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# PAH and PCB Levels in *Malva sylvestris* L. Specimens Collected from Kocaeli, Turkey

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**Abstract:** In this study, polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) contaminations in the leaf, stem and root tissues of common mallow (*Malva sylvestris* L.) were investigated by using gas chromatography to give an insight into the bioaccumulation of these persistent pollutants. The sampling stations are located in the Dilovası and İzmit Districts of Kocaeli Province in Turkey. Total PAH concentrations varied between 10.44 and 61.15 pg g<sup>-1</sup> dw (dry weight). The most dominant PAH congeners were Acenaphthene and Acenaphthylene which are low molecular weight. Total PCB concentrations were found to be between 326.79 and 4496.42 pg g<sup>-1</sup> dw. PCB 66, PCB 110, PCB 153 and PCB 180 were found to be the most dominant congeners. Detected concentrations in root tissues showed the plant's ability in accumulating these pollutants. Therefore, these findings suggest that *Malva sylvestris* can reflect the contamination levels which might be used to monitor soil and ecological pollution levels caused by these persistent pollutants.

**Keywords:** Bioaccumulation, Biomonitoring, Kocaeli, *Malva sylvestris*, PAH, PCB

## 1 Introduction

In industrial histories of developing countries, it has always been a problem to keep organic pollutants under control, which may contribute to serious health issues as well as air and soil pollution. As one of these organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are widely distributed chemicals in the environment which

might be produced by natural sources such as forest fires and volcanoes and/or by anthropogenic sources including wood burning and fossil fuel consumption [1]. In addition to direct deposition in soils, PAHs can be deposited on plants or absorbed by them, from which they can be washed by rain and thus get oxidized. Furthermore, they can be deposited indirectly in soils as a result of plant decay. PAHs have long been recognized as toxic compounds for humans and mammals, birds, fish, amphibians, invertebrates and plants [2]. Also, several PAHs are known to have the potential to cause cancer [3]. As another type of organic pollutant, polychlorinated biphenyls (PCBs) are a group of highly toxic chlorinated industrial chemicals. PCBs are mixtures of different congeners of chlorobiphenyl. Depending on the number of chlorine atoms and their position, 209 types of PCB congeners are possible. The highest environmental concentrations of PCBs are associated with paper mills, refineries and other industrial sites. PCBs are extremely persistent in the environment and bioaccumulate throughout the food chain. They can be spread by atmospheric transport and remain in the soil for extended periods due to their long half-life [4]. These organic pollutants can be accumulated by plants in their tissues, on leaves or in root systems which are directly in contact with soils [5]. Therefore, widespread plant species which remain green during winter season, especially those with larger leaves and well-developed root systems, should be used in biomonitoring studies of these pollutants.

*Malva sylvestris* L. (Malvaceae), usually known as common mallow, is a cosmopolitan, medicinal and edible plant native to Europe, North Africa and Asia. Medicinal applications of the common mallow can treat specified disorders of several systems of the body, such as the digestive, respiratory, genitourinary, muscular and skeletal system, as well as skin disorders and injuries [6]. The plant has a wide distribution in the Marmara, Black Sea and Mediterranean Regions of Turkey.

Kocaeli, the city located in the Marmara Region, is known for its dense industrialization. In this study, we hypothesized that this cosmopolitan plant should

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reflect the potential PAH and PCB pollution levels through accumulation on its leaves, stems and roots. Therefore, the aim of this study is to monitor PAH and PCB contaminations in several tissues of *M. sylvestris* to understand the potential usability of the plant in biomonitoring studies.

## 2 Material and methods

PAH and PCB contaminations in roots (R), stems (S) and leaves (L) of *M. sylvestris* specimens collected from three different spots of Kocaeli were determined. The plant collection areas (Fig. 1) are as follows; around Dil Creek (D; a contaminated creek), around facilities (M; heavy industry/metallurgy) and city forest (F; probably less contaminated area). The collection areas D and M are located in Dilovası District which is known by its intensive industrialization and air pollution. F is located 12 km away from dense urbanization and industrialization at an approximate altitude of 380 m in İzmit District.

Fifteen grams of tissue samples from three specimens were collected per site, wrapped in aluminum foil and transported to the laboratory in jars at 4°C and then stored at -20°C until analysis. The samples were then washed under distilled water. Fresh leaf, stem and root tissues were used in analyses conducted according to methods modified from EPA 8082A [7] and EPA 8100 [8]. Water contents of the tissues were determined before the analysis. The samples (10 g) were shredded in a blender, then subjected to ultrasonic extraction at 25°C after PAH and PCB surrogate standards and solvents (acetone:hexane,

1:1) were added. Following the ultrasonic extraction, samples were cleaned up in a column containing 3 g silicic acid (activated with 3% deionized water) and 2 g alumina (activated with 2% deionized water). The obtained extracts were concentrated to 1 ml under a gentle stream of nitrogen. The concentrate was then analyzed using GC (gas chromatography; Agilent 7890A) equipped with an ECD (electron capture detector) and FID (flame ionization detector). The data were given as pg g<sup>-1</sup> dw (dry weight). The limit of detection per substance is reported in Tables 1 and 2. To calculate summary values, measurement data below the limit of detection were set to zero.

## 3 Results

PAH (9 of 16 congeners listed as “primary pollutants” by the EPA) [9] and PCB (19 congeners) levels were individually determined. Concentrations of nine PAH congeners (Acenaphthylene (ACY), Acenaphthene (ACP), Fluorene (FLR), Pyrene (PYR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo[g,h,i]perylene (BghiP), Dibenzo(a,h)anthracene (DahA) and Indeno(1,2,3-cd)pyrene (IcdP)) detected in tissue samples are given in Table 1. ΣPAH concentrations were found to be between 10.44 and 61.15 pg g<sup>-1</sup> dw. Among the congeners, the most dominant ones were found to be Acenaphthene and Acenaphthylene. The highest ΣPAH concentration (61.15 pg g<sup>-1</sup> dw) was detected in the root samples of the specimens collected from station M while the lowest ΣPAH concentrations were detected in the root (10.44 pg g<sup>-1</sup> dw) and stem samples (10.70 pg g<sup>-1</sup> dw) of the specimens collected from station D and F, respectively. PYR, BbF, DahA and IcdP congeners were not detected in any samples. Also, BkF was only detected in leaf samples of the specimens collected from M station.

ΣPCB concentrations were found to be between 326.79 and 4496.42 pg g<sup>-1</sup> dw (Table 2). Evaluation of the data obtained from specimens collected from the three stations showed that the least contaminated organ of the plant was the stem. Among the considered congeners, PCB 66, PCB 110, PCB 153 and PCB 180 were found to be the most dominant ones. However, PCB 66 and PCB 180 congeners were not detected in the leaf and stem samples of the specimens collected from F station. The highest ΣPCB concentration was found to be 4496.42 pg g<sup>-1</sup> dw in the root samples of collected specimens from station D, while the lowest ΣPCB concentration was detected in stem samples of the specimens collected from station F. PCB44 congener was detected only in the roots and leaves of the specimens collected from F and D station.

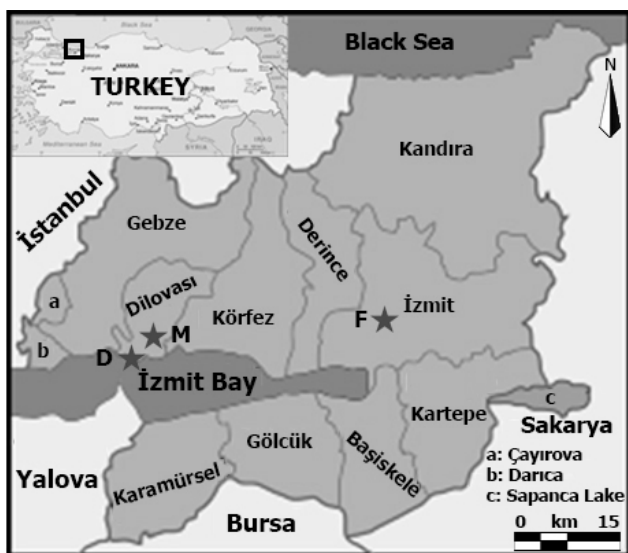


Figure 1. Locations of the sampling stations in Kocaeli province of Turkey

**Table 1.** Concentrations of PAH congeners in different tissues of *M. sylvestris* specimens

PAHs	M-L	M-R	M-S	F-L	F-R	F-S	D-L	D-R	D-S	LOD
ACY	2.58	39.75	n/d	n/d	7.17	n/d	2.93	n/d	n/d	2.00
ACP	n/d	21.40	12.35	29.01	2.97	10.70	8.53	10.44	11.97	2.40
FLR	n/d	n/d	n/d	n/d	8.50	n/d	2.85	n/d	n/d	2.55
PYR	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	2.00
BbF	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	2.30
BkF	4.91	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	2.00
DahA	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	2.20
lcdP	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	2.20
BghiP	15.67	n/d	n/d	n/d	n/d	n/d	8.42	n/d	10.39	2.10
$\Sigma$ PAH	<b>23.17</b>	<b>61.15</b>	<b>12.35</b>	<b>29.01</b>	<b>18.64</b>	<b>10.70</b>	<b>22.73</b>	<b>10.44</b>	<b>22.36</b>	

\*n/d: not detected or value is lower than detection limit, the data were expressed as  $\text{pg g}^{-1}$  dw

**Table 2.** Concentrations of PCB congeners in different tissues of *M. sylvestris* specimens

Congeners	M-L	M-R	M-S	F-L	F-R	F-S	D-L	D-R	D-S	LOD
PCB 1	n/d	n/d	n/d	63.49	53.45	34.97	26.82	27.33	n/d	2.80
PCB 5	172.69	n/d	50.43	n/d	11.73	n/d	150.63	n/d	13.48	2.50
PCB 18	184.23	160.02	101.66	58.24	45.50	82.27	75.97	28.73	80.42	3.12
PCB 31	317.74	222.42	108.15	29.83	85.99	33.59	159.28	n/d	57.97	3.00
PCB 52	126.83	n/d	156.35	n/d	50.04	47.34	159.65	459.69	130.30	4.52
PCB 44	n/d	n/d	n/d	n/d	77.44	n/d	128.76	n/d	n/d	6.80
PCB 66	353.82	327.94	164.76	n/d	62.36	n/d	243.53	571.94	109.20	8.12
PCB 101	181.06	n/d	107.29	29.00	14.48	25.84	14.44	536.71	64.88	4.50
PCB 87	164.34	303.68	84.10	72.44	n/d	n/d	103.04	333.62	84.76	6.16
PCB 110	257.63	302.97	131.17	54.81	57.55	68.80	146.85	597.54	94.13	5.20
PCB 151	197.79	n/d	98.71	n/d	67.11	n/d	66.55	212.37	50.49	6.10
PCB 153	300.84	339.46	313.41	18.04	18.02	33.98	81.51	277.83	44.22	12.06
PCB 141	114.68	n/d	119.18	n/d	n/d	n/d	92.18	197.88	98.37	10.24
PCB 138	n/d	n/d	105.98	n/d	n/d	n/d	80.39	196.68	n/d	6.12
PCB 187	79.28	281.21	90.59	n/d	68.82	n/d	68.46	164.61	69.95	6.00
PCB 183	84.36	n/d	n/d	n/d	n/d	n/d	79.02	175.85	85.54	8.22
PCB 180	131.81	382.39	157.99	n/d	96.86	n/d	114.32	254.43	114.22	10.10
PCB 170	109.07	n/d	115.66	82.49	93.40	n/d	102.04	243.26	104.24	7.60
PCB 206	n/d	395.30	93.46	n/d	n/d	n/d	n/d	217.94	n/d	12.00
$\Sigma$ PCB	<b>2776.19</b>	<b>2715.40</b>	<b>1998.91</b>	<b>408.34</b>	<b>802.77</b>	<b>326.79</b>	<b>1893.43</b>	<b>4496.42</b>	<b>1202.15</b>	

\*n/d: not detected or value is lower than detection limit, the data were expressed as  $\text{pg g}^{-1}$  dw

## 4 Discussion

In general, the congeners with higher molecular weight could not be detected, while congeners with low molecular weight such as Acenaphthene and Acenaphthylene were found to be the highest accumulated PAHs. Perwak et al. [10] declared that Acenaphthylene production is triggered more by wood combustion in residential areas than other PAHs. Furthermore, this congener is known to be found in soils and underground waters. Therefore, this statement is in line with our findings since root samples from M station were found to be the most contaminated with Acenaphthylene. Contaminations found in root tissues of the plant are thought to be an indicator of rain water drain and/or soil contamination. Additionally, low molecular weight PAHs detected in leaves can be explained by wind-blown transportation of ashes or pollutant vapors. PAHs with low molecular weight may be accumulated in leaves by absorption through stomata.

Due to their lipophilic properties and their long half-lives, PCB 138, 153 and 180 are the PCB congeners that are accumulated the most during transfer along the ecological food chains [11]. In a previous report, it was suggested that due to their hydrophobicity, PCBs and other persistent organic pollutants were unlikely to be taken up from soil and translocated within plants [12]. However, in other studies conducted on *Cucurbita pepo* spp. *pepo*, it was reported that this species can translocate and accumulate significant concentrations of PCBs [13-15] in its tissues. The higher concentrations observed in root tissues of specimens from all stations indicated that *M. sylvestris* has also the potential to accumulate PCBs in its root system. Also, contaminations in the stem and leaf tissues might be attributed not only to atmospheric transportation but also to the mobilization ability of PCBs between plant's tissues and organs. Compounds like PAHs and PCBs that can persist for a long time in the environment are generally found in industrial zones. The presence of considerable amounts of these compounds in non-industrial areas can be explained by atmospheric transportation.

*Malva sylvestris* can be biennial or perennial, and remain leafy during the winter season [16]. Thus, the plant may accumulate these pollutants for several years. Generally, a plant that is used in biomonitoring studies should have a wide distribution all over the world and display large contact surface with pollutants. *Malva sylvestris* has these two properties, and besides, it is an edible and commonly-used medicinal plant. Decoctions, infusions, cataplasms, ointments or external compresses prepared by using flowers, leaves, stems or roots of the

plant are used to cure gastrointestinal disturbances, dermatological ailments, haemorrhoidal inflammations, menstrual pains, urological and vaginal disorders, respiratory complaints and oral diseases [17]. Therefore, consumption and usage of contaminated parts – either dietary or medicinally – might bring health risks. In order to clarify these doubts, a risk assessment study on usage of such contaminated and widely-used medicinal plants should be carried out. Consequently, bioaccumulation by vegetation provides a critical step in the accumulation of persistent organic pollutants in terrestrial food chains, and forms a pathway to human and animal exposure.

In conclusion, since most of the investigated PAHs remained under the detection limit, this plant species has very limited potential to monitor PAH contaminations. But our data demonstrates that *M. sylvestris* has potential to be used in PCB biomonitoring studies. However, this preliminary study is not enough to explain the influence of xenobiotic factors which play a role in bioaccumulation of the studied pollutants. Additionally, PAH and PCB contaminations in the air, soils and waters of the sampling areas should be examined to find out their correlations with contaminations detected in tissues of the plant.

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