

The Fate of Phthalates in Surface Waters during Humus Removal by Precipitation

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Abstract: Phthalates are esters of aromatic 1,2 di-carboxylic acids and are widely found in surface waters and their removal is necessary because of their effects on human health. Humic material in water can adsorb phthalates and may be precipitated along with phthalates. The fate of phthalates in surface waters during humus removal by precipitation has been investigated in the laboratory with well characterised humic substances from the “NOM typing project” (Natural Organic Matter typing project from Norway). Water samples have been prepared with humus samples from the project to mimic natural surface waters and a mixture of phthalates containing di-methyl, di-ethyl, di-propyl, di-butyl and di- (2-ethyl) hexyl phthalates (DEHP) were added to the water samples. After a week standing the humic material in the samples was precipitated by alum flocculation. After filtration, the remaining water was analysed for phthalates using solid phase extraction and Gas Chromatography. The results show that all the phthalates except DEHP were removed together with humic material in water. The concentration of DEHP can still exceed the allowed limit for phthalates and alternative techniques are needed to remove DEHP before the water is free from phthalates for human consumption.

Keywords: Phthalates, humus, Precipitation, Gas Chromatography

Introduction

Phthalates are esters of aromatic 1,2 di-carboxylic acids and are widely used as plasticisers since their introduction in the 1920's. Plasticisers are combined with thermoplastic resins to increase the flexibility, extensibility and workability of the polymer. The flexible polyvinyl chloride (PVC) plastic industry is one of the beneficiaries of the plasticisers. PVC is unique in its acceptance of plasticisers being compatible with a wide range of plasticiser structures at a variety of temperatures and conditions.

Of the one million tonnes of plasticisers used in Europe, approximately 0.9 million tonnes is phthalate esters and a half million tonnes of it is Di (2-ethyl) hexyl phthalate (DEHP) which is a common plasticiser in PVC. The main regions of phthalate ester consumption are in building and construction, home furnishings, transportation, clothing, food packaging and medical products. The worldwide production of DEHP has been increasing during the past few decades and out of the one million tonnes of DEHP produced, about 1/3 is produced in Europe and 1/3 is produced in the USA.

The use of Phthalates as plasticisers has raised concern regarding their medical implications. Their effects on male fertility and their suspected oestrogenic activity are some of the raised concerns [1]. The intake of phthalates by humans appears to take place through two different routes. 1) food and 2) water.

Phthalates used as plasticisers in the food packaging material do not form a chemical bond with the polymer and lie freely in the polymer matrix. They can migrate into the food stuff from the food packaging material. Raw food stuffs like meat, fish and vegetables and consumer products such as confectioneries, biscuits and cakes use packaging materials containing phthalate plasticisers. Furthermore, phthalate esters are used in the aluminium foil-paper laminates that are used in packing butter and margarine [2] and in the packaging and processing of cream and cheese [3]. The phthalates such as di-butyl phthalate (DBP) and DEHP used in the outer surface of the packaging materials have been shown to migrate to the inner surface and even into butter and margarine [3]. The extent of the penetration of phthalates into food stuff depends on the duration of contact with the wrapper, temperature and the type of plasticiser involved.

Environmental contamination of phthalates is another concern. The surface water is contaminated by phthalate esters leaking from the plastic products disposed in the environment. Furthermore, water disposed from industries is contaminated by phthalates because of the usage of plastic tubings and products in the processing industries. Various levels of phthalates are shown to be present in different water sources [4,5]. The air in urban areas is also polluted by phthalates. This is due to the plasticised products, which may be disposed in a landfill site or incinerated. Some phthalates remain stable at high temperatures during incineration and are lost to the atmosphere and carried down to water sources by rain.

Phthalates in surface water can also arise from non-anthropogenic sources. Phthalic acid is present in wood, oxidation products of lignin, microorganisms, humic substances and coal. Furthermore, phthalates are common constituents of plant material and are intermediates in biochemical pathways. Aliphatic alcohols present in plant waxes together with phthalic acids lead to phthalates in nature.

The discussions above clearly show that the water sources of an urban water supply are contaminated by phthalates. The health concerns require their removal or reduction in their concentrations to an accepted level ($6\mu\text{g}/\text{dm}^3$) [6] before the water is supplied to consumers.

There are many ways to remove phthalates from surface water. UV photolysis in combination with hydrogen peroxide oxidation [7], Reverse osmosis, nanofiltration and ultrafiltration [8] can be applied to remove phthalates. Furthermore, wastewater treatment processes can also remove phthalates [9]. The removal efficiency may vary depending on their structures.

Surface water contains humic material originating from soluble organic residues from plants and animals. It may also contain pollutants from industry, pesticides

and other contaminations from the environment. Humus present in surface water is complex, poly-functional and has the ability to adsorb molecules and ions. The efficiency of adsorption depends on the chemical nature of the molecules and the surface functionalities of the humus molecules in water. Generally, the humus molecules are highly polar and hence attract highly polar molecules. Humus molecules function as adsorbent to some of the organic molecules and inorganic ions in water and these may be precipitated along with humus during purification process.

A study of adsorption of phthalates by humic material in water solutions should involve quantitative determination of phthalates after removing the humic material by chemical or physical means. Phthalates in water have been quantitatively determined by traditional solvent extraction followed by GC or GC-MS analysis [10,11]. They have also been quantitatively determined using solid phase extraction technique with different sorbants followed by GC or GC-MS analysis [6,12-14]. It was opted to use solid phase extraction with C-18 modified silica gel as adsorbant because of the high recovery of dialkyl phthalates [10] that needed quantification in this study. Quantification of phthalates was then carried out by gas chromatography.

The aim of this paper is to investigate whether phthalates are effectively removed during humus precipitation. The humic samples used in this study have been well characterised under the "NOM typing" project and their composition may reveal some characteristics related to phthalate adsorption in relation to their chemical properties. The adsorption characteristics of humus involve several physical and chemical parameters and chemometrics, a multivariate analytical methodology is obviously a candidate for the characterisation and correlation analysis in this work.

Experimental

Water samples were prepared by using humic material from seven different water sources [15,16] that were used in the "NOM typing" project. The humus samples were isolated from eight different locations in the southern part of Norway. The nature of the corresponding catchments differs; however, all samples were from areas with no influence of agriculture or local industry [15,16]. Nine bottles were filled to contain each with 1dm³ milli-Q water. Eight of the water bottles were dissolved isolated humus material from the above mentioned water sources. Dissolved amount of each humus sample is given in Table 1. No humic material was added in the ninth water sample.

Five different phthalates namely di-methyl, di-ethyl, di-propyl, di-butyl and di-(2-ethyl) hexyl phthalates were used as samples representing phthalates in water. The phthalates were purchased from Sigma-Aldrich Norway AS and used without further purification potassium-aluminium sulphate [KAl (SO₄)₂.12H₂O] also known as alum was purchased from Merck, Darmstadt, Germany.

Table 1. Details regarding the water samples, their total isolate content, Dissolved Organic Carbon content and the amount of humus dissolved in the water samples used in this study.

Water sample	Total isolate mg/dm ³	DOC mg/dm ³	Dissolved amount of humus in mg/dm ³
Trehørningen	24.3	4.8	11
Hellerudmyra (May)	57.2	17.7	10.4
Aurevann	24.5	4.8	11
Maridalsvann	20.9	2.7	11.5
Birkenes	24	3.4	10.5
Humex B	25	7.4	10.6
Gjerstad (limed)	25	4.2	10.7
Gjerstad (unlimed)	23.8	5.6	11.1

Standard solution of phthalates was prepared by mixing particular amounts of phthalates (Table 2) in methanol. One half cm³ of phthalate mixture was added in all the nine bottles so that the concentration of phthalates in each of the water sample was approximately 20 µg/dm³. After a week standing the water samples were prepared for humus precipitation by flocculation. Six of the samples (200 cm³ portions) were placed in six 1 dm³ beakers and were added 1 cm³ of 1M alum. The addition of alum caused a decrease in the pH and the pH of the solutions was adjusted in between 5.5-6.5. The samples were then stirred for 2 hours using a Flocculator (Flocculator SW1, Stuart Scientific, England). The flocculator was set to a speed of 100 rpm. The same procedure was repeated with remaining two humus samples. The last plain water sample was left to stand without further treatment. This sample would serve as a reference. After two days of standing, gelatinous precipitate was settled out and the water above became perfectly clear. All the eight samples treated with alum solution were filtered through a Buchner filter funnel.

Table 2. Concentration of phthalates in water samples

Phthalate	Concentration of phthalate in standard solution mg/100 cm ³	Concentration of phthalate in water samples µg/dm ³
DMP	5.9	29.5
DEP	4.233	21.165
DPP	4.103	20.5
DBP	3.215	16.075
DEHP	4.01	20.05

Bond elut column containing C-18 modified silica gel (500mg) from Analytichem International was used for the extraction of remaining phthalates in the filtered water samples. For each extraction, a bond elut column was conditioned using 10 cm³ methanol and 10 cm³ water. The water sample (200 cm³) was passed through the column at a rate of 4 cm³/min by using a water aspirator (Fig. 1). The column was then dried by letting the aspirator on for 10 minutes. Phthalates from the bond elut column were eluted using a VAC-ELUT apparatus from Analytichem International using 1 cm³ of methanol containing di-nitryl phthalate as reference standard. Eluted phthalates were collected in glass tubes and then concentrated by a stream of nitrogen.

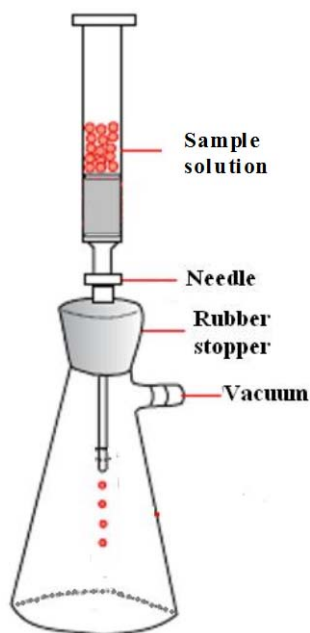


Fig. 1. Apparatus used for solid phase extraction

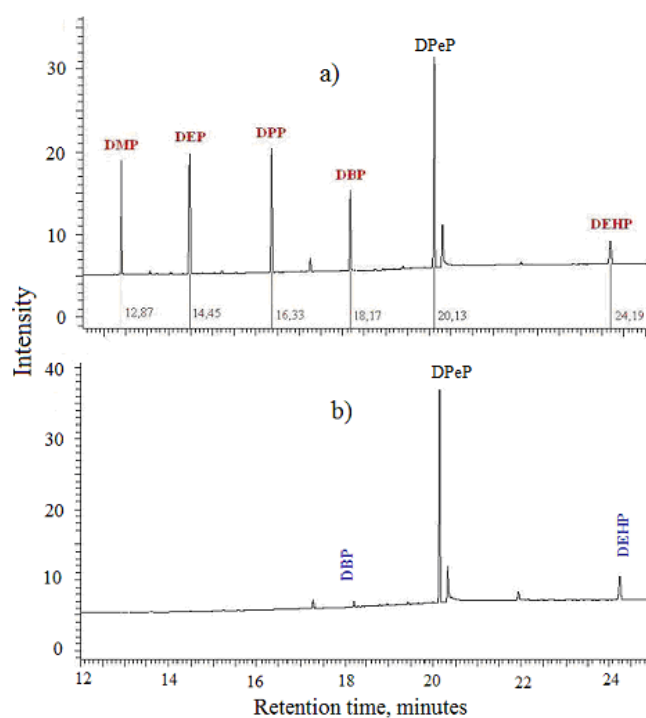
The gas chromatographic analysis was carried out on a Hewlett Packard 5890 series II gas chromatograph with a 0.32 mm (internal diameter) 30 m cross linked methyl silicone column with FID detection. A temperature program with an initial temperature of 60 °C at 1 minute and then a temperature rate of 10 °C/min up to 250 °C and then a final time of 10 min at 250 °C was used. The concentrated solutions were then analysed by gas chromatography.

The peaks in the chromatograms were integrated and quantified with respect to the reference standard.

Results and discussion

Facts regarding the water samples used in this work can be found elsewhere [15, 16]. Chromatograms of the phthalates extracted from the reference water sample and phthalates extracted from a water sample after precipitation of humic material are given in Fig. 2 a and 2 b respectively.

The numbers clearly reveal that the phthalates are preferentially adsorbed by humic material in the water sample. During precipitation by alum flocculation these phthalates are brought down together with the humic material present in the water sample. The concentrations of phthalates added to the water samples containing humic material are given in Table 2. The quantities of phthalates adsorbed by different humic material in water samples in $\mu\text{g}/\text{dm}^3$ and in percentage of the started amount of phthalates are given in Table 3 and 4 respectively.



A closer look at the table clearly shows that DMP, DEP, DPP and DBP are almost completely removed during precipitation. Only the DBP in two humus samples had around 90% adsorbed. However, the results from the DEHP shows that the adsorption by humic material ranged from 5-55% with exception of one sample which adsorbed around 70% of the DEHP.

These results are in agreement with several articles indicating the persistence of DEHP in surface waters [13, 17]. This is also giving us a clue that the higher concentrations of DEHP reported in the surface waters may be partially due to the moderate ability of humus towards adsorption of DEHP molecules.

Table 3. Quantity of phthalates adsorbed during humus removal by precipitation in $\mu\text{g}/\text{dm}^3$.

$\mu\text{g}/\text{dm}^3$	DMP	DEP	DPP	DBP	DEHP
1. Trehørningen	29,432	21,078	20,445	15,461	7,940
2. Hellerudmyra (May)	29,403	20,997	20,482	14,988	1,0309
3. Aurevann	29,390	21,009	20,408	14,287	5,499
4. Maridalsvann	29,453	21,035	19,656	14,047	7,301
5. Birkenes	29,441	21,132	20,361	15,580	7,469
6. Humex B	29,468	21,146	20,484	16,025	11,109
7. Gjerstad (limed)	29,472	21,142	20,480	15,979	13,854
8. Gjerstad (unlimed)	29,472	21,143	20,452	15,886	11,217
9. Reference sample	29,5	21,165	20,5	16,075	20,05

Humus is the most important source of organic carbon in the environment. Its colloidal character and high surface functionality make them excellent adsorbents of molecular pollutants and facilitate the processes of mobilization/immobilization of these in the environment. Humus consists of a large variety of organic molecules [18]. Furthermore, they contain micro-porous structure in their bulk matrix. The adsorption characteristics of humus samples depend on the surface functionalities. There is another process partition [19] can also influence the uptake of organic molecules by humic material. The organic molecules penetrate in the pores and held there by Van der waals forces. The efficiency of the partition process depends on the size and size distribution of the micro-pores. The DEHP molecules are large and bulky because of their side chains and only the large pores can accommodate these molecules.

The moderate ability for the humus to take up DEHP is a concern because DEHP is one of the phthalates that is used in very large quantities for the production of plastic and plastic related material for consumer goods. The availability of DEHP in water can cause health problems in humans and can be toxic for water living creatures. Special Chemical/physical methods are necessary to bring down the concentration of DEHP to an acceptable limit ($6\mu\text{g}/\text{dm}^3$). Water sources that are present in industrial areas may contain higher concentrations of DEHP that may be health hazardous.

Table 4. Quantity of phthalates adsorbed during humus removal by precipitation in %.

%	DMP	DEP	DPP	DBP	DEHP
1. Trehørningen	99,760	99,590	99,733	96,181	39,599
2. Hellerudmyra (May)	99,670	99,204	99,912	93,241	5,142
3. Aurevann	99,627	99,264	99,550	88,875	27,425
4. Maridalsvann	99,841	99,384	95,884	87,384	36,414
5. Birkenes	99,801	99,842	99,322	96,921	37,254
6. Humex B	99,893	99,909	99,920	99,688	55,405
7. Gjerstad (limed)	99,905	99,893	99,903	99,403	69,096
8. Gjerstad (unlimed)	99,906	99,897	99,765	98,823	55,944

A cross-validated Partial Least Squares (PLS) analysis [20-22] was carried out with percentages of phthalates adsorbed by the humus samples as dependent variables and DOC (dissolved organic carbon) values as dependent variables. Furthermore, a second calibration was carried out with poly hydroxyl aromatics (PHA), one of the bio-polymer constituent [16] in the humic materials as dependent variable. A plot between measured and predicted DOC for all the 8 samples are shown in Fig.3a. The plot clearly shows that the sample five is an outlier. A new calibration without sample 5 gives a linear correlation ($R^2=0.86$) between measured and predicted DOC values (Fig.3b). This correlation clearly indicates that the adsorption of phthalates depend on the organic carbon content of the humic material in the solution. It is also an indication that the adsorption of phthalates increases with the aromatic content of the humic material. This fact is revealed by the third calibration mentioned above. A linear correlation shows that the adsorption of phthalates increases with increasing PHA content (Fig. 4) of the humic material in the water samples.

The adsorption of phthalates by humic material is one of the important processes for transport of phthalates in surface waters.

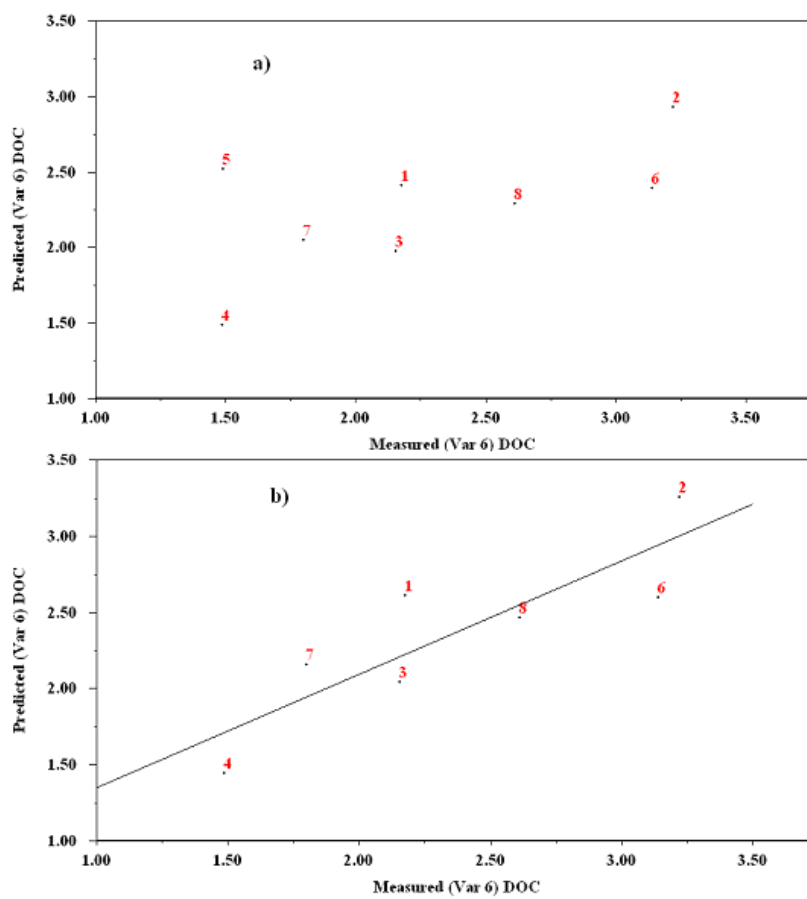


Fig. 3. A plot of measured versus predicted DOC from PLS analysis. a) with sample 5 b) without sample 5.

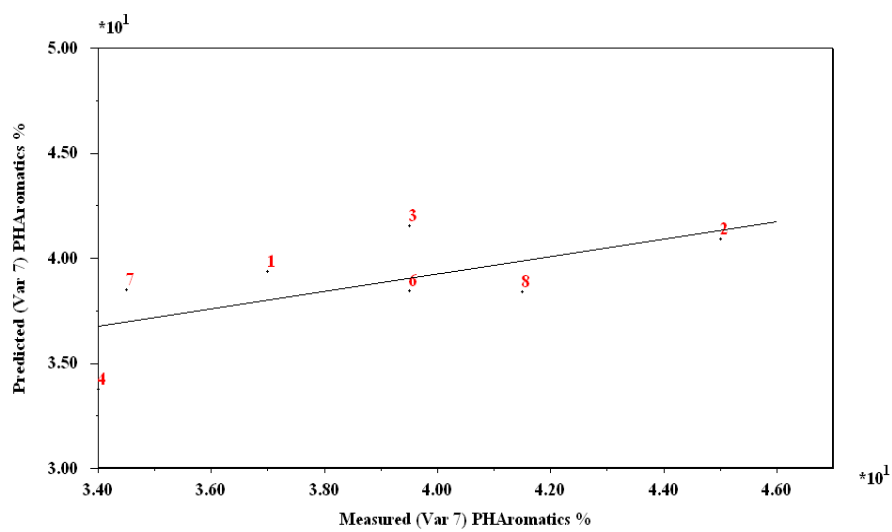


Fig. 4. A plot of measured versus predicted PHA from PLS analysis

Conclusion

It has been shown in this paper that the phthalates can be adsorbed and remain bound to the humus matrix. The whole complex matrix can be precipitated by using alum and thereby remove phthalates from surface waters. Most of the phthalates found in surface waters can be removed by precipitation technique. Di-(2-ethyl) hexyl phthalates are not effectively adsorbed onto the humic matrix. This can be due to several factors such as its solubility in water, its bulky size and the availability of the groups containing oxygen atoms to form hydrogen bonds with the humic material.

The only mechanism that operates between DEHP and humic material is the weak Van der Waals forces. The weak adsorption mechanism of phthalates onto humic material is clear from the fact that the phthalates are solvent extractable because they do not form any strong bond with humus molecules.

The concentration of DEHP remaining in water ranges from 7 to 13 $\mu\text{g}/\text{dm}^3$. The difficulty in complete removal of some higher phthalates by precipitation clearly illustrates the need for other techniques in addition so that the concentration of the phthalates can be brought under the allowed limit. The analyses also illustrate that the organic carbon content of the humic material or in other words the aromatic content of the humic material plays an important role in the adsorption of phthalates.

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