respirometry test (OECD 301F), BPA is "readily biodegradable" (5), which is also evident from many other studies which test BPA degradation. It has been shown that microorganisms metabolise BPA to use it as carbon source, these organisms have been isolated and examined in some studies (6,7).

A study from Ike et al, 2006 (8) revealed that the biodegradation of BPA under anaerobic conditions cannot be completed. An additional study from Voordechers et al. 2002, (9) tested the fate of BPA under anaerobic conditions in estuarine sediment samples from the USA. Methanogenesis, sulphate-, iron(III)- or nitrate-reducing conditions were produced in these samples by addition of inorganic anaerobic medium. There was no significant loss of BPA after the end of monitoring period (162 days).

Kang and Kondo (2002), (10), studied the BPA fate in surface water samples from 13 rivers in Japan. The degradation was shown to change according to the temperature and the bacteria present in water. The degradation half-life for BPA was between 4 to seven days at T=20˚C. A study on BPA fate in soil was also conducted by Fent et al. (2003) (11) by detecting the labelled C[14]. BPA was completely removed after three days. These results are in contrast with the half-life value of BPA that EUSES[1] suggests at 30 days with first rate constant of 0.0231d[-1]. It is supposed that the covalent bond of BPA can by catalysed by biological media and degraded into the soil matrix, such as phenolic compounds catalysed by soil microorganisms and enzymes (12).

Lobos et al. (1992) (13), tested the biodegradation of BPA in sludge from wastewater treatment plant using gram-negative aerobic bacteria (strain MV1). The results showed that 60% of BPA carbon was mineralized. The metabolites from the degradation pathway were 2,2-bis(4-hydroxylphenyl)-1-propanol, 4-hydroxyacetophenone and 2,3-bis(4-hydroxyphenyl)-1,2-propanediol with small amounts of 4-hydroxybenzoic acid. Figure 8 demonstrates the degradation pathway of BPA by bacteria under aerobic conditions.
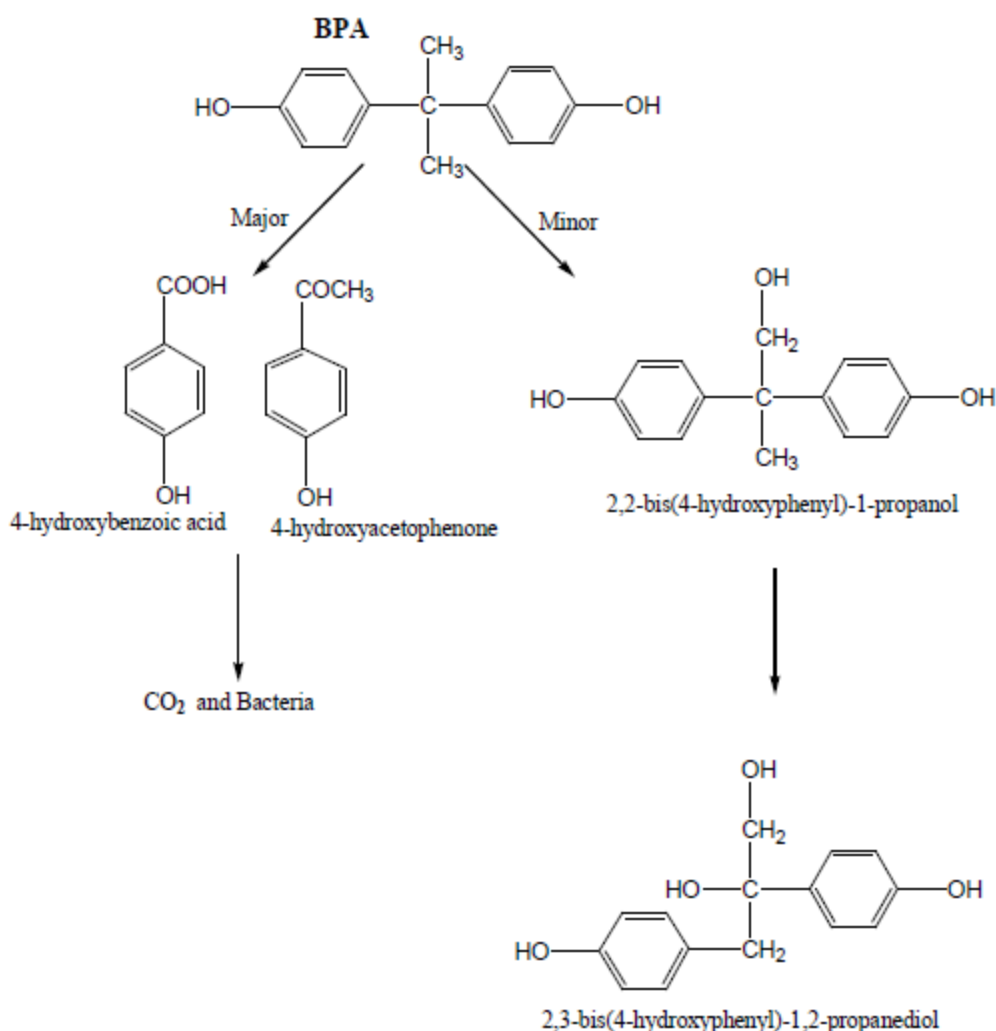

Figure 8 Aerobic degradation of BPA using bacteria, Lobos et al. 1992

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[1] EUSES: European Union System for the evaluation of Substances

References

1. European Chemicals Bureau, European Union risk assessment report, 4,4'-isopropylidenediphenol (bisphenol-A), 1-302

2. I.T. Cousins, C.A. Staples, G.M. Klecka, D. Mackay, A multimedia assessment of the environmental fate of bisphenol A, Human Refer. Popul, Environ Health Perpectives, 113, 4, 391-395, 2005

3. A.C. Belfroid, P. DeVoogt, A.D. Vethaak, Van der Zande, A.J. Schafer, W.P. Cofino, Occurrence of estrogenic compounds in the environmental matrices, Society of Environ. Toxic. And Chem. Europe 8th Annual Metting Abstract book, 246, 1998

4. J. Saiki, J. Yonekubo, Leaching of bisphenol A (BPA) to seawater from polycarbonate plastic and its degradation by reactive oxygen species, Chemosphere, 51, 55-62, 2003

5. R.J. West, P.A. Goodwin, G.M. Klecka, Assessment of the ready biodegradability of BPA, Bulletin Environ. Toxic. and Chem., 61, 106-112, 2001

6. J. Spivak, T.K. Leib, J.H. Lobos, Novel pathway for bacterial metabolism of BPA, Journal of Biol. Chem., 269, 7323-7329, 1994

7. M. Ike, C.S. Jin, M. Fujita, Biodegradation of BPA in the aquatic environment, Water Sci. and Techn., 42, 7-8, 31-38, 2000

8. M. Ike, M.Y. Chen, E. Danzil, K. Sei, M. Fujita, Biodegradation of a variety of bisphenols under aerobic and anaerobic conditions, Water Sci and Techn., 53, 6, 153-159, 2006

9. J.W. Voordeckers, D.E. Fennell, K. Jones, M.M. Haggblom, Anaerobic biotransformation of tetrabromobisphenol A, tetrachlorobisphenol A, and bisphenol A in estuarine sediments, Environ. Sci and Techn., 36, 4, 696-701, 2002

10. J.H. Kang, F. Kondo, Effects of bacterial counts and temperature on the biodegradation of bisphenol A in river water, Chemosphere, 49, 493-498, 2002

11. G. Fent, W.J. Hein, M.J. Moendel, R. Kubiak, Fate of BPA in soil, Chemosphere, 51, 735-746, 2003

12. J. Dragun, The soil chemistry of hazardous materials, Hazardous Materials Research Insitute, Silver Spring, MD, USA, 1-458, 1988

13. J.H. Lobos, T.K. Leib, T.M. Su, Biodegradation of PBA and other bisphenols by a gram-negative aerobic bacterium, Appl. Environ. Microb., 58, 1823-1831, 1992

> *Metformin*

Diabetes is one of the most common diseases affecting the metabolism of glucose and having more than 200 million patients worldwide. Many pharmaceuticals to treat diabetes have been developed but the most common is called Glucophage in the market and is specialized for type 2 diabetes. The real name is Metformin, it is an oral administrative drug and can be used to treat all stages of diabetes disease. In the 1950s it was introduced in the European pharmaceutical market. The median dose is 2 g/day (WHO,2012) (1) and considered to be one of the most prescribed drugs. In United Kingdom, Metformin was prescribed at a total mass of 205 tons in 2000 as it is described by Sebastine and Wakeman, (2003) (2). Metformin is not considered as a toxic compound to humans even at high doses. Chemical properties of metformin are shown on table 4.

IUPAC name	*N,N*-Dimethylimidodicarbonimidic diamide	
CAS number	657-24-9	
Molecular formula	$C_4H_{11}N_5$	
Molar mass	$129.16 \text{ g mol}^{-1}$	
Vapour Pressure	$1.3\pm0.3 \text{ mmHg}$ (25°C)	
Solubility in water	Freely soluble as HCl salt	

Table 4 Chemical Properties of Metformin

Metformin is not metabolized in humans, so it is excreted via urine in its initial form. Due to the huge consumption of this drug it ends in the sludge treatment plants in great amounts. Its extent usage may result in entrance of this compound to the environment. The environmental fate of metformin is still under investigation. The vapor pressure determines that can be in the air phase at the ambient environmental conditions, but cannot volatilize from dry soil. Henry's constant, $k_H=7.6 \times 10{-16}$ atm*L/mol), indicates that the volatilization from the soil and water surface is not favourable. In addition, the distribution coefficient of metformin, $K_{oc}=110$, indicates that when it is released in the soil compartment it may have high mobility, as it is not expected to be absorbed to soil compartment. Merbel et. al (3) experimentally found the pk_a of metformin to be 11.5, indicating that metformin is a positively charged ion at pH range 5-9.

Many pharmaceuticals used the last 60 years have been found in drinking water and surface water. Figure 9 demonstrates the possible environmental route of metformin.
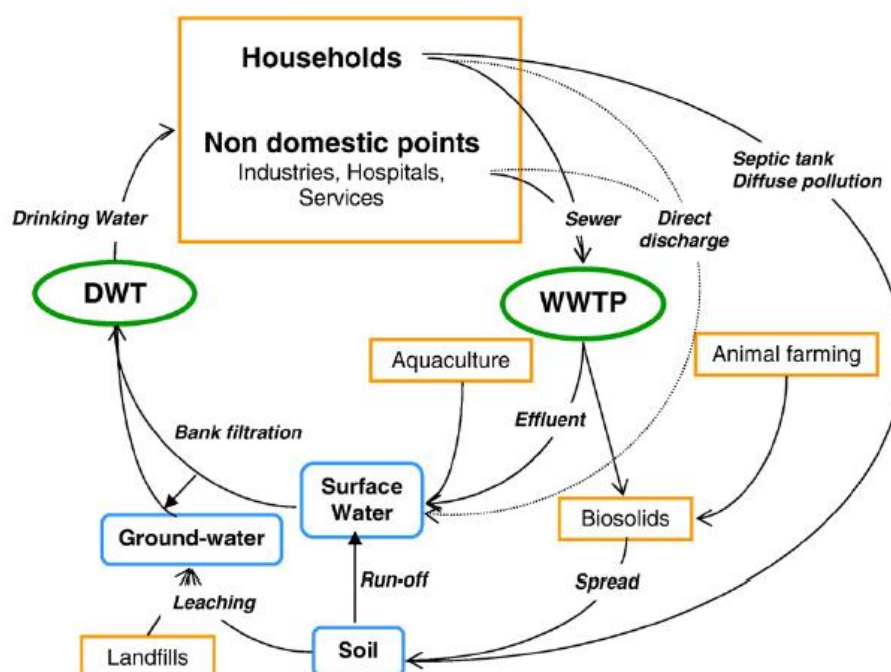

Figure 9 The possible routes of a pharmaceutical compount in the environment, Petrovic et al (11)

Scheurer et al. (2009) (4), have reported that metformin was detected in surface waters in Germany at 100 ng/L and 1700 ng/L in Rhine and Elbe river, respectively. They also tested pK_a of metformin and estimated the values of 10.3 and 12.3, indicating that metformin is a double charged cat-ion. Another recent study showed that metformin was present in all sewage treatment plants in Belgium at a concentration range of 20 ug/L to 94 ug/L (5). Metformin is highly polar which can easily reach to drinking water, as the conventional treatment techniques are not capable to remove it efficiently. The Federal Environmental Agency of Germany (6) has evaluated the substances in drinking water and has reported acceptable values of genotoxic or non-genotoxic substances based on that. The allowed concentration for non-genotoxic is 3 ug/L.

Many studies have been conducted the last years to investigate the fate of metformin in the environment. One very important study was the one from Trauwein and Kummerer (2011) (7) where the aerobic degradation of metformin was investigated using three different tests. These tests tried to represent real environmental conditions and were: the Closed Bottle test (OECD 301D) which simulates the conditions of surface water, the Menometric Respiratory test (OEDC 301F) which uses bacteria and the third was the Zahn-Wellens test (OEDC 302B) (8) which uses samples with activated sludge. The results from this study showed that metformin is not a readily biodegradable substance. In the last test, metformin was partially biodegraded. As it was observed by HPLC analysis, metformin since the ninth day was completely eliminated, till the end of the experiment (30 days), but not mineralized as a new peak was found, which was identified as Guanylurea. This result is shown in figure 10 below.
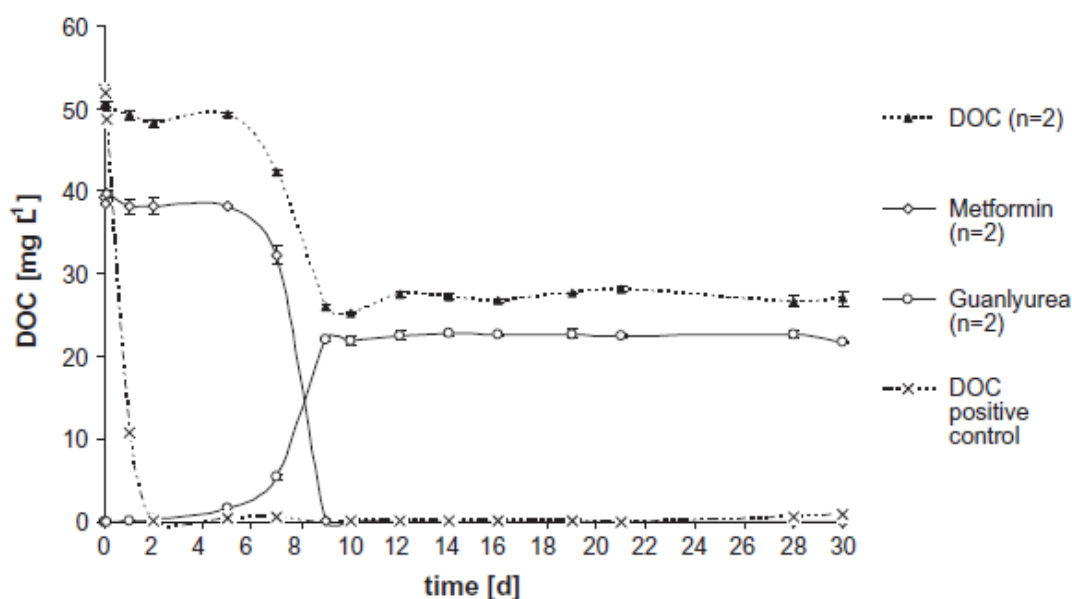

Figure 10 Aerobic degradation of metformin and formation of Guanylurea, using Zahn-Wellens test, Trautwein and Kummerer, 2011

Guanylurea is not formed as a metabolite by humans, but only by aerobic transformation in activated sludge. That is a very interesting investigation, while this metabolite can be present for years in the water environments without any knowledge. In the same study the degradation of Guanylurea was tested, with negative photodegradation and biodegradation results. That should be investigated more, while this compound cannot be degraded in water treatment plants where treatment by UV irradiation is used and it is also highly polar so can escape easily from water disinfection techniques. In addition, a further study of degradation of the parent compound metformin and its metabolite Guanylurea showed that they are not completely eliminated by ozonation (9). By using Zahn-Wellens test, they determined that metformin was fully eliminating after 2 to 4 weeks.

In a study by Scheurer et al. (2012) (10) the fate of metformin and its metabolite guanylurea under different treatment techniques of raw waters was tested based on laboratory batch experiments. The elimination of these compounds using flocculation and activated carbon filtration was not efficient. However, the most effective technique appeared to be chlorination, which is not a permissible disinfection technique in Germany. Ozonation also was tested with good removing results. In addition, the effectiveness of river bank filtration and artificial ground water recharge was studied in a monitoring program of three waterworks and proved to be the best removal technique. An additional test for sorption of these compounds to soil matrix was conducted by using three different soils but the results showed a neglected sorption. The river bank filtration tests demonstrated a lag-phase for metformin's degradation close to 35 days, but in wastewater treatment plants higher removal rates have been reported. Even guanylurea does not showed to be degraded during the test period of 60 days, it is considered that should have be degraded in the duration of a river bank filtration which lasts few weeks to several months. Figure 11 depicts the degradation of metformin during river bank filtration's simulation. In case of direct deduction of surface raw water, without any underground passage, there is the possibility these compounds to be present. Because of the limiting on soil, it is assumed that the degradation could be though biological media.
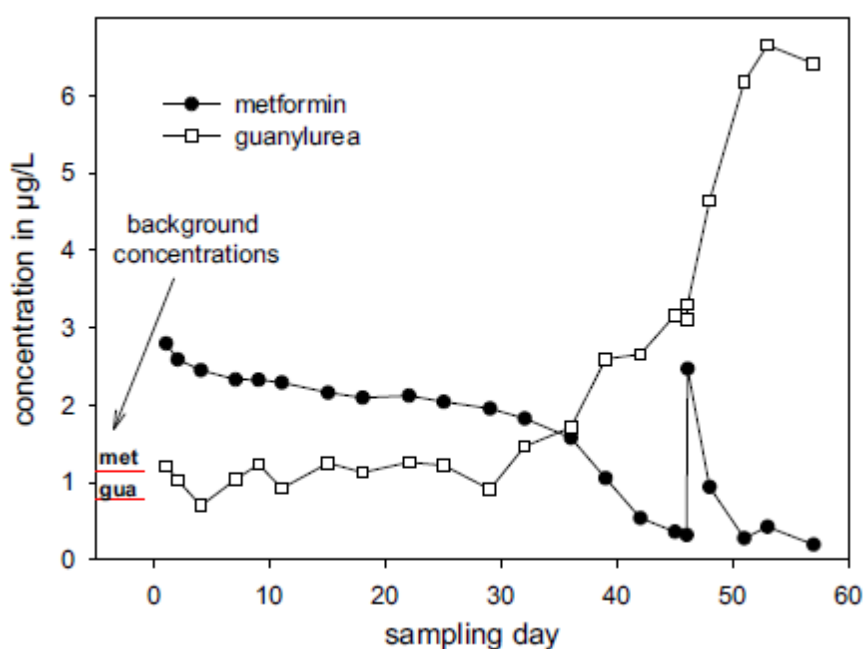

Figure 11 Degradation of metformin in a river bank filtration test, Scheurer et al. 2012

References

1. WHO, 2012, http://www.whocc.no/atc_ddd_index/?code=A10BA02
2. I. Sebastine, R. Wakeman, Consumption and environmental hazards of pharmaceutical substances in the UK, Process Saf. Environ., 81, 4, 229/235, 2003
3. N.C. Merbel, G. Wilkens, S. Fowles, B, Oosterhuis, J.H.G. Jonkman, LC phases improve, but not all assays do: Metformin bioanalysis revisited, Chromatographia, 47, 9-10, 542-546, 1998
4. M. Scheurer, F. Sacher, H. Brauch, Occurrence of the antidiabetic drug metformin in sewage and surface waters in Germany, Journal of Environ. Monitor., 11, 9, 1608, 2009
5. A.L.N. Nuijs, I. Tarcomnicu, W. Simons, L. Bervoets, R. Blust, P.G. Jorens, H. Neels, A. Covaci, Optimization and validation of hydrophilic interaction liquid chromatography-tandem mass spectrometry method for the determination of 13 top/prescribed pharmaceuticals in influent wastewater, Anal. Bioanal. Chem., 398, 5, 2211-2222, 2010
6. German Federal Environmental Agency, Evaluation from the oint of view of health of the presence in drinking water of substances that are not (yet) possible or only partially possible to evaluate, 2003
7. C. Trautwein, K. Kummerer, Incomplete aerobic degradation of the antidiabetic drug Metformin and identification of the bacterial dead/end transformation product Guanulyrea, Chemosphere, 85, 765-773, 2011
8. OECD 302B, Zahn-Wellens/EMPA test. OECD Guideline for testing of chemicals, 21 July 1992
9. S. Gartiser, C. Hafner, K. Kronenberger-Schafer, O. Happel, C. Trautwein, K. Kummerer, Approach for detecting mutagenicity of biodegraded and ozonated pharmaceuticals, metabolites, and transformation products from a drinking water perpective, Environ. Sci. Pollut. Res., 19, 3597-3609, 2012
10. M. Scheurer, A. Michel, H/J. Brauch, W. Ruck, F. Sacher, Occurrence and fate of the antidiabetic drug metformin and its metabolite guanylurea in the environment and during drinking water treatment, Water Research, 46, 4790-4802, 2012
11. M. Petrović, S. Gonzalez, D. Barceló, Analysis and removal of emerging contaminants in wastewater and drinking water, Trends Anal Chem., 22,10,685–696, 2003

> *Metolachlor*

Metolachlor belongs to the acetanilide herbicides, and it is a racemic mixture (1:1) of two stereoisomers. The R-isomer has no active herbicidal activity but S-isomer is widely used for weed control in corn, soybean and cotton production. It was developed by Ciba-Geigy, a Swiss chemical company and was released in the market in 1977. It is one of the most used herbicides in Europe and the United States and can be detected in surface water and groundwater. Its estimated average usage in US is 25 million kilos per year (1). Table 5 summarizes some chemical properties of metolachlor.
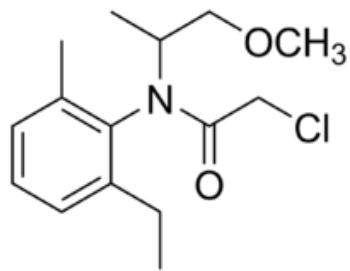
IUPAC name	(RS)-2-Chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-2-yl) acetamide	
CAS number	51218-45-2	
Molecular formula	$C_{15}H_{22}ClNO_2$	
Molar mass	283.79 g mol^{-1}	
Vapour Pressure	1.3 x 10^{-5} mmHg (20˚C)	
Solubility in water	530 ppm (20 °C)	

Table 5 Chemical properties of metolachlor

The environmental fate of this compound depends on many factors, such as the location and the hydrogeological properties of the site where the application was, the application rate, the rainfall degree and the mobility of the compound in the water and soil. Metolachlor is a very persistent herbicide (2) and due to its high solubility in the water and low $logK_{oc}=200$ ml/g, it can reach groundwater and be a potential risk for human health. In addition, the vapour pressure and the Henry's constant (2.44 x 10^{-8} atm*L/mol) values are relative low, so they determine that no significant amount of metolachlor can be in air phase (1). Metolachlor has been found in the range of 0.08 – 4.5 ug/L in Wiscosin and Pensylvania (3). It has been found that metolachlor has two major degradation products, ethane sulfonic acid (ESA) and oxalic acid (OA). These two compounds can be found in higher concentration in surface waters and groundwater and are more persistent than their parent compound metolachlor, as Huntscha et al (2008) (4) described. In a study of De Guzman et al. (2005))(5), ESA and OA was detected at 106 and 63 tested sites respectively. Figure 12 demonstrates the environmental fate of herbicides after their application.
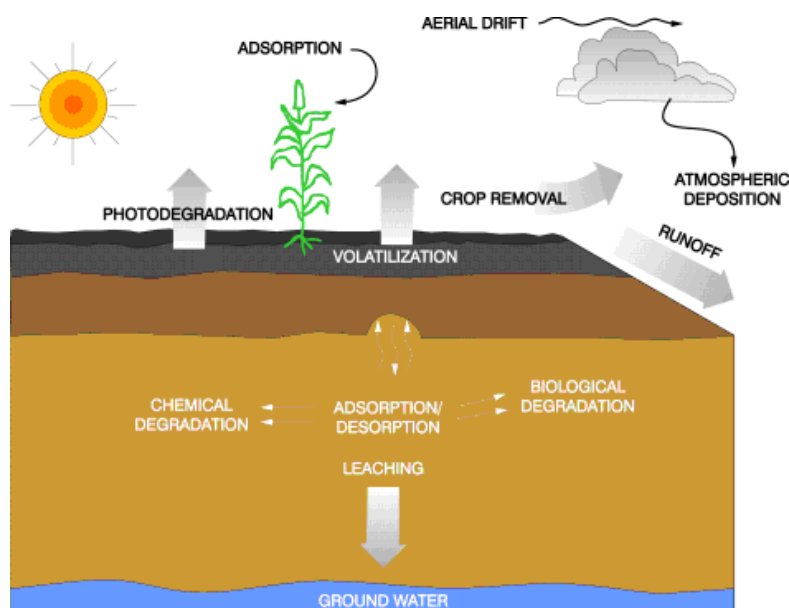

Figure 12 Environmental fate of herbicides, adapted from Alberta.ca

A geological survey was conducted in the United States to evaluate the environmental fate of pesticides using the National Water-Quality Assessment (NAWQA) program (6). Based on this survey Dalton and Frick (7) studied the fate and transport of pesticides in the upper Floridan aquifer (UFA). Metolachlor was the most frequently found pesticide in this aquifer. As it was discovered, biodegradation rates of metolachlor in a shallow unsaturated aquifer were higher than in the saturated aquifer. Data from the age of the pesticides in groundwater estimated presence of these compounds more than 30 years before sampling (8). A possible explanation is that while the compound moves downwards from oxic conditions in the unsaturated zone to more anoxic conditions in the saturated zone the biodegradation rate slowly decreases and later stops leaving the pesticides to remain in the soil or water in the aquifer.

In a later study, the dissipation of metolachlor with time and depth was tested (2). They found that the dissipation rate constant of metolachlor followed first-order kinetics. Dissipation took place at all soil depths and the rates were higher in the top soils than at lower depths. Figure 13 demonstrates the dissipation of metolachlor with time and depth. Metolachlor could be classified as moderately persistent at depths 0-2m and highly persistent to 2-5m, under the classification of Comfort et al. (9). It was assumed that the lower dissipation in subsoil affected from the lower number of microorganisms. Regression showed that degradation of metolachlor depends on total carbon and biomass content. That results from the fact that in rich organic content soils the number of heterotrophic microorganism is greater.
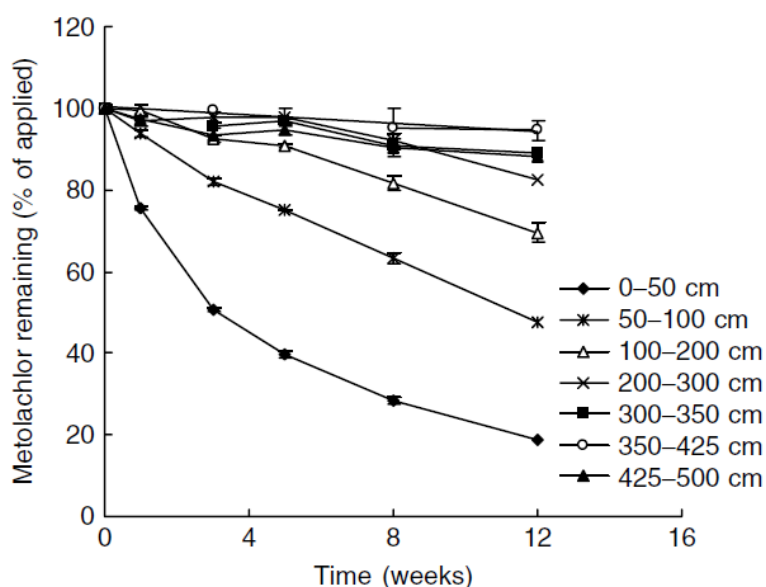

Figure 13 Metolachlor dissipation over time and depth, Y Si et al., 2009

A study from Huntscha et al. (2008) (4) referred to an Arrhenius type of degradation equation of metolachlor and its degradation product ESA from surface water in Lake Greifensee, Switzerland. This equation derived from indirect photolysis and another loss process, eventually biodegradation, with half-lives, during summertime, 160-300 days and 60-150 days respectively. Konopka and Turco (10,12), investigated that metolachlor (0.6-9 ppm) was not degraded in vadoze zone samples in laboratory experiments. In another study of Konopka (11), they found that metolachlor could be degraded under anaerobic conditions with inorganic sulphide. The results showed higher than 85% of the initial concentration of metolachlor to be degraded in sewage sludge samples in incubation period of 30 days.

References

1. L. Rivard, Environmental fate of metolachlor, Sacramento April, 2003
2. Y. Si, K. Takagi, A. Iwasaki, D. Zhou, Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils, Pest Manag. Sci. , 65, 956-962, 2009
3. G. Chesters, G.V. Simsiman, J. Levy, B.J. Alhajjar, R.N. Fathulla, J.M. Harkin, Environmental fate of alaclor and metolachlor, Rev. Environ. Contam. Toxic., 110, 1/74, 1989
4. S. Huntscha, H. Singer, S. Canonica, R.P. Schwarzenbach, K. Fenner, Input Dynamics nad fate in surface water of the herbicide metolachlor and of ist highly mobile transformation product metolachlor ESA, Environ. Sci. Techn. 42, 5507-5513, 2008
5. N.P. De Guzman, P. Hendley, D. I. Gustrafon, I. van Wesenbeeck, A. J. Klein, J.D.Fuhrman, The acetochlor registration partnership state ground water monitoring program, J. Environ. Qual., 34, 793-803, 2005
6. R.J. Gilliom, J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, D.M. Wolock, The quality of our nations´ waters-Pesticides in the Nation´s streams and groundwater, 1992-2001, U.S. Geological Survey Circ, 1291, 172 p. USGS, Washington, DC, 2006
7. E.A. Frick, M.S. Dalton, Alachlor and two degradates of alachlor in groundwater and surface water, southwest Georgia and adjacent parts of Alabama and Florida, 1993-2005. In T.C. Rasmussen et al. Proceedings of the 2007 Georgia Water Resources Conf., Athens, Ga., Universtiy of Georgia, 27-29, 2007
8. F. Spurlock, K. Burrow, N. Dubrovsky, Chlorofluorocarbon dating of herbicide-containing well waters in Frasno and Tulare Countries, California, J.Environ. Qual., 29, 474-483, 2000
9. S.D. Comfort, P.J. Shea, F.W. Roeth, Understanding pesticides and water quality in Nebraska, Nebraska Cooperative Extension Publication, EC 94-135,16, 1994
10. A. Konopka, R. Turco, Biodegradation of organic compounds in vadose zone and aquifer sediments, Appl. Envir. Microb., 57, 2260, 1991
11. A. Konopka, Anaerobic degradation of chloroacetanilide herbicides, Appl. Micorbiol. Biotechnol., 42, 440, 1994
12. D.M. Stamper, O.H: Tuovinen, Biodegradation of the acetanilide herbicides alachlor, metolachlor,and propachlor, Critical Reviews in Microbiol., 24, 1-22,

> ➤ *Mecoprop (MPCC)*

Mecoprop (MPCC) is a phenoxyalkanoic acid herbicide with a wide usage in agriculture. It was introduced into the market in 1964 and since then has been used in agriculture and households' gardens to control the growth of weeds in autumn and spring. It is a chiral compound with equal proportion of isomers and only the (R)-enantiomer is an active herbicide. In 1980, the production of the active isomer was succeeded and sold as mecoprop-p. It is estimated according to EPA[2] that 0.5 – 2.5 million kilos of mecoprop are being used in the United States each year. In a study of Poiger et al. (2003) (1), mecoprop racemic mixture or even a slight enrichment with the second isomer was found in water samples from Greifensee lake, in Switzerland. The amounts of mecoprop were correlated with the effluents of wastewater treatment plants. Later, it appeared that the second isomer ((S)-enantiomer) was used on sealing and roofs to prevent plant roots penetration. Figure 14 depicts the structure of mecoprop enantiomers. Chemical properties of mecoprop are shown in Table 6.
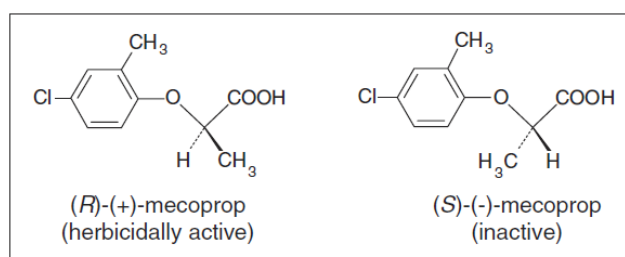

Figure 14 Stucture and configuration of MCPP enantiomers, Poiger et al. 2003

IUPAC name	(*RS*)-2-(4-Chloro-2-methylphenoxy) propanoic acid	
CAS number	93-65-2	
Molecular formula	$C_{10}H_{11}ClO_3$	
Molar mass	214.65 g mol^{-1}	
Vapour Pressure	1.2 x 10^{-6} mmHg (25˚C)	
Solubility in water	900 mg/L (20 °C)	

Table 6 Chemical properties of mecoprop (MPCC)

Due to the usage in agriculture mecoprop can easily be transferred into the surface waters, groundwater and aquatic environment. It has been reported that mecoprop concentrations in groundwater, used for drinking water, exceeds the EU guideline value of 0.1 ug/L (2). The carbon-water partition coefficient has been found to be K_{oc}=20-43 in 4 different soils by European Commission (EC) (3) and thus, mecoprop has a high mobility in soil. It is a weak acid and is expected to adsorb greater into the soil matrix at low pH values. Its vapour pressure determines that the evaporation into the air phase is not favourable at ambient conditions. In order to investigate the degradation of mecoprop, many studies have been conducted so far. Janniche et al. (2010) (4), studied the natural mineralization of mecoprop at environmentally low concentrations (<10 ug/L) in a deep unsaturated limestone and sandy aquifer. The results after 8 months of incubation showed 19-44% mineralization for mecoprop in soil. It was found that mineralization decreases with depth and a half-life for mecoprop in unsaturated limestone and in the deep limestone was estimated at 1-2 years and more than 9.5 years, respectively. This process is considered to be biological under aerobic conditions. Mecoprop did not show mineralization under anaerobic conditions after 231 days of incubation. These results are similar with other studies in shallow anaerobic sandy aquifers (5,6).

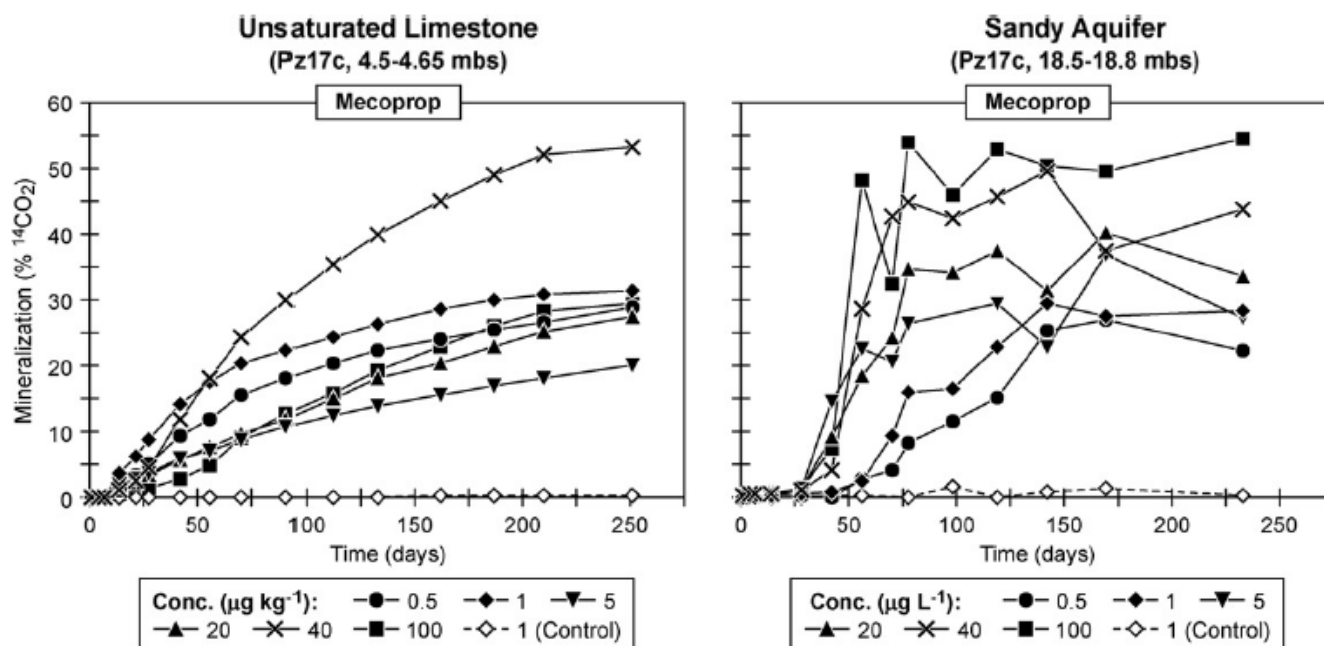
[2] EPA: Environmental Protection Agency

Figure 15 Mineralization kinetics at different initial concentrations, Janniche et al. 2010

Figure 15 demonstrates that with increasing initial concentration the mineralization of mecoprop increases too, so it was important to conduct the study with environmental low concentrations to have representative results for degradation rates. The results from another study did not show degradation of mecoporop in chalk and low limestone.

A study from Rodriguez et al. (2006) (7), demonstrates that 50% degradation of mecoprop can occur in the upper layer of soil by microorganisms and also the rate of this process increases with the multiplication of the degraders. However, the results showed that degradation decreases with soil depth. Considering the low sorption of mecoprop in soil the cause for the low degradability in the deep soil depends on the presence and number of the degraders. Another study of Rodriguez et al. (2010) (8), investigates the degradation of mecoprop-p according to the depth and the contribution of tfdA genes in degradation. They observed increment in number of tfdA genes in soils which was correlated with the degradation of mecoprop-p.

Sojic et al.(2010) (9) tested mecoprop herbicide by photocatalytic degradation. In the presense of Fe and N-doped TiO_2 under visible light irradation the results were positive for decomposition of mecoprop. Abramovic et al. (2009) (10) examined the photocatalytic activity of Nitrogen-doped TiO_2 to the degradation of mecoprop using various light sources. The outcome showed much slower degradation under sunlight than under artificial radiation. These studies are interesting to evaluete and estimate the degradation of this compound during disinfection of water.

References

1. T.Poiger, H-R Buser, M.D. Muller, M.E. Balmer, I.J. Buerge, Occurrence and fate of organic micropollutans in the environment± regional mass balances and sources apportioning in surface waters based on laboratory incubation studies in soil and water, monitoring, and computer modelling, Chimia, 57, 492-498, 2003
2. European Environmental Agency, Groundwater quality and quality in Europe, 1999
3. European Commission (EC), Health and consumer protection directorate-general, mecoprop, 2003
4. G.S. Janniche, E. Lindberg, C. Mouvet, H.-J. Albrechtsen, Mineralization of isoproturo, mecoprop and acetochlor in deep unsaturated limestone and sandy aquifer, Chemosphere, 81, 823-831, 2010
5. K. Rugge, P.L. Bjerg, H. Mosbaek, T.H. Christensen, Fate of MCPP and atrazine in an anaerobic landfill leacheate plume, Water Res., 33, 2455-2458, 1999
6. L. Larsen, J. Aamand, Degradation of herbicides in two sandy aquifers under different redox conditions, Chemosphere, 44, 231-236, 2001
7. M.S. Rodriguez-Cruz, J.E. Jones, G. D Bending, Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics, Soil Biol. And Biochem., 38, 2910-2918, 2006
8. M.S. Rodriguez-Cruz, J. Baelum, L.J. Shaw, S.R. Sorensen, S. Shi, T. Aspray, C.S. Jacobsen, G. D. Bending, Biodegradation of the herbicide mecoprop-p with soil depth and its relationship with class III tfdA genes, Soil Biol. And Biochem., 42, 32-39, 2010
9. D.V. Sojic, V.N. Despotovic, N.D. Abazovic, M.I.Comor, B.F. Abramovic. Photocatalytic degradation of selected herbicides in aqueous suspensions of doped titania under visible light irridation, Journal of Hazardous Material, 179, 49-56, 2010
10. B.F. Abramovic, D.V. Sojic, V.B Anderluh, N.D. Abazovic, M.I. Comor, Nitrogen-doped TiO_2 suspensions in photocatalytic degradation of mecoprop and (4-chloro-2-methylphenoxy)acetic acid herbicides using various light sources, Desalination, 244, 293-302, 2009

Conclusion

To make a conclusion, for all the results that were shown and described in this review study for the five compounds, a summary of the environmental fate and degradation of these chemicals is shown below:

- MTBE: is a gasoline oxygenate with high water solubility and low biodegradability. It is persistent in the environment and the best way to recover polluted sites with MTBE is the natural attenuation. Some filed studies indicate that the degradation of MTBE can be done under methanogenic conditions with half-life 23-843 days.
- Bisphenol-A: BPA release into the environment is mostly to the soil phase. It has been classified as a "readily biodegradable" compound. It is also completely removed during wastewater treatment. However, it is not degradable under anaerobic conditions.
- Metformin: is completely transformed into its metabolite, Guanylurea, when it is released in the environment with an average half-life 15 days. It is important to investigate the transport and environmental fate of this metabolite because it could affect the safety of drinking water.
- Metolachlor: is a persistent herbicide which could biodegrade at low rates in shallow aquifers and even slower at deeper aquifers. There is evidence that more than 85% of added metolachlor can be degraded under anaerobic conditions through the action of sulphide.
- Mecoprop: a second herbicide, which is also persistent in water and soil aquifers. It also has low degradation rates in shallow aquifers, decreasing with depth. The estimated half-life in unsaturated limestone is 1-2 years and in saturated deep limestone more than 9.5 years. Mecoporop did not show mineralization under anaerobic conditions in a test period of 231 days.

As it is obvious, the environmental fate of each compound and the biodegradation rates depends on the chemical structure of each compound and its chemical properties. In addition, the soil properties and redox conditions influence the microbial population and activity, so the biodegradation rates of the organic compound. It is important to study the transport and distribution of a chemical into the environment to assess the quality of the water and to prevent water contamination by chemicals.

Acknowledgments