FATE AND BEHAVIOR OF TOXIC ORGANIC POLLUTANTS IN PLANT, SOIL AND IRRADIATED SEWAGE SLUDGE

RAWIA EL-MOTAIUM, MOHAMED EL-SAYED HASHIM

Plant Research Department, Nuclear Research Center, Atomic Energy Authority,
11787 Cairo, Egypt, rawiae@yahoo.com

GIOVANNI CARIA

Institute National de la Recherche Agronomique (INRA), LAS. 273, Rue de Cambrai,
62000 Arras, France

Abstract. This study was conducted to determine the toxic organic pollutants, Polycyclic Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyls (PCB) in Navel orange fruits, soil, and sewage sludge. The fruits were collected from 20 years old trees grown at three different farms at El-Gabal El-Asfar. The three farms received sewage water for irrigation for different periods of time: 20, 50, 90 years. The control farm is located in Anshas area, which received canal water for irrigation. The soil samples were collected from the same locations as for the fruits. The raw sludge samples were colleted from the drying beds of El-Gabal El-Asfar farm, whereas the digested sludge samples were collected from the drying beds of El-Gabal El-Asfar Wastewater Treatment Plant. The results indicated that long-term irrigation with sewage water induced the accumulation of toxic organic pollutants (PAHs and PCBs) in the Navel orange fruits and soil. The accumulation of PAHs in the fruits is less than PCBs due to their lower water solubility and hence uptake by the plant roots. The same pollutants tend to accumulate more in the top soil layer (0–20 cm) and decrease with the soil depth. Gamma irradiation (dose = 6 kGy) of raw sludge showed degradation effect on several PAHs and PCBs congeners. However, the extend of the degradation vary between the different compounds. In the digested sludge the PAHs and PCBs concentrations stay more or less similar for irradiated and non-irradiated samples indicating the lower degradation effect of gamma irradiation on the digested sludge than on the raw sludge.

Keywords: PCBs, PAH, irrigation, pollutant’s uptake.

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1. Introduction

Sewage wastewater and sludge are used for irrigation and fertilization of agricultural soils. They contain several toxic organic pollutants that are harmful to human health and the environment. The legislative control of the environmental contaminants, which enter the food chain, is of a great concern to the public. Thus, it is important to investigate the fate and behavior of such pollutants in plant, soil, and sewage sludge.

The main organic pollutants that exist in the sewage sludge and sewage water are polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The organic pollutants accumulation in soil varies between the different group of compounds, PAHs or PCBs, and between the specific congeners within each group. The accumulation increase gradually in the order: PCBs > CB (chlorinated benzenes) > PAHs > PCDD/F [11].

PCBs are one of the most important xenobiotics and persistent organic pollutants in the environment [2]. There is a relationship between the metabolism and the structural properties of PCBs [9]. Chlorination grade, substitution, and molecular configuration play an important role in PCBs metabolism in plants. The lower the chlorination grade the higher is the metabolic rate in plants [14]. The solubility of these compounds decrease as the number of rings increase. Plant uptake of PCBs can occur through two pathways, the root system or atmospheric deposition [15].

PAHs are non-polar (hydrophobic), soluble in organic solvents, and difficult to mobilize due to their low water solubility. Their water solubility decreases with increasing molecular weight, whereas the resistance to oxidation, reduction, and vaporization increases. They are lipophilic and accumulate in soils by binding to the organic matter [11]. The lower molecular weight PAHs of two or three ring groups such as naphthalene, fluorene, phenanthrene, and anthracene are toxic, their toxicity tends to decrease with increasing molecular weight. There is a concern about PAH existence in the environment due to the fact that the higher molecular weights PAHs cause cancer to human beings. Pyrene is a product of incomplete combustion of fossil fuels and has been identified in surface and drinking water, numerous foods, and ambient air [10, 12, 13]. Polycyclic aromatic hydrocarbons – although non-polar – can be assimilated by intact plants [9].

Information is lacking on toxic organic pollutants' transfer and fate in plants and soils under sewage water irrigation regime. Also, the effect of gamma irradiation on their fate in sewage sludge needs to be studied. The ultimate goal of this study is to ensure the safe utilization of sewage water and sludge in agricultural soils.

2. Materials and methods

This study was conducted to determine the toxic organic pollutants on the Navel orange fruits and soils from four different farms. In addition, two different kinds of sewage sludge were analyzed for their PAHs and PCBs content. The four farms used different kinds of water, canal water and sewage water, for irrigation. One farm received canal water, the other three farms received sewage water for different periods of time: 20, 50, 90 years. The kinds of sludges used were raw sludge collected from El-Gabal El-Asfar farm and digested sludge collected from El-Gabal El-Asfar Wastewater Treatment Plant, both are located North -East of Cairo city.

The raw sludge from El-Gabal El-Asfar Farm was originated from the domestic sewage water and received no treatment. At El-Gabal El-Asfar WWTP the domestic sewage water received primary (sedimentation) and secondary (biological) treatments in addition to anaerobic digestion process at 35°C for 27 days in digesters.

2.1. Sludge irradiation treatment

The sludge samples were divided into two equal portions. One portion was sent to the National Center for Research and Radiation Technology, Atomic Energy Authority, for irradiation treatment. The samples received the radiation dose of 6 kGy at a dose rate of 5.6 kGy h^{-1}.

2.2. Determination of PAHs and PCBs in fruits, soil and sludge

This method was developed and conducted at the Institute National de la Recherche Agronomique (INRA), Laboratoire d'analyses des sols, Arras (France) as follows.

2.2.1. Extraction

PAHs and PCBs in soil [6,7] and sludge [3] were extracted using Pressure Liquid Extraction with an Accelerated Solvent Extractor (DIONEX ASE 200).

Twenty gram of soil or 2 g of sludge was weighed and added to 5 g of celite. The mixture was placed in a metallic cell of ASE 200, which was filled with pure sand. Each cell prepared was carried in the ASE 200 sampler and extracted at three types of conditions: temperature 150°C, pressure 103,4 Bar and organic solvent mixture acetone/hexane/dichloromethane (50/25/25; v/v). About 40 ml of extract was obtained in a glass tube and transferred in a graduated flask in order to adjust the final volume at 50 ml with pure acetone. Two 20 ml-volumes of final extract were transferred in two different conical flasks. The first flask was called PAH extract and the second PCB extract. 0.5 ml n-dodecane at 1% in hexane was added as keeper in each conical flask containing the PAH and PCB extracts.

PAHs and PCBs were extracted from fruits using Liquid–Liquid Extraction (LLE) [4, 5]. Twenty millilitre of fruit juice and 3 g of sodium chloride (NaCl) were measured and added in a glass conical funnel of 250 ml for LLE. The mixture was shaken first for 15 min and, after addition of 100 ml of dichloromethane, shaken for another 30 min. The conical funnels were left at vertical position in order to perform the decantation of the mixture. The lower chlorinated phase was transferred into a glass conical flask of 250 ml through a funnel filled with glass wool and anhydrous sodium sulfate.

The residual aqueous phase was extracted another time with 100 ml of hexane and shaken for 30 min. The mixture was left in vertical position for decantation. The lower aqueous phase was discarded and the hexane phase was transferred in the same conical funnel (which contained the chlorinated extract) through the same funnel. The volume of the final extract was adjusted to 250 ml in a graduated glass flask and this extract was divided in two equal volumes measured with a graduated glass test tube and distributed in two different glass flasks. The PAH and PCB extracts were then obtained. 0.5 ml n-dodecane at 1% in hexane was added as keeper in each conical flask containing the PAH and PCB extracts.

2.2.2. Purification and Determination of PAHs

The PAH extract was reduced partially in a rotary evaporator and then to dryness with a low flow of nitrogen. Then 2 ml of methyl alcohol was added to the conical flask to dissolve the dried residue. After a contact time between 30 and 45 min, the extract was filtered through a fritted disk (0.45µm of porosity). The sample was kept in a small vial for PAHs determination. PAH solution mixture “Accu – Standard Inc.” and High Pressure Liquid Chromatograph (Varian) equipped with Fluorescence Detector (FD) were used for measurement.

2.2.3. Purification and Determination of PCBs

The PCB extract was reduced partially in a rotary evaporator and then to dryness with a low flow of nitrogen. 4 ml of hexane was added and left in contact between 30 and 45 min to dissolve the dried residue. The extract was purified using a glass filtration system which consists of 50 cm narrow tube with a tape in the bottom and a piece of glass wool, 5 g of magnesium silicate, 2 g of anhydrous sodium sulfate and filled with hexane. The extract was put on the column and purified through the sorbent with 80 ml of hexane. The filtrate was received into conical flask~~s~~. It was evaporated partially to 5 ml using rotary evaporator. 20 ml sulfuric acid was added to the 5 ml extract in the conical flask. The mixture was transferred into a separation funnel, shaken for 5 min and left some time to obtain the separated layers. The lower aqueous layer was discarded. The upper layer was received in a conical flask after passing through anhydrous sodium sulfate to purify it from sulfuric acid residue. Copper wire was added till it covers the sample~~s~~ and left for 15 min in contact without shaking. The mixture was filtered on glass wool to separate hexane solution and copper wire, which was rinsed with a few volume of hexane. The hexane phase was evaporated partially using rotary evaporator and then to dryness with a low flow of nitrogen. The dried residue was dissolved with

2 ml of internal standard (PCB 202 in hexane at 50 μg/l). The contact time was between 30 and 45 min before transferring the extract into small vial (2 ml).

Quantitative determination of PCBs was performed using PCB standard "Accu Standard Inc." and a gas chromatograph (GC 3400, Varian) equipped with an Electron Capture Detector (ECD).

3. Results and discussion

3.1. Plant

The concentrations of PAHs in Navel orange fruits were 9.9, 16.3, 21.4, 26.5 $\mu g \cdot kg^{-1}$ for canal water, 20, 50 and 90 years of irrigation using sewage water, respectively. Whereas, the concentrations of PCBs in Navel orange fruits were 165.8, 255.8, 282.0, 455.3 $\mu g \cdot kg^{-1}$ for fresh water, 20, 50 and 90 years of irrigation using sewage water, respectively. It was noticed that the longer the irrigation period the higher were the concentrations of these pollutants in the fruits. PAHs concentration in fruit is less corresponding to PCBs. This implies that there is little uptake and transport of PAHs through the plant. The results agree with [11]. This could be due to their low water solubility, which prevents their uptake by plant roots. In addition, PAHs are lipophilic, which make them immobile by bounding to soil organic matter in the upper soil layers [11].

The average PAHs and PCBs concentrations in the two top soil layers (0–20 and 20–40 cm) are shown in Table 3.1.1. These two layers represent the soil where most of the active root system exists.

Table 3.1.1. Average of total PAHs and PCBs in the top soil layer (0-40) mg kg^{-1}.

	F.W.	20 years	50 years	90 years
PAHs	0.11	0.26	0.52	2.68
PCBs	6.1	21.9	37.1	120.1

The percent recoveries of PAHs and PCBs by orange fruits are shown in the Table 3.1.2. Both compounds showed reduction in the percent of recovery as the irrigation period increased. This indicates that, in the long term, there is a substantial accumulation of these compounds in the soil relative to their concentrations in plants. The highest recovery was under the fresh water irrigation regime. This could be due to the low concentrations of the organic pollutants in the soil relative to their concentration in plants. On the contrary, under high soil concentrations of these compounds, as a result of prolonged irrigation with sewage water, the recovery by plant was low.

Table 3.1.2. Recovery of PAHs and PCBs by fruit.

Compounds	F.W. (%)	20 years (%)	50 years (%)	90 years (%)
PAHs	9.4	6.3	4.1	1.0
PCBs	2.7	1.2	0.8	0.4

3.2. Soil

The concentration of PAHs and PCBs congeners varies according to the type of irrigation water, the irrigation period and the soil depth. The data given in Tables 3.2.1 and 3.2.2. indicate that, the longer the irrigation period the higher the concentrations of all congeners are. The soil irrigated with canal water exhibited the lowest congener's concentrations in all soils layers. The concentrations of all congeners are higher at the surface soil layer (0–20 cm) and decrease with the soil depth. Some transport of PAHs and PCBs from the upper soil layer into the lower layers was observed. The reason for being concentrated at the soil upper layer is that, the prolonged application of sewage water at El-Gabal El-Asfar Farm has increased the organic matter content particularly at the surface soil layer. Organic matter is the major sorptive material of organic pollutants in the soil [8], which explain their accumulation in the surface soil layer. The distribution of the different compounds in the soil indicated that, the total PCBs were much higher than the total PAHs in all soil layers.

The higher molecular weight of the congeners (Benzo(a)anthracene ‘230.27’, Benzo(k)fluoranthene ‘252.32’, Benzo(ghi)perylene ‘252.31’) revealed higher concentrations, indicating more persistence relative to the lower molecular weight congeners (Naphthalene ‘128.17’, Acenaphthene ‘154.21’, Fluorene ‘166.22’). The data reveal the long-term effects of sewage water on PAHs and PCBs contents in the soil. The long term (90 years) application of sewage water to the soil showed 22 and 20 time increase in the top soil layer (0–20 cm) of PAHs and PCBs, respectively, relative to the control.

Table 3.2.1. Total soil PAHs as affected by the kind of water and irrigation period ($mg{\cdot}kg^{-1}$).

Soil depth (cm)	F.W.	20 years	50 years	90 years
0–20	0.13	0.33	0.59	2.91
20–40	0.08	0.19	0.46	2.45
40–60	0.07	0.15	0.29	0.80
60–80	0.05	0.11	0.21	0.47
80–100	0.04	0.09	0.16	0.29

Table 3.2.2. Total soil PCBs as affected by the kind of water and irrigation period ($mg \cdot kg^{-1}$).

Soil depth (cm)	F.W.	20 years	50 years	90 years
0–20	6.5	28.8	44.1	131.8
20–40	5.7	15.1	30.0	108.5
40–60	4.4	10.5	13.0	55.0
60–80	2.9	6.1	8.3	37.6
80–100	1.8	4.7	5.5	20.7

It is obvious from the data in the Table 3.2.3 that percent transport of PCBs congeners varies according to their chlorination grade and substitution pattern. As for the chlorination grade, after 90 years of irrigation, almost 50% of the top soil (0–20 cm) concentration of 2,4-dichlorobiphenyl was transported to the lower soil layer (80–100 cm), whereas, for the 2,2,4,5,5-pentachlorobiphenyl congener no translocation (0.0%) was recorded to the lower soil layer (80–100 cm). Regarding the substitution, the 2,3,4,4,5-pentachlorobiphenyl congener recorded 25% translocation to the lower layer (80–100 cm) comparing with 0.0% of the 2,2,4,5,5-pentachlorobiphenyl.

Table 3.2.3. Concentrations of some soil PCBs congeners as affected by the kind water, irrigation period and the depth of the soil profile ($mg \cdot kg^{-1}$).

Depth (cm)	2,4 Dichlorobiphenyl				2,2,4,5,5-Pentachlorobiphenyl				2,3,4,4,5-Pentachorobiphenyl			
	C.W.	20 years	50 years	90 years	C.W.	20 years	50 years	90 years	C.W.	20 years	50 years	90 years
0–20	4.1	8.1	10.0	20.4	0.0	7.3	11.6	25.8	0.0	0.4	1.4	8.2
20–40	3.1	6.3	7.4	15.9	0.0	1.3	8.5	22.6	0.0	0.3	0.9	8.1
40–60	3.0	6.3	6.5	12.4	0.0	0.0	0.0	2.3	0.0	0.0	0.0	4.3
60–80	2.4	4.4	5.5	10.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3
80–100	1.6	3.6	4.2	9.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1

3.3. Sewage sludge

3.3.1. PAHs

The data in the Table 3.3.1.1 show that PAHs congeners (fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene) are dominant in the raw sludge, whereas, in the digested sludge the dominant congeners are naphthalene, acenaphtene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene. Chrysene and pyrene exhibited the highest concentration in raw sludge and digested sludge, respectively. Anthracene and benzo(a)pyrene exhibited the lowest concentrations in raw and digested sludge, respectively. Most congeners recorded higher concentrations in the digested sludge than in the raw sludge.

The effects of gamma radiation treatment on organic pollutants vary according to the compound. The concentrations of some compounds stay the same after irradiation, whereas the concentrations of other compounds were reduced. . Several compounds in raw sludge such as phenanthrene, fluoranthene, pyrene, and chrysene exhibited higher concentrations in non-irradiated sludge than in irradiated sludge. The results indicate the degradation effect of gamma irradiation on these compounds. The results agree with former findings in the literature [1]. However, the different compounds showed differences in the magnitude of degradation in response to 6 kGy of gamma irradiation. In raw sludge, the reductions were as follows: 25% for phenanthrene, 22% for fluoranthene, 51% for pyrene, and 17% for chrysene. In the digested sludge, the concentrations of these compounds were more or less similar in irradiated and non-irradiated sludge. This indicates that the digestion processes have caused some degradation of PAHs during the processes of methane gas formation, thus no further significant degradation could occur by radiation.

Table 3.3.1.1. Toxic organic pollutants (PAHs) in different kinds of irradiated and non-irradiated sludges (μg·kg^{-1}).

Compounds	Raw sludge		Digested sludge	
	PAHs		PAHs	
	Irradiated	Non-irradiated	Irradiated	Non-irradiated
Naphthalene	<LOD*	<LOD*	350	330
Acenaphthene	<LOD*	<LOD*	520	500
Fluorene	130	<LOD*	670	640
Phenanthrene	860	1,150	1,310	1,300
Anthracene	110	110	410	430
Fluoranthene	460	590	550	570
Pyrene	301	630	2,450	2610
Benzo(a)anthracene	<LOD**	<LOD**	<LOD**	<LOD**
Chrysene	2,710	3,250	2,070	1,460
Benzo(b)fluoranthene	<LOD*	180	320	330
Benzo(k)fluoranthene	<LOD*	<LOD*	<LOD*	<LOD*
Benzo(a pyrene	270	280	190	230
Dibenzo(ah)anthracene	560	<LOD**	<LOD**	<LOD**
Benzo(ghi)perylene	<LOD**	990	<LOD**	<LOD**
Indeno(123 cd)pyrene	<LOD**	<LOD**	<LOD**	<LOD**
Total	5,410	7,180	8,840	8,400

*LOD = 0.11.

**LOD = 0.54.

3.3.2. PCBs

The data in the Table 3.3.2.1 show that PCBs congeners (PCB 77, PCB 101, PCB 52) are dominant in the raw sludge, whereas, in the digested sludge the dominant congeners are PCB 77, PCB 153, PCB 101, PCB 118, and PCB 66. The congener PCB 77 exhibited the highest concentrations in both raw and digested sludge. However, it recorded higher value in digested than in raw sludge, whereas PCB 101 recorded higher value in raw than in digested sludge.

The different compounds showed differences in the magnitude of degradation in response to 6 kGy of gamma irradiation and the kind of sludge. PCBs congeners exhibited higher concentrations in non-irradiated than in irradiated raw sludge. The results indicate the degradation effect of gamma irradiation on these compounds. However, PCBs congeners exhibited almost similar concentrations in

Table 3.3.2.1. Toxic organic pollutants (PCBs) in different kinds of irradiated and non-irradiated sludges ($\mu g \cdot kg^{-1}$).

Compounds	Raw sludge		Digested sludge	
	PCBs		PCBs	
	Irr	Non-irr	Irr	Non-irr
PCB 8 (2,4 Dichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 18 (2,2,5-Trichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 28 (2,4,4-Trichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 52 (Tetrachlorobiphenyl)	10.9	22.4	<LOD	16.0
PCB 44 (2,2,3,5-Tetrachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 66 (2,3,4,4-Tetrachlorobiphenyl)	<LOD	<LOD	7.0	6.5
PCB 101 (2,2,4,5,5-Pentachlorobiphenyl)	37.5	41.5	12.5	10.0
PCB 77 (3,3,4,4-Tetrachlorobiphenyl)	38.7	40.8	46.4	44.1
PCB 118 (2,3,4,4,5-Pentachlorobiphenyl)	<LOD	<LOD	7.8	7.0
PCB 153 (2,2,4,4,5,5-Hexachlorobiphenyl)	<LOD	<LOD	20.3	16.6
PCB 105 (2,3,3,4,4-Pentachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 138 (2,2,3,4,4,5-Hexachlorobiphenyl)	<LOD	<LOD	21.9	16.0
PCB 126 (3,3,4,4,5-Pentachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 187 (2,2,3,4,5,5,6-Heptachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 128 (2,2,3,3,4,4-Hexachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 180 (2,2,3,4,4,5,5-Heptachlorobiphenyl)	<LOD	<LOD	11.1	6.5
PCB 170 (2,2,3,3,4,4,5-Heptachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 195 (2,2,3,3,4,4,5,6-Octachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 206 (2,2,3,3,4,4,5,5,6-Nonachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 209 (2,2,3,3,4,4,5,5,6,6-Decachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
Total	87.1	104.7	127.0	138.7

LOD = 5.4.

non-irradiated and irradiated digested sludge. This indicates that the digestion processes caused the degradation of the most PCBs congeners thus no further significant degradation could occur by irradiation. Gamma irradiation seems to have pronounced effect on PCB 52; it reduces the initial concentration by 50% in raw sludge and by 100% in digested sludge.

Several PAHs and PCBs congeners were not detected as they are below the limit of detection (LOD < 0.11 $\mu g \cdot kg^{-1}$ and < 0.54 $\mu g \cdot kg^{-1}$) for PAHs and (LOD < 5.4 $\mu g \cdot kg^{-1}$) for PCBs.

4. Conclusion

Precaution must be taken when applying sewage water and sludge to agricultural soils due to their content of organic and inorganic contaminants. These contaminants, even at low concentrations, represent a negative impact on crop quality, human health, and the environment.

Lower concentrations of PAHs were recorded in orange fruits and soils than of PCBs. PAHs are hydrophobic compounds, which are difficult to mobilize (uptake) due to their low water solubility. The existence of these compounds in the fruits indicates their transfer into the food chain and the subsequent harmful effects on human health. Their persistence in soil can result in the pollution of the ecosystem. Gamma irradiation of sewage sludge could be a useful tool to reduce the levels of sludge contamination with toxic organic pollutants.

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