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Calculating analysis of seasonal changes and degradation reactions of pesticides in surface waters feeding Süleymanpasa district, Tekirdag

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In this study, the possible reaction paths of 2,3,4,5,6-pentachlorotoluene, benzylbenzoate and demeton molecules with OH radicals were determined. Optimized geometries were drawn with Gauss View 5. Later, with the Gaussian 09 program, geometric optimization was made and the lowest energy states were found. Geometric structure analysis was done and bond lengths and bond angles were calculated. The purpose of this study is to determine the most likely way of interaction of 2,3,4,5,6-pentachlorotoluene, benzylbenzoate and demeton molecules with OH in gas phase and in aqueous medium. The effect of solvent water was studied, COSMO was used as the dissolution model which had a stabilizing effect in reducing the energy in the reactions. The molecule with the lowest energy has the most stable structure. Apart from these studies, the seasonal changes of the 3 pesticides mentioned in the water samples taken in 4 different seasons from the Naip Dam, which feeds the central neighborhoods of Süleymanpaşa district of Tekirdağ Province, were examined. These results will guide experimental studies and determine the fragmentation mechanism.

Keywords: Pesticides, quantum mechanical methods, Gaussian 09

INTRODUCTION

Water is the basic building block for all living things in nature. The fact that three-quarters of the world is covered with water and that 75% of living things are made up of water clearly reveals the importance of water for life. While water consumption and need are constantly increasing, the importance of efficient use of water resources has become more evident due to the pollution of resources by external factors and droughts due to global warming. It has been reported that water consumption worldwide has doubled in recent years [1].

With the increase in population in recent years, the amount of need for nutrients has increased. Since the yield of food products has decreased due to reasons such as weeds and pests, there has been a need to take serious measures in the fight against this issue. Researches show that the loss of productivity in this way is equivalent to the 1-year food requirement of 150 million people [2]. For this reason, various methods are used to increase the durability of foodstuffs and productivity in agriculture, and chemical control in this regard is carried out with pesticides.

Especially in populated areas, water resources are polluted due to factors such as agricultural activities and industrialization [3]. Pesticides used in the fight against pests in agricultural areas are mixed with surface waters by wind, rain and drift. From past to present, premature deaths have occurred due to water pollution [4]. Pesticides, which are quite resistant to degradation by natural means, accumulate in nature and cause soil and water pollution. In this case, with the pollution of water resources, it causes a decrease in the number of water resources that can be used and negatively affects aquatic organisms [5, 6]. When used as a chemical weapon, it is very effective on the target creature. However, due to its accumulation, effects are also seen on non-target organisms [7, 8].

In recent years, pesticide accumulations in the USA and European Union countries have been closely monitored in agricultural activities and food products, and accumulation over a certain limit is not accepted. The self-cleaning period of the surface water source, whose authenticity is deteriorated by such deposits, is long enough to adversely affect living things.

In this study, computational analysis was used to assess seasonal changes of 3 pesticides determined as possible pollutants in surface waters. The priority environmental pesticides investigated were: 2,3,4,5,6-pentachlorotoluene, benzylbenzoate, benzo(a)fluorene. Possible reaction pathways of these pesticides with OH radicals were determined.

METHODOLOGY

The mathematical expression of energy derived from dihedral angles (atomic positions) of molecular atoms, cartesian coordinates, bond lengths and angles, atomic types and and interatomic bond arrangements depending on atomic radii and positions is called molecular modeling.

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All computational manipulations used to mimic or model the behavior of molecules fall within molecular modeling. Many computer programs are available for these models. As a result of solving the Schrödinger equation with different methods, different programs have emerged. Especially in the field of chemistry and in the pharmaceutical sector, computer software is widely used in areas such as new drug development.

In this study, the Gaussian 09W package program, which is a product of the Gaussian series of Gauss 09 programs, was used. Gaussian 09W is a very comprehensive program that includes semi-experimental molecular mechanics and *ab initio* methods. With the Gaussian 09W program, the energies of atoms and molecules can be calculated, geometric optimizations can be made and energy-dependent force constants, vibration frequencies and dipole moments can be calculated. The conformation analysis of the molecules of 2,3,4,5,6-pentachlorotoluene, benzylbenzoate and demeton, which should be monitored in the surface waters examined in this study, was performed with the previously explained molecular mechanical modeling method and the most durable conformer was determined. Gaussian 09W package program was used for molecular modeling and molecular mechanics calculations. Molecular orbital calculations of the most stable conformer found as a result of the molecular mechanics method were made by DFT/B3YLP/6-31G* methods. Gaussian 09W package program was used in all molecular orbital calculations.

RESULTS AND DISCUSSION

2,3,4,5,6-Pentachlorotoluene

The lowest energy and most durable structure of 2,3,4,5,6 pentachlorotoluene molecule is shown in Figure 1 according to the conformer analysis performed by the molecular mechanical method. Possible reaction pathways of 2,3,4,5,6 pentachlorotoluene were identified as C-Cl bond breaking and benzene ring breaking. The reaction sites were determined according to the Mulliken charge distribution of the molecule.

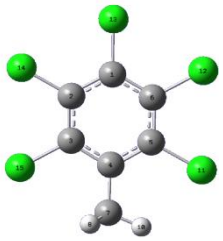


Figure 1. Optimized geometric structure of 2,3,4,5,6 pentachlorotoluene *via* DFT method. (grey: C; white: H; green: Cl).

As a result of DFT calculations, 2,3,4,5,6 pentachlorotoluene's total energy in the gas phase is -1612336.958 kcal/mol, enthalpy -1612336.365 kcal/mol, gibbs free energy -1612369.534 kcal/mol. In addition, the total energy in the water phase, enthalpy and Gibbs free energy, respectively: -1612338.889 kcal/mol, -1612338.296 kcal/mol, -1612371.556kcal/mol.

Table 1 Optimum geometric parameters of the 2,3,4,5,6-pentachlorotoluene

DFT Bond Lengths (Å)		DFT Bond Angles (°)	
12Cl-6C	1.76000	12Cl-6C-1C	120.00800
13Cl-1C	1.76000	13 Cl-1C-2C	119.99722
14 Cl-2C	1.76000	14Cl-2C-3C	120.01055
15 Cl-3C	1.76000	15Cl-3C-4C	119.99304

Table 2. Mulliken loads of 2.3.4.5.6-pentachlorotoluene

1 C 0.599646	10 C -0.116954	19 C -0.167128
2 O -0.495734	11 H 0.136152	20 C -0.167117
3 C 0.048045	12 H 0.137244	21 C -0.129929
4 C -0.159733	13 H 0.136130	22 H 0.133597
5 C -0.151231	14 O -0.476466	23 C -0.129930
6 C -0.137532	15 C -0.126853	24 H 0.133599
7 H 0.160805	16 H 0.165318	25 C -0.125980
8 C -0.138939	17 H 0.165316	26 H 0.133822
9 H 0.162449	18 C 0.144383	27 H 0.133822

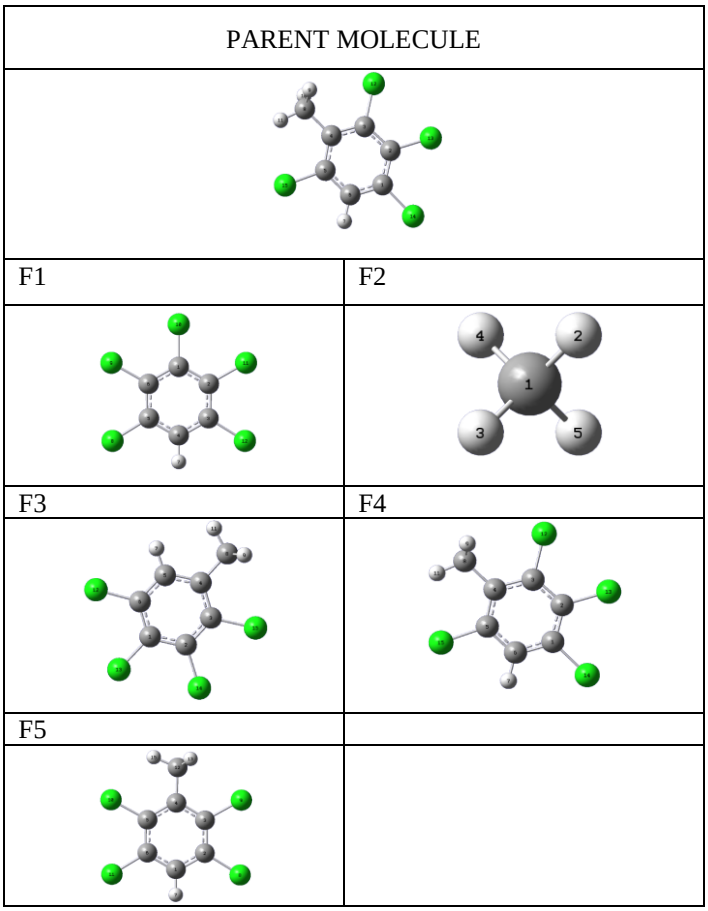


Figure 2. Possible reaction pathways of 2.3.4.5.6-pentachlorotoluene

Optimum parameters of 2,3,4,5,6-pentachlorotoluene, whose optimum shape is shown in Figure 1, are shown in Table 1. Parameters of pentachlorotoluene obtained by the DFT/B3LYP/6-31G(d) method which was found as the most appropriate method. are shown in Table 2.

Looking at the data in Table 3, fragment 1 (F1) of the possible decomposition pathways of 2.3.4.5.6-pentachlorotoluene has the lowest energy, in other words, it has the most stable structure. This fragment is formed by the detachment of the methyl molecule from the benzene ring to which the electronegative Cl atoms are attached.

In this study, possible reaction pathways were determined in the reaction between 2.3.4.5.6-pentachlorotoluene and the OH radical. The decomposition reaction requires energy. OH radicals are used to degrade pesticides in water.

As seen in the obtained fragments, 2.3.4.5.6-pentachlorotoluene was reduced to F5 and became harmless to the environment. Our aim was to break down the pesticides that enter the waters down to the smallest harmless substances and to remove their toxic effects from the waters. As can be seen from the results. this fragmentation occurred theoretically.

Benzylbenzoate

The durable geometric structure of benzylbenzoate obtained as a result of molecular modeling calculations and optimized by DFT/B3LYP/6-31G(d) methods is shown in Figure 3. As a result of DFT calculations, benzylbenzoate's total energy in the gas phase is -433573.210 kcal/mol, enthalpy -433572.617 kcal/mol, Gibbs free energy -433606.845 kcal/mol. In addition, the total energy in the water phase, enthalpy and Gibbs free energy are, respectively, -433577.433 kcal/mol, -433576.840 kcal/mol and -433612.461kcal/mol.

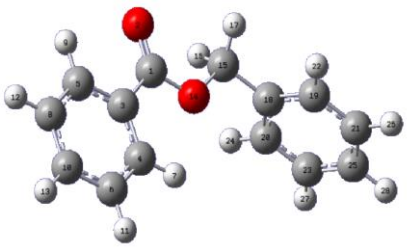
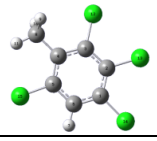
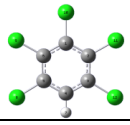
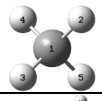
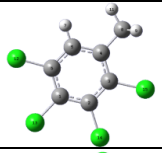
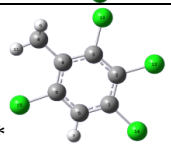
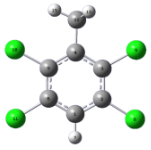


Figure 3. Optimized geometric structure of 2.3.4.5.6-pentachlorotoluene *via* DFT method (grey: C; white: H; red: O).

Table 3. Energy, enthalpy, Gibbs free energy of compounds

Compounds		Phase	ΔE Energy (kcal/mol)	ΔH Enthalpy (kcal/mol)	ΔG Gibbs Free Energy(kcal/mol)
2.3.4.5.6-pentachloro toluene		Gas	-1612336.958	-1612336.365	-1612369.534
		Water	-1612338.889	-1612338.296	-1612371.556
F1		Gas	-1587684.513	-1587683.921	-1587714.764
		Water	-1587686.412	-1587685.820	-1587716.718
F2		Gas	-25395.484	-5394.892	-25408.153
		Water	-25395.708	-25395.115	-25408.377
F3		Gas	-1323938.213	-1323937.620	-1323968.591
		Water	-1323940.550	-1323939.957	-1323970.956
F4	 *	Gas	-1323939.252	-1323938.660	-1323969.831
		Water	-1321041.305	-1321040.713	-1321071.048
F5		Gas	-1323939.213	-1323938.620	-1323969.906
		Water	-1323941.132	-1323940.539	-1323971.874

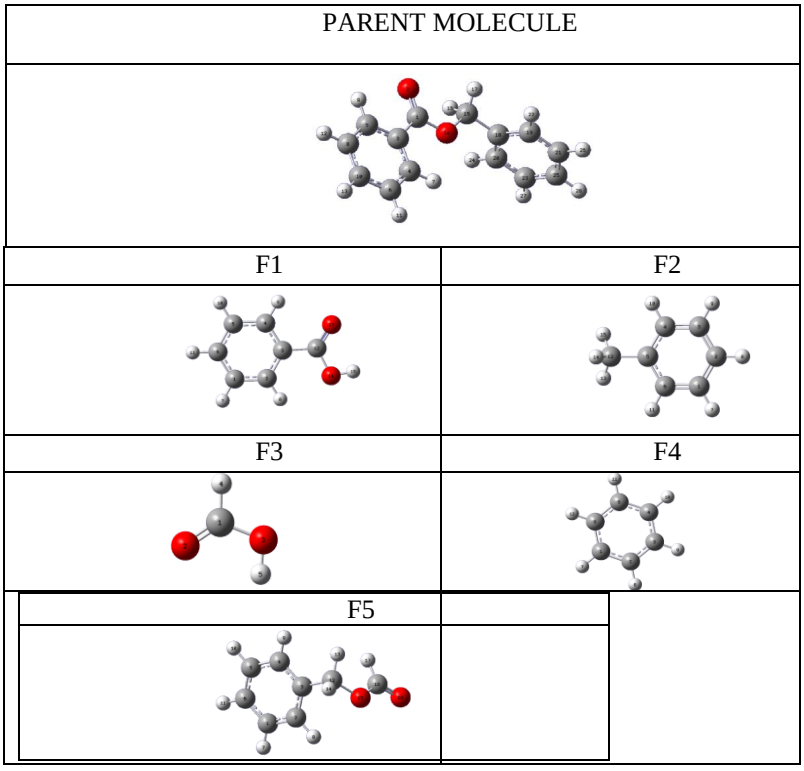


Figure 4. Possible reaction pathways of benzylbenzoate

Possible reaction pathways of benzylbenzoate were identified as breaking of C-C. C-O and aromatic ring bonds. The reaction sites were determined according to the Mulliken charge distribution of the molecule. According to the data in Table 3, the decomposition reaction occurred due to the electronegativity of O.

Table 4. Mulliken loads of benzylbenzoate

1 C 0.599646	10 C -0.116954	19 C -0.167128
2 O -0.495734	11 H 0.136152	20 C -0.167117
3 C 0.048045	12 H 0.137244	21 C -0.129929
4 C -0.159733	13 H 0.136130	22 H 0.133597
5 C -0.151231	14 O -0.476466	23 C -0.129930
6 C -0.137532	15 C -0.126853	24 H 0.133599
7 H 0.160805	16 H 0.165318	25 C -0.125980
8 C -0.138939	17 H 0.165316	26 H 0.133822
9 H 0.162449	18 C 0.144383	27 H 0.133822

Looking at the data in Table 5, fragment 1 (F1) of the possible degradation ways of the benzylbenzoate molecule has the lowest energy, in other words, it has the most stable structure. This fragment is formed by the bond breaking of the C to which the electronegative O atom is attached.

In this study. possible reaction pathways were determined in the reaction between benzylbenzoate and OH radical. The decomposition reaction requires energy. OH radicals are used to degrade pesticides in water. As seen in the resulting fragments, benzylbenzoate was reduced to F5 and became environmentally safe. Our aim was to break down the pesticides that enter the waters down to the smallest harmless substances and to remove their toxic effects from the waters. As can be seen from the results, this fragmentation occurred theoretically.

Demeton

According to the conformer analysis made by the molecular mechanics method, the lowest energy and most durable structure of the demeton molecule is shown in Figure 5. The most durable geometric structure of demeton, obtained as a result of MM calculations, was optimized with DFT/B3LYP/6-31G(d) methods.

As a result of DFT calculations the total energy of demeton in the gas phase is -1053887.648 kcal/mol, its enthalpy is -1053887.056 kcal/mol and its Gibbs free energy is -1053933.845 kcal/mol. In addition. the total energy, enthalpy and Gibbs free energy in the water phase are, respectively, -1053897.525 kcal/mol, -1053896.932 kcal/mol and -1053943.972 kcal/mol. The geometric structure of demeton, which was optimized by DFT/B3LYP/6-31G(d) methods, is shown in Figure 6 and its geometric parameters are shown in Table 6.

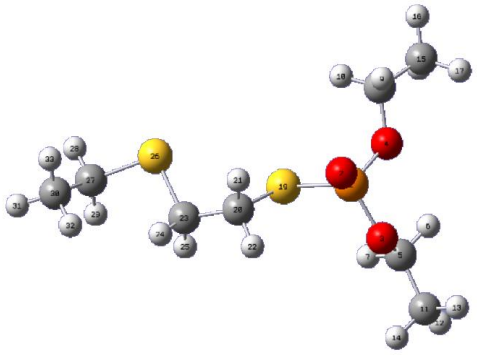


Figure 5. Optimized geometric structure of demeton *via* DFT method. (grey: C; white: H; red: O; yellow: S; orange: P).

Looking at the data in Table 7, fragment 4 (F4) among the possible fragmentation paths of demeton has the lowest energy, in other words, it has the most stable structure. This fragment is formed by bond breaking from the S atom.

In this study, possible reaction pathways were determined in the reaction between demeton and OH radical. The decomposition reaction requires energy. OH radicals are used to degrade pesticides in water. As seen in the resulting fragments, demeton has been downgraded to F5 and has become harmless to the environment. Our aim was to break down the pesticides that enter the waters down to the smallest harmless substances and to remove their toxic effects from the waters. As can be seen from the results, this fragmentation occurred theoretically.

CONCLUSIONS

In this study. the possible reaction paths between 2.3.4.5.6-pentachlorotoluene, benzylbenzoate and demeton molecules and the OH radicals were determined. Optimized geometries were drawn with Gauss View 5. Then, the lowest energy states were found by geometric optimization with the Gaussian 09 program. These results will guide experimental studies and determine the fragmentation mechanism.

These pesticides have been identified as primary endocrine disruptors in surface waters to be used as drinking water. Considering that classical biological enhancement methods are insufficient for the removal of these endocrine disrupting molecules, computational analysis of the degradation reactions of priority pesticides in surface waters, which will guide the application of alternative treatment methods to increase treatment efficiency was carried out.

In this work, besides theoretical studies, seasonal concentration differences of the aforementioned 4 pesticides in Naip dam were tried to be determined. These experimental studies were carried out in the Çınar Çevre Laboratory and it was found that all 4 pesticides did not show seasonal changes (Figs. 7-9).

Table 5. Energy, enthalpy, Gibbs free energy of compounds

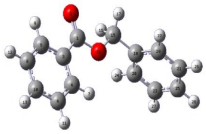
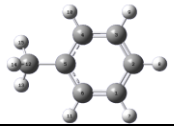
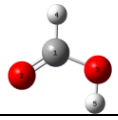
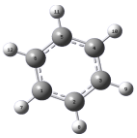
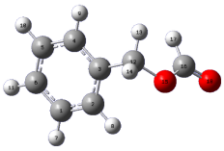
Compounds		Phase	ΔE Energy (kcal/mol)	ΔH Enthalpy (kcal/mol)	ΔG Gibbs Free Ennergy (kcal/mol)
Benzyl benzoate		Gas	-433573.210	-433572.617	-433606.845
		Water	-433577.433	-433576.840	-433612.461
F1		Gas	-263992.485	-263991.892	-264017.011
		Water	-263997.061	-263996.468	-264021.664
F2		Gas	-169174.769	-169174.176	-1691983.905
		Water	-170327.810	-170327.218	-170350.841
F3		Gas	-119049.983	-119049.391	-119067.075
		Water	-119054.193	-119053.601	-119071.294
F4		Gas	-145672.132	-145671.540	-145692.120
		Water	-145673.820	-145673.227	-145693.803
F5		Gas	-288626.528	-288625.935	-288654.281
		Water	-288632.525	-288631.932	-288660.627

Table 6. Optimum geometric parameters of demeton

DFT Bond Length (Å)		DFT Bond Angle (°)	
26S-23C	1.83980	27C-26S-23C	99.99185
19S-20C	1.85785	20C-19S-1P	98.08497
19S-1P	2.11478	2O-1P-4O	117.86752
1P-2O	1.48060	3O-1P-4O	101.00592
1P-4O	1.61568	2O-1P-3O	112.72439
1P-3O	1.60744	1P-3O-5C	122.86610
3O-5C	1.44850	1P-4O-8C	119.41604
8C-4O	1.45384	19S-1P-4O	101.99261

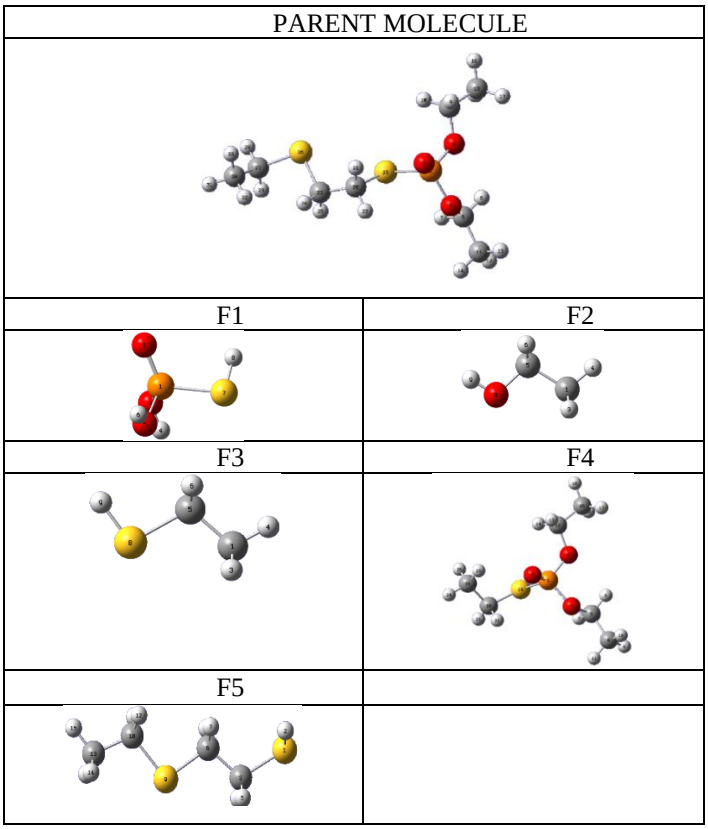
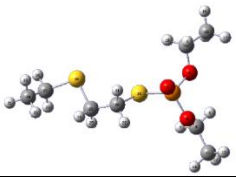
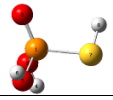
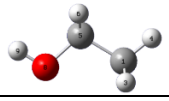
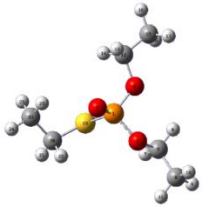
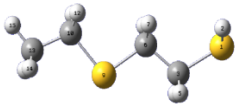


Figure 6. Possible reaction pathways of demeton

Table 7. Energy, enthalpy, Gibbs free energy of compounds

Compounds		Phase	ΔE Energy (kcal/mol)	ΔH Enthalpy (kcal/mol)	ΔG Gibbs Free Energy (kcal/mol)
Demeton		Gas	-1053887.648	-1053887.056	-1053933.845
		Water	-1053897.525	-1053896.932	-1053943.972
F1		Gas	-606820.745	-606820.153	-606844.561
		Water	-606830.41	-606829.817	-606853.893
F2		Gas	-97232.029	-97231.437	-97250.612
		Water	-97235.139	-97234.546	-972537.576
F3		Gas	-299907.151	-299906.558	-299926.956
		Water	-299909.648	-299909.056	-299929.512
F4		Gas	-754725.733	-754725.141	-754763.088
		Water	-754725.111	-754724.519	-754762.634
F5		Gas	-599071.678	-599071.085	-599099.515
		Water	-599075.779	-599075.187	-599103.911

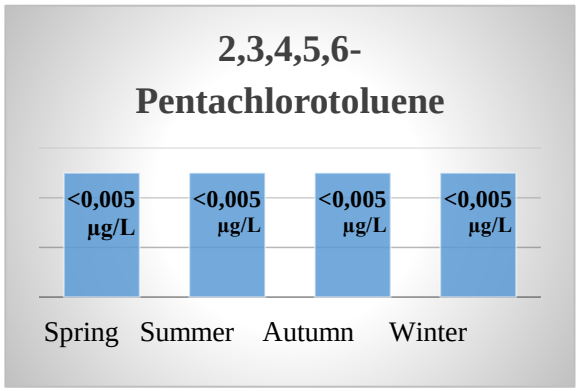


Figure 7 Concentration of 2.3.4.5.6-pentachlorotoluene in Naip Dam in four different seasons

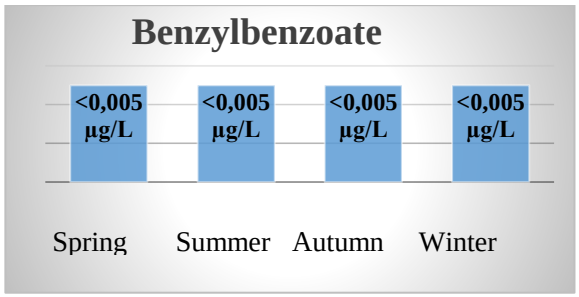


Figure 8 Concentration of benzylbenzoate in Naip dam in four different seasons

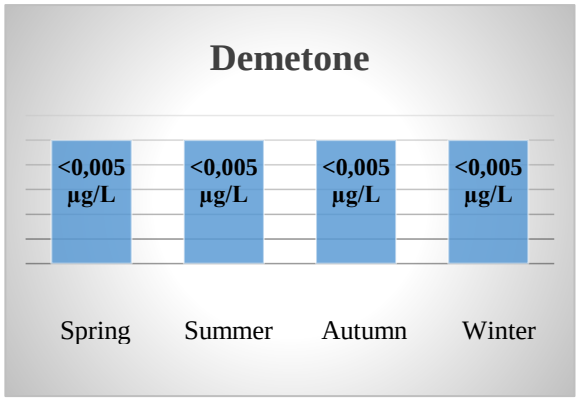


Figure 9. Concentration of demetone in Naip Dam in four different seasons

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