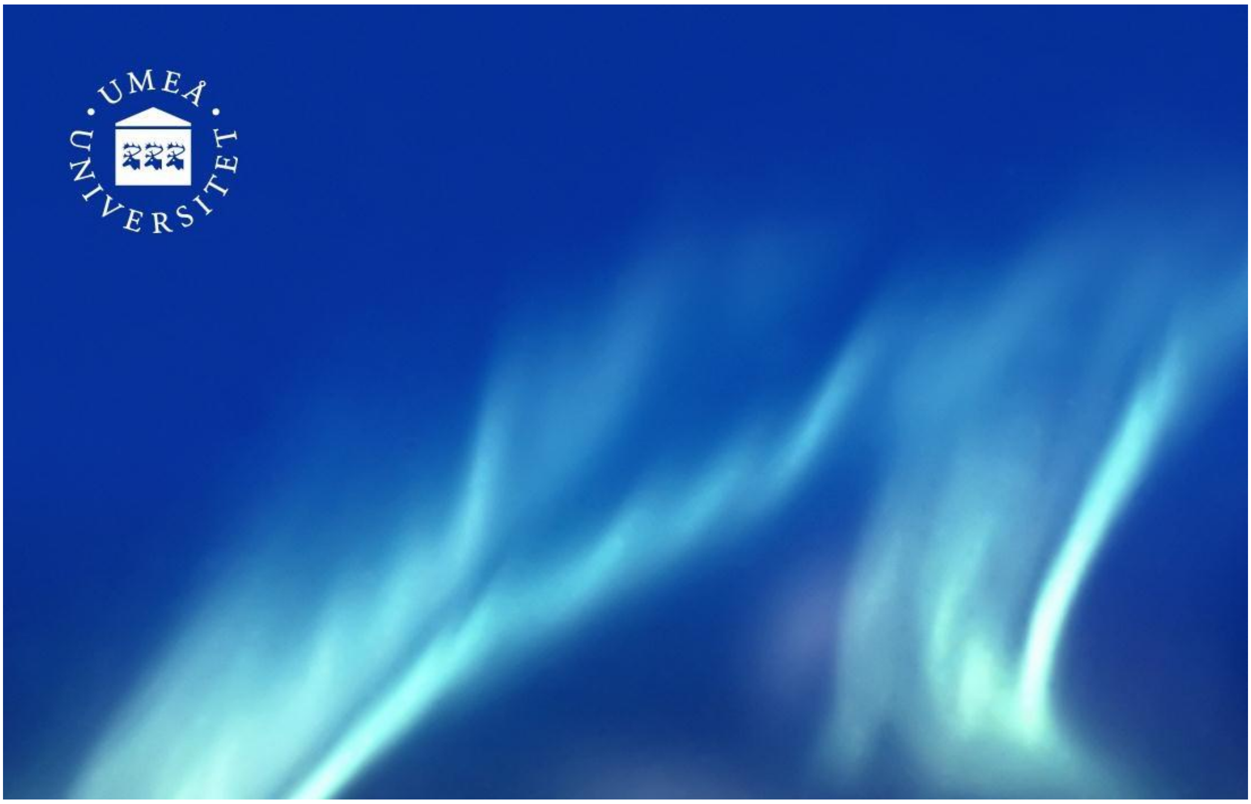

Leachability of Polychlorinated Biphenyls (PCBs) from Naturally Aged Soil in Relation to the Composition and Concentration of Dissolved Organic Matter (DOM) at Different pH

Majid Mustafa

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Department of Chemistry, Umeå University
Supervisor: Mats Tysklind
Assistant Supervisor: Silviu-Laurentiu Badea
Examinar: Peter Haglund
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Abstract

Industrially contaminated soil commonly contains persistent organic pollutants (POPs) such as polychlorinated Biphenyles (PCBs), polychlorinated dioxins (PCDDs) and dibensofurans (PCDFs). PCBs being a class of contaminants with very persistent very and bio-accumulative properties have adverse effects on both human and wildlife and hence highly prioritized for remediation. One important aspect in the risk assessment is the mobility and leaching behavior from soil/sediments to surface and ground water. The present study comprised of three parts i) Evaluation of leaching of PCBs from soil to water phase at different pH using batch leaching test and GC-HRMS analyses, ii) Characterization of dissolved organic matter (DOM) by FTIR analysis, and iii) Exploration of possible correlation between leachability and DOM by Multivariate Data Analysis (MVDA). For this purpose, the seven indicator PCBs (28, 52, 101, 118, 138, 153, 180) and additional PCB congeners (PCB 66, 105, 156, 187) were selected. Batch leaching tests were conducted to evaluate the aqueous leachability of PCBs. It was observed that the log k_d-values for all PCBs were decreased with the increase of pH (3 to 9). In addition, all PCBs were highly influenced by the release of total organic carbon (TOC), except the lower chlorinated PCB 28. However, PCB 28 and PCB 52 showed the highest leachability 5160±1240 ng/L and 2530±723 ng/L respectively at pH 9.3±0.1 and TOC 465±115. The ratio of concentration of ortho-PCBs (mono to di-ortho and di to tri-ortho) was calculated to investigate the influence of molecular structures on leachability. Only, ratio of concentration of PCB 180 (di-ortho) to PCB 187 (tri-ortho) indicated a possible influence of the ortho-chlorine substitution through pH effect on leachability of PCB 187.

In the second part of the project, characterization of DOM by FTIR spectroscopy, showed clear changes in carboxylate and C-H aliphatic functional groups peaks from lower pH (i.e. pH 3) to higher pH (i.e. pH 9). Amide/Amine peaks became more prominent and intense at higher pH. A slight shift (towards lower wavelengths) in the peaks of aromatic C=C and C=O from lower to higher pH was observed, indicating de-protonation of carboxyl groups and the release of intra-molecular hydrogen bonds between keto-groups and the neighboring carboxyl groups of DOM. Furthermore, principal component analysis (PCA) modelling explained the differences in DOM in pH gradient, showing that functional group O-H from alcohol/phenol or amine amide was the most influential at lower pH (pH 3 - 5). Similarly, C-O stretching of ester and/or O-H deformation of COOH and/or saturated C-N stretching was the most influential at higher pH (pH 6 - 9). The predicted explained variance (Q2) for three significant components was 97.0 %. For exploring the possibility to establish a model describing relationship between the leachability of the different PCB congeners and the characteristics of the DOM (FTIR signal att different pH), a OPLS model was created. Predictive component 1 of OPLS model explained 50.3% and orthogonal component showed 42.7% variation in the data. Moreover, PCX-Y model indicated the different behaviour of PCB 28 from all other PCBs.

Key Words: leachability, PCBs, DOM, TOC, k_d, ortho-PCBs, FTIR

List of Abbreviations

DL-PCBs	dioxin like **-** polychlorinated biphenyls
FTIR	Fourier transform infrared spectroscopy
GC-HRMS	gas chromatography – high resolution mass spectrometry
I-PCBs	indicator PCBs
m-o PCBs	mono-ortho polychlorinated biphenyls
DOM	dissolved organic matter
K_d	soil-water distribution coefficient
Kow	octanol-water partition coefficient
LAS	linear alkylbenzene sulfonate
NDL-PCBs	non-dioxin like polychlorinated biphenyls
OPLS	Orthogonal projections to latent structures
PCA	Principal component analysis
PCBs	polychlorinated biphenyls
PCDDs/Fs	polychlorinated dibenzo-*p*-dioxins/furans
POPs	persistent organic pollutants
TEQ	toxic equivalent
TOC	Total organic carbon

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1. INTRODUCTION

During the last decades, increasing scientific and public concerns have given risks associated to contaminated soils and soil as a secondary source of contamination. Extensive activities have been taken to reduce the release of pollutants to water and air, which in many cases resulted in general decreasing levels of contaminants in the environment. These efforts now also increase the awareness that secondary sources such as contaminated soils can act as a significant source not only on a local or regional scale. Soil also receive contaminants from other compartments, e.g. via long-range diffuse emissions [1]. From the soil, these pollutants may be mobilized and transported to aquatic ecosystems through ground water or water run-off. Additional pathways can be through re-volatilization to air in gas-phase or the spread of particles.

In Europe, as many as approximately 3 million sites are estimated to be contaminated of which more than 240.000 sites are estimated to be an object for remedial actions [2]. Inventories coordinated by the Swedish Environmental Protection Agency reported approx. 80,000 contaminated sites throughout Sweden [3] of which approximately 1200 sites are classified as being in the highest risk class. Specific classes of contaminants found at the highest risk class are e.g. heavy metals and persistent organic pollutants (POPs) such as polychlorinated dioxins (PCDDs) and dibensofurans (PCDFs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

Crucial in the management of the large number of sites is improved risk assessment and cost effective procedures for many groups of contaminants. It is a challenging task to address the complex issues related to contaminated soils in order to accomplish the risk reduction needed for the protection of humans and wildlife. Especially, risk assessment for persistent organic pollutants (POPs) have been of immense concern, regardless of production and usage bans. For these compounds increased knowledge of the fundamental processes determining the environmental transport is especially important owing to their persistence nature and high concentrations even in remote ecosystems [4].

The present study focuses on one of the classes of POPs, viz. the polychlorinated biphenyl (PCBs), a well-known class of pollutants included in the Stockholm Convention [5]. Consequently, they have been listed in the “priority pollutants” implemented by e.g. US Environmental Protection Agency (USEPA), European Commission (EC) and the State Environmental Protection Administration (SEPA) in China [6]. PCBs are very persistent, very bio-accumulative contaminants and have adverse effects on both human and wildlife [5]. Although, the PCB production and usage have been banned, their ubiquitous nature and toxicity in combination with large reservoirs in secondary deposits, such as landfills and industrially contaminated sites, still makes them highly relevant for scientific community and environmental policy makers [7].

1.1 Aim

The present study focuses on understanding the environmental conditions determining the mobility of PCBs in soils and sediments. The mobility is the key factor for environmental risk and fundamental understanding of PCBs can also be extrapolated to other classes of POPs with similar physico-chemical properties. The main objectives were to study the pH-dependency of PCBs as well as dissolved organic matter (DOM) and to explore the possible relation between PCB and DOM leachability.

The specific aims of this project were:

- To study and describe the pH-dependent leachability of selected PCBs
- To establish pH-specific K_d-values based on the concentration of PCBs at different pH values
- To characterize the pH-dependent leachability of DOM depending on pH
- To characterize the composition of DOM-fractions at different pH using FTIR spectroscopy
- To using multivariate data analysis explore possible correlation between DOM and leachability of PCBs

An overall preview of complete project is shown in figure 1.

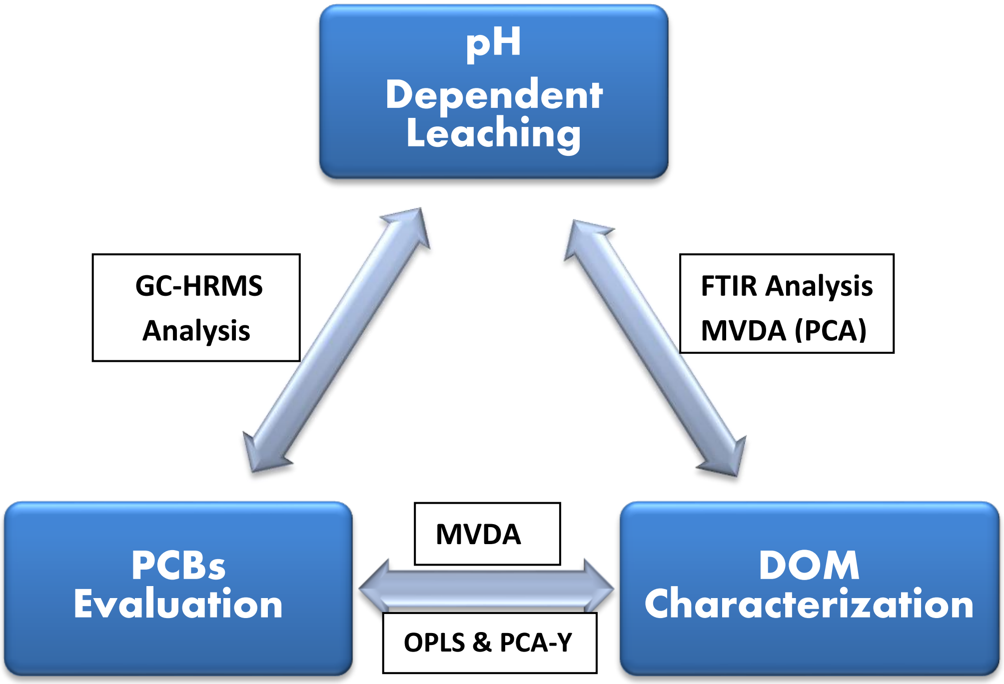


Figure 1: Schematic sketch over the study

1.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls, are organic aromatic compounds, belonging to one class of pollutants with chemical formula C12H10−*n*Cl*n*, n ranging the chlorine atoms from 1 to 10 (see Fig. 2).

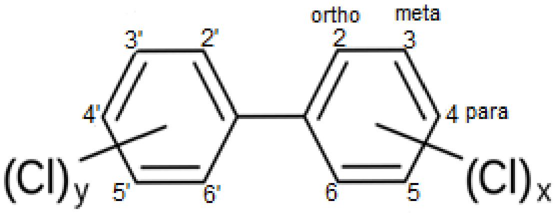


Figure 2: PCBs Structural formula

Depending on the number of Cl-atoms attached to two rings, 209 congeners of PCBs are theoretically possible. However, only approximately 130 congeners have been identified in commercial PCB products [4]. These specific congeners are named according to the Cl-atoms position on the two rings of biphenyls, respectively [8]. The PCBs are numbered according to IUPAC giving each specific congener a number which are the common way of expressing specific PCB compounds. Alternatively the substation pattern is given by indicating the carbon atoms substituted with chlorine. IUPAC names and the corresponding substitution patterns of the PCBs included in current study are listed in Table 1 below.

All congeners of PCBs can be divided into two sub-groups on the basis of their toxicity. The first group contains 12 PCBs congeners, called dioxin like-PCBs (DL-PCBs) or planer PCBs. The name assigned to them is determined by their toxicity resemblance to dioxins (PCDD/Fs). The second group, called non-dioxin-like PCBs (NDL-PCBs) comprises rest of 197 congeners (compounds)[9]. These NDL-PCBs have other toxicological profile. DL-PCBs are considered more toxic because it is related to their binding and activation of the aryl hydrocarbon receptor (AhR) signal transduction pathway. For the NDL-PCBs, having Cl-atoms in the ortho-position, the interaction with AhR is weak [10]. NDL-PCBs have also been shown other toxicological effects that are independent of the AhR-mediated toxixity and follow multiple other toxic pathways. For example endocrine, neurological, immunological neuroendocrine, and carcinogenic effects have been observed [11].

From an environment point of view, the major part of PCB research has focused on seven congeners of PCBs, the so-called Indicator PCBs (I-PCBs, congeners nos. 1 – 7 in Table 1). These I-PCBs are abundant and widespread compounds in the environment and animal tissues and markers of the major components of the technical mixtures of PCBs used. In addition, in the present study, four otho-PCBs were selected to investigate the influence of molecular structures on leachability. Literature studies also show that the selected ortho-PCBs i.e. 66, 105, 156 and 187 are abundant in maternal blood and other human tissues [12, 13].

Table 1. IUPAC number and IUPAC names for selected PCBs.

No.	IUPAC no.	IUPAC name
1	**28**	2,4,4’-Trichlorobiphenyl
2	**52**	2,2’,5,5’-Tetrachlorobiphenyl
3	**101**	2,2’,4,5,5’-Pentachlorobiphenyl
4	**118**	2,3’,4,4’,5-Pentachlorobiphenyl
5	**138**	2,2’,3,4,4’,5’-Hexachlorobiphenyl
6	**153**	2,2’,4,4’,5,5’-Hexachlorobiphenyl
7	**180**	2,2’,3,4,4’,5,5’-Heptachlorobiphenyl
8	66	2,3’,4,4’-Tetrachlorobiphenyles
9	105	2,3,3',4,4'-Pentachlorobiphenyl
10	156	2,3,3’,4,4’,5-Hexachlorobiphenyl
11	187	2,2',3,4',5,5',6-Heptachlorobiphenyl

Moreover, comparing the DL-PCBS and the NDL-PCBs, the maximum toxic equivalent quantity (TEQ) level for DL-PCBS is set at 2.3 pg/kg/day but for the ND-PCBs, no restrictions have been specified [10]. Studies had shown that human exposure to the sum of I-PCBs exceeds especially in gestating women [14]. Thus NDL-PCBs are e.g. listed in the priority of food contaminants monitored by Global Environmental Monitoring System (GEMS) (WHO Regional Office for Europe, 2004).

It is reported that approximately 99% of environmental PCBs mass are found in soil [6] . Therefore, from environmental point of view, it is significant to study the aspect of PCBs disappearance and transport rate from soil by various mechanisms to other compartments of the environment.

1.2.1 Use and Production

PCBs have been used industrially for various applications in the form of different commercial mixtures like Sovol, Clophen, Aroclor, Phenoclor, etc. These industrial chemicals have been used for the period 1930s to the 1979, in electrical transformers and capacitors, as cooling fluid, as lubricants and hydraulic fluid, and also in plasticizers and adhesives [15]. Larry and Larry. (2001) reported the uses and applications (in percent) of PCBs in US during 1930-1975 based on work by Durfee *et al*. (1976) and others [16, 17] (See Fig. 3).

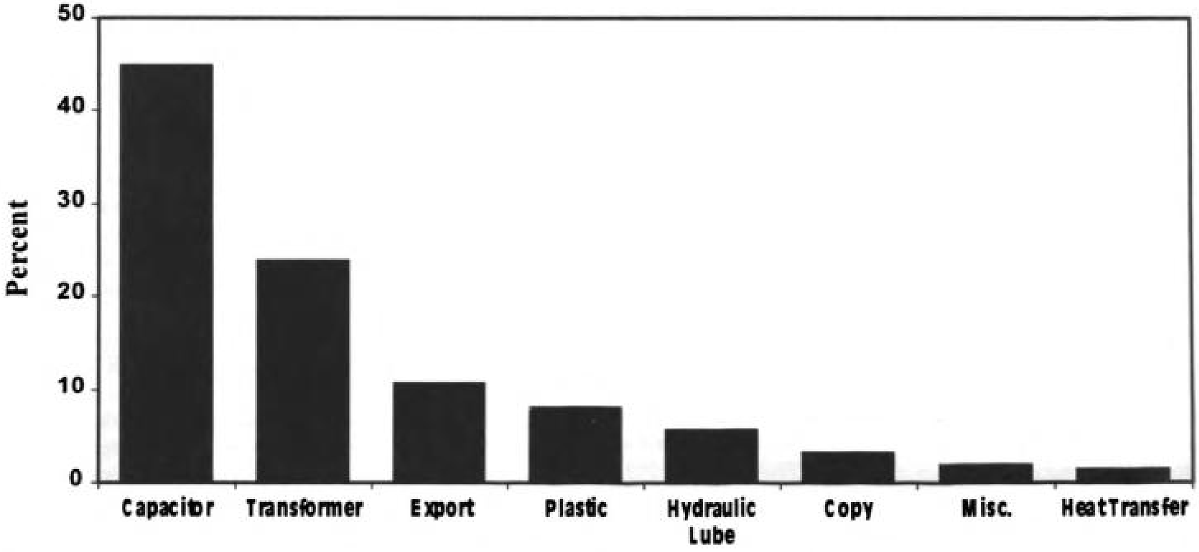


Figure 3: Applications of PCBs in United States based on Sales Records 1930-1975

The overall global PCBs production is estimated to be more than 1 million tones [18]. Although the total production of PCBs is unknown but the production of Spain, France and Italy have been estimated approximately 3 x 10^5 t during 1954-1984 [19]. In China, about to 10000 t of PCBs were produced from 1965-1974, with 9000 t as trichlorobiphenyl and 1000 t as pentachlorobiphenyl [1].

1.2.2 Legislative regulations

Health and environmental issues upshot the legislative regulations which finally provoked the cease of PCBs production in developed countries by the late 1970s [20]. USA, western Europe and Japan reduced and completely banned the PCBs production in the 1970s and early 1980s, while in Russia the production was only stopped in 1993 [21].

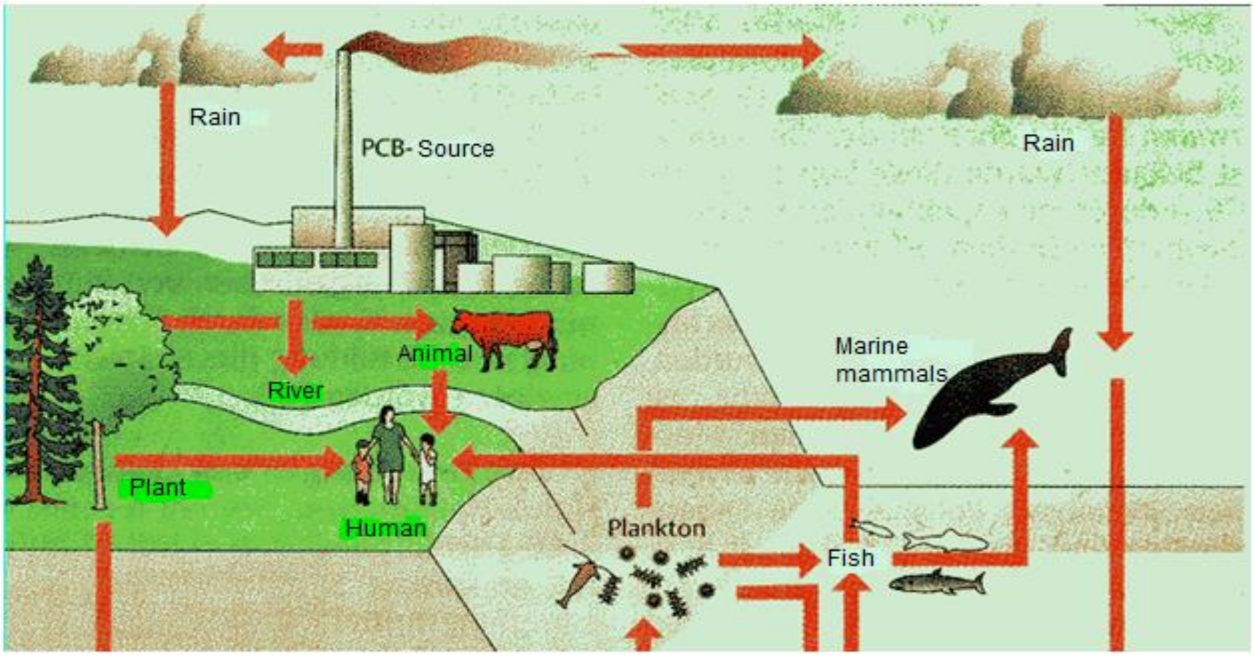
In Sweden, the first step was taken in 1971 to restrict PCBs by introducing the Act on PCB and they were completely banned in 1972 (http://www.chem.unep.ch/pops/POPs_Inc/proceedings/bangkok/WAHLS1.html) while USA banned PCBs in 1979 ((http://www.epa.gov/epawaste/hazard/tsd/pcbs/pubs/about.htm) and China in 1974 [1].

1.2.3 Fate and Distribution

Fate and distribution of PCBs are not only controlled by their source, but also by multi-factors such as atmospheric depositing, mixing, pH, sorption and partitioning in sediments and water column [22] . It is also intimately associated with the mobility of organic carbon (OC) because PCBs sorption processes are strongly influenced by OC [23]. Soil being a major source of PCBs may responsible for transport to the other compartments of the environment (biotic and abiotic). Thus, in some cases, PCBs are leached into ground water not only as dissolved phase but also as a suspended phase, either in an emulsion with other solubilizing agents or sorbed onto the mobile soil colloids [24]. Similarly, volatilization is another major pathway for PCB loss that is [23].

Further, marine sediments also behave as an important reservoir for PCBs in the ecosystem [25]. This is because; PCBs being hydrophobic partitioned itself to particulate matter in the aquatic environment and settled down through water column to the sediments which ultimately makes coastal marine sediments their final sink [22]. Tatsukawa and Tanabe (1990) stated that large proportions of escaped PCBs into the environment reside in open-ocean waters and coastal sediments[26]. For example, Jian shen *et al*. (2012) reported that tetra-, penta- and hexa-PCBs are dominant homolog in the Baltimore Harbor accounts for 61.7% and 60.1% of the total PCB concentration in the bottom sediment and water column, respectively [23].

Figure 4 shows a schematic overview of the cycling of PCBs in the environment and exposure pathways. Generally, it is agreed that dietary intake is the main route of human exposure to PCBs. Plant is the most first link in the food chain [6] however of lower importance as direct exposure pathway for humans. Intake of fish, meat and milk, however are recognized as the principal routs of human exposure to PCBs [27]. Li *et al*. (2001) reported that animals accumulate specific PCBs while metabolizing others [28]. For example, PCB congeners 118, 138 and 153 represent 12-39, 32-34, 22-25, 37-46 and 30-55% of the sum of PCBs in the fish, sediment, coral, crab and eel, respectively[29].



http://www.eco-knowhow.eu/basin/pop-monitoring.htm

Figure 4: Schematic illustration of the environmental transport of PCBs

1.2.4 Toxicity and Hazard

In humans, a broad range of health toxic effects have been associated to high exposure of PCBs. Some PCBs disrupt reproductive cycles of wildlife and humans because they are considered to behave as environmental hormones [30]. Particularly, it has been speculated since last two decades that numerous human male reproductive disorders, such as cryptorchidism, low sperm counts, hypospadias and testicular germ cell cancer, might be linked to increased PCBs exposure in early human life [31]. Evidences exist that chlorinated biphenyls disrupt the reproduction of aquatic animals as well [32].

Moreover, PCBs have been revealed to cause cancer and non-cancer effects. In non-cancerous effects, developmental effects, hormonal dysfunction, chloracne, endometriosis and reduced mental performance [33], nervous system alterations, ocular effects, liver damage, endocrine disruption immune deficiency and gastrointestinal system bleeding [34] have been reported.

1.3 Methodology

1.3.1 Leaching tests

Contaminated soils may be the secondary sources of PCBs in the environment. Therefore, their mobility from the contaminated soil must be estimated through risk assessment of site. The measurement of PCBs in soil is a complicated task, especially when their concentration is low (ppb to ppq) and contemporarily, other interfering compounds are present at higher concentration. To overcome these problems, various leaching tests have been developed estimate the mobile fractions of organic compounds in the soil [35]. Generally, all leaching tests are designed to provide the concentration of contaminants in water in contact with the solid material. The concentration may significantly depend on the contact time between water and respective solid material. Moreover, all tests follow the same chemical laws and mass transfer principles [36].

Leaching tests may comprise of two types, viz. A) Batch leaching tests, and B) Column leaching tests. Generally, both test designs can be considered to have different possibilities and limitation depending on the purpose of the investigation. In general, batch test is simple and column test is more practical approach and close to the field process. Batch leaching test was originally developed for sewage sludge [36].

In different countries, different leaching tests are used for different purposes. In Sweden, the most popular and utilized leaching methods are the European standards that are employed for the characterization of waste entering landfills as inert, acceptable, non-hazardous or hazardous. The procedure comprises two parts: a two-step batch (static) leaching test and an up-flow column leaching test. In both tests, de-ionized water is used but after a new amendment released by the international organization for standardization [37] 0.001 M CaCl2 (a weak ionic solution) is consumed instead of de-ionized water to reduce the leaching of dissolved organic matter (DOM) and to mimic the ionic strength of soil solution [38].

1.3.2 Batch leaching test

In the batch leaching procedure, the eluent is constantly in contact with the sample of the granular sample. The purpose of this procedure is to set up pseudo equilibrium conditions. The equilibrium is manipulated by the solubility of the compounds present in the solid [39]. The quantity of leached contaminant strongly depends on the time during which material (soil) is in contact with the leachant until the equilibrium is established [40]. Once equilibrium is stabilized, release of compound is dependent on the chemistry of the liquid phase and the geochemistry of the solid material rather than contact time [39].

1.3.3 Leaching dependency /Factors affect the leachability

Generally, the factors that affect the leachability are classified as: (a) factor relating to sample such as loss on ignition, geometry and contents of pollutants; (b) leachant concerning factors, such as redox potential, pH level, co-existing matter, ionic strength and temperature, and; (c) factors such as Liquid to Solid ratio (L/S ratio) and contact time [41]. Sorption has also been known as an important parameter to retard the movement of organic compounds [42]. In addition, sorption is one of the fundamental processes that decide the fate of the hydrophobic compounds in ground water. It is normally described in simple manner by using K_d concept.

Sorption is reversible and instantaneous and can be explained by K_d value. Sorption process is not affected by other organic compounds because there is no competition for sorption sites among different organic compounds [43].

In the present study, the general considered factors are contact time (shaking time), temperature, ionic strength and L/S ratio but more specifically pH and co-existence of dissolved organic matter (DOM) to know there effect on leachability.

1.3.3.1 pH

pH is one of the key factors that decide the mobility of organic compounds in the soil/sediments because many important processes such as sorption, dissolution, speciation etc, are pH dependent or may indirectly associate with pH [42]. Consequently, small change in pH can directly result considerable difference in the pollutant mobility. For example at neutral pH, the overall sorption has been found predominated by sorption of the dissociated fraction [44]. Furthermore, Kalbe *et al.* (2008) clearly demonstrated that importance of knowing the buffering capacity of contaminated material in studies of pH-effects in batch leaching test [45].

1.3.3.2 Dissolved Organic Matter (DOM)

Leachability of organic compounds in soil/sediments is directed by the sorption/desorption and dissolution processes in relation with DOM [45]. Organic contaminants release slowly in porous soil because release is often dependent on diffusion [46]. DOM may be transported through the soil as colloids [47] and hence may increase the release rate of hydrophobic organic compound (HOCs) from soil [48]. Therefore, if colloidal facilitated release is not considered there will be a risk of underestimation of the dispersal of HOCs [49]. Compounds of concern may contain halogenated biphenyls, polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene, dibenzofurans, halogenated dibenzodioxins and others [50]. Schramm *et al.* (1995) determined the leachibility of PCDD/F in fly ash column and soil eluted with linear alkylbenzene sulfonate (LAS) water and pure water. He observed significant increase in leachability by using LAS [51].

1.4 Multivariate Data Analysis (MVDA)

Rapid development of science and technology has promoted the use of advance methods and instruments for research and development, for example NIR, UV, HPLC, GC, MS, NMR, Gene array etc. Typically, these methods, when applied to complex samples, produce data with hundreds of variables and observations. To extract the useful and systematic information from this data regarding our problem, we need to use appropriate data analytical tools in reasonable time. Different tools and methods have been used for this purpose like univariate method (UV), Multiple Linear regression (MLR) and Multivariate Data Analysis (MVDA). Further, we need methods which in short time analyze our data and approaches including changing one variable at a time cannot handle the complexity of present problems and processes and thus sophisticated and computer based techniques must be used. MVDA is one of them which solves these kinds of problem and provides reliable results.

MVDA, enables efficient ways of getting overview the data, classify data and to obtain regression models seeking correlation between complex data tables. Basically, MVDA methods are projection techniques, in which we assume different observation (samples) as a swarm of points and then project them onto the latent variable in a hyper plane. MVDA also allows us to vary the variables simultaneously and systematically. Different tools of MVDA are used to deal with different types of problem. For example, Zbytniewski *et al.* (2002) applied multivariate analysis to compare naturally occurring organic matter and compost origin organic matter (in soils and natural amendments). They concluded that it is possible to discriminate samples from different origin in an unequivocal manner by utilization of MVDA [52].

1.4.1 Principal Component Analysis (PCA)

PCA represent a multivariate data set as a low dimensional plane, most often consisting of 2-5 dimensions, in such a way that overview of the data is obtained. In Particular, PCA distinguish the relationships and find the trends among large number of samples [52] (see Fig. 5).

On the basis of data set, new variables are calculated by the linear combination of the measured original parameters [52]. These new non-correlated variables are called principal components (PCs) or latent variables. They (PC) are consisting of *scores*, t_i and *loadings*, p_i. First PC explains the largest variation in the data, 2nd PC orthogonal to first PC express the 2nd largest variation in the data and so on [53]. All systematic variation is explained by the model and non-systematic variation can be expressed by the model residue. Mathematical relationship of fitted model is given below;

$$\mathbf{X} = \mathbf{TP}' + \mathbf{E}$$

T: matrix of score vectors **P:** matrix of loading vectors **E:** residual matrix

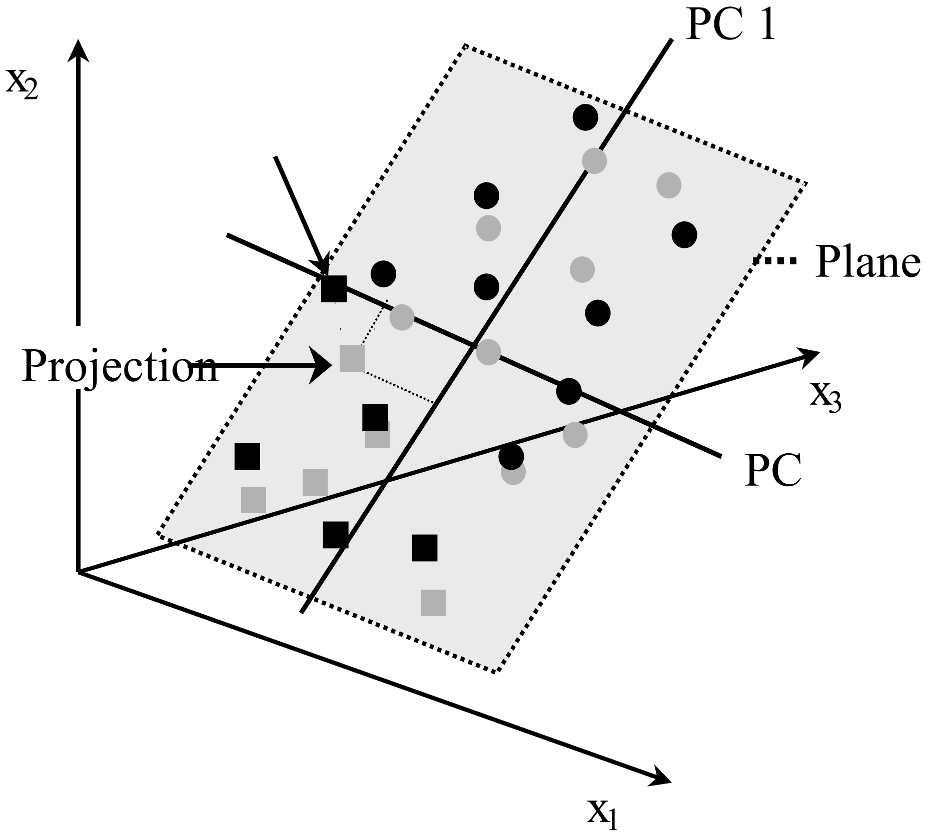


Figure 5: This figure illustrates the Principal components (PCs) with observations and variables in the plane. Observations are projected onto the PCs and give scores while loadings are the angels of variables to the PCs. Overall this is a schematic diagram of PCA.

The number of significant PCs is determined by cross-validation [54] and also by eigenvalue [52].

1.4.2 Orthogonal Projection to Latent Structures (OPLS)

Orthogonal projection to latent structures (OPLS), an extended form of Projections to latent structures (PLS) is developed by Trygg and Wold in 2002. It enables us to remove systematic variation from data X not correlated to the response Y. In other words, OPLS allows separate modeling of Y-orthogonal and Y-predicted variation in data X [55] and all correlated information in concentrated in one principal component i.e. Y-predicted. This thing reduces the model complexity and facilitates interpretation. Although, variation in Y-orthogonal can be useful and interesting but for instance it is unrelated to the question at hand (i.e. the model predictions) [56], Hence may disturb our model.

Mathematically, the OPLS model of Data matrix X is given in the following Equation:

$$\mathbf{X}=\mathbf{T}\mathrm{p}\mathbf{P}\mathrm{Tp}+\mathbf{T}\mathrm{o}\mathbf{P}\mathrm{To}+\mathbf{E}$$

Tp: Y-predictive score matrices, **T**o: **Y**-orthogonal score matrices, **P**p and **P**o are corresponding loading matrices, **E**: the residual matrix [56].
More Schematic overview of OPLS explained by Trygg and Wold (2002) is given in Figure 4.

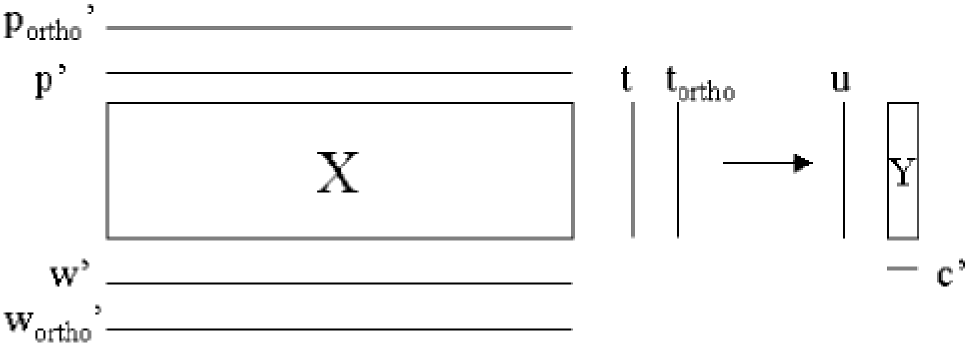


Figure 6: This figure illustrates the schematic diagram of all the steps in OPLS

At the moment, OPLS has been employed extensively in various investigations utilized in chemometrics, transcriptomics and metabolomics including NIR spectral data, GC-MS data, NMR data and HPLC-MS data [57]. A study conducted by [58], revealed that by applying this method (OPLS) model clarity was enhanced and interpretation of model was improved significantly for both non-correlated and correlated variation in NIR Spectra [58].

1.5 Fourier transforms infrared (FTIR) Spectroscopy

Since last decade, an explosive growth in utilization and application of FTIR spectroscopy has been occurred. Because relative low cost of instrumentation, simple sample preparation and methodology has lifted FTIR up to the category of the promising approaches. Although, other sophisticated techniques are also present but they however, are expensive and time consuming techniques.

FTIR spectroscopy is a generally used technique to distinguish the type of organic matter in soil such as carbohydrate, cellulose, lipids, etc through vibration of their structure chemical bond [59]. High variability of organic matter in soil and rapid demand of results make other high-tech techniques less favorable. On the other hand, procedure used for characterization of DOM by FTIR gives satisfactory results by giving information about structure and composition of DOM and does not require complicated and extensive sample preparation. In addition, FTIR spectroscopy offered such a method that can complement already existing procedures. Kim and Yu (2005) used FTIR to characterize the organic fractions of DOM at a conventional water treatment plant. They observed that aliphatics increased and aromatics decreased in the organic fraction of organic matter [60].

Moreover, different procedures can be followed for sample preparation of FTIR. Freeze drying is one of the possibilities that is used to investigate the small amount of DOM composition in water samples [61].

2. MATERIALS AND METHODS

2.1 pH static test

A batch leaching tests were performed on 50 g aliquots of PCBs contaminated soil sampled from Västervik (Sweden) contaminated site, homogenized prior the test. Samples from L1-L8 were prepared for the individual leaching experiments at pH 3-9 respectively, performed in replicates. The tests were performed in 0.5 L Schott bottles at a liquid to solid ratio (L/S) of 10, which was reached by using 0.5 L of an aqueous solution containing 0.001 M $CaCl_2$. The pH was measured with a METTER DELTA 320 pH meter equipped with a Thermo Fischer electrode and adjusted to pre-selected set points in the range of 3-9 with HCl or NaOH solutions of 1, 0.1 and 0.01 M. About 50 g of PCBs contaminated soil was weighted and added into the above mentioned 0.5 L Schott bottles containing the pre-selected pH solutions. 50 g of clean OECD soil added in 0.5 L Scholl bottle was used as blank. Each test was performed in duplicates at the following pH: 3, 5, 7, 8 and in triplicates at the pH 4, 6 and 9. Due to buffering capacity of the soil, the pH was measured again and adjusted to the initial values when was appropriate. The totally 18 bottles were put in a horizontal shaker, run at 120 rpm, for 48 hours, in order to obtain equilibrium between contaminants in solution and contaminants in the soil. The pH of every leachates ware measured again at the end of the test, prior to filtration. After this, the leachates were separated from the soil by filtration, first using a cellulose filter followed by vacuum filtration through a glass fiber filter with the pore diameters of about 0.7 μm (Sartorius Stedim Biotech GmbH, Gottingen, Germany).

2.2 Extraction of soil leachates

After separation the leachates were spiked with 40 μL of Internal Standard (IS) solution containing ^{13}C-labeled PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180. All compounds were purchased from LGC Standards (Borås, Sweden). 400 mL of each leachate were then extracted by sequential liquid-liquid extraction with 3 X 50 mL dichloromethane using separator funnels. The organic extracts were evaporated using a rotavapor and were dried on columns with anhydrous sodium sulfate (Na_2SO_4). The rest of leachates were saved for further DOC measurements.

2.3 Extraction of soil samples

Five grams samples (dry weight) of the original PCBs contaminated soil were transferred in triplicates to pre-washed Soxhlet thimbles. The samples were then spiked with 100 μL ^{13}C-

labeled PCB 80 solution to check the efficiency of the Soxhlet extraction, after which they were extracted with toluene using Soxhlet Dean-Stark extractors for 24 hours. Due to the high levels of PCBs from the soil, only a fraction of about 1: 400 (by weight) from the organic extract was used further for clean-up and analysis of PCBs. The extraction procedure for the soil particles trapped on the filter was identical to that for the soil samples.

2.4 Clean-up and analysis of PCBs

The aliquots of the extracts intended for PCB analysis was spiked with 40µL of the same ^{13}C-labeled Indicator PCBs as the ones used for the leachates and 50µL of tetradecane, after which they were evaporated until near dryness (the residual volume of tetradecane) using a rotavapor. The residual extracts were dissolved in 2-3 mL n-hexane and transferred to multi layer silica columns for clean up [62]. The columns consisted of, 16 mm i.d. glas columns packed with the following components from top to bottom: 1cm layer of Na_2SO_4, 4cm of H_2SO_4 acidified silica, 4 cm of neutral silica, 4 cm of KOH alkaline silica and 2 cm of glass wool. The PCBs and were eluted with 50 mL of n-hexane which was collected in round flasks and evaporated again until near dryness (the residual volume of 50µL tetradecane). The bulk PCB fractions were spiked with 40 µL of recovery Standard (RS) solution containing ^{13}C-labeled PCB 97 and PCB 188. The PCBs fractions was evaporated until only the tetradecane remained, and were then transferred to 200 µL GC-vials for analysis.

The PCBs were analyzed by high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS). The system used was an Agilent 6890N gas chromatograph coupled to a Waters Autospec Ultima NT 2000D mass spectrometer, the latter with a mass resolution of 10000. The mass spectrometer was operated in electron impact ionization (EI) /selected ion monitoring (SIM) mode. Analyses were performed on non-polar DB-5 MS column (60 m x 0.25 mm x 0.25 µm from J&W Scientific, CA, USA). The GC oven temperature program started at 190°C for, then increased by 3 °C/min to 260 °C, then 10 °C/min to 325 °C and hold for 0.4 min.

2.5 Total organic carbon analysis

Total and dissolved organic carbon was determined using a Shimadzu TOC-5000 high temperature catalytic oxidation instrument with NDIR detection. Samples were acidified and sparged prior to analysis. Calculation of carbon concentrations was made with potassium hydrogen phthalate as standard substance.

2.6 Fourier transforms infrared (FT-IR) measurements

To characterize the DOM, the extracted leachates from soil were placed in the refrigerator for 24hours at -20^{0}C. The frozen leachates were put in the freeze drier. Pressure and temperature were maintained at 0.2-0.1m Pa and -40^{0}C to -50^{0}C, respectively with strong vacuum. Samples were completely dried in powder form.

After freeze drying, 4 to 10 mg of dry samples were mixed with KBr and made total weight about to 400 mg. They were ground and homogenized by pestle and mortar. Spectra were recorded by using FT-IR (BRUKAR) instrument. The scanning conditions were as follow: 128 scans, a resolution of 4 cm^{-1} and a spectral range of 4000–400 cm^{-1}.

2.7 Calculation of the distribution coefficient

The distribution of the contaminant between the solid and the liquid phase was described by the soil-water distribution coefficient (K_d), which is defined as follows:

$$K_d = \frac{C_s}{C_w}$$

Where C_s is the concentration of a compound in the soil (µg/Kg), and C_w the concentration of the same compound in the aqueous phasing (ng/L). The use of homogenously PCBs contaminated soil analyzed in triplicates allows the calculation of the soil-water distribution coefficient (K_d) based only the concentration of the compounds in the aqueous phase.

3. RESULTS AND DISCUSSIONS

3.1 PCBs Results:

3.1.1 Assessment of the distribution coefficients of PCBs

The logarithmic values of the distribution coefficient (log K_d) for all target PCBs are summarized in Table 1. The log K_d-values of all target PCBs decreased with the pH values, the highest values being recorded at the initial pH 3.32±0.01 and the lowest at initial pH 9.3±0.1. Overall, the log K_d-values recorded for all PCBs were highly influenced by total organic carbon (TOC), while the K_d-values recorded for PCB-28 were less influenced by TOC likely due to its higher solubility in water (0.085 mg/L) comparing with the other selected PCBs in this study and therefore they varied in lower range (3.3-5.5). The highest variation of K_d-values with TOC was recorded for PCB 187 (3.2-6.1) due to its high log K_{ow} (7.17) and very low water solubility (4×10^{-4} mg/L).

At the initial pH of 3.3 ±0.0 the log K_d-values were varying in the range 5.47±0.0 for PCB 28 to 6.6±0.0 for PCB 156, while at pH 9.3±0.1, the log K_d-values varied from 3.2±0.1 both for PCB 180 and PCB 187 to 3.9±0.1 for PCB 156. Overall, from the log K_d-values of PCBs recorded at the same pH, the log K_d-values of PCB 156 were always the highest comparing with the rest of PCBs. The results from Table 1 confirmed the previously literature studies [63, 64] and they showed that the tendency to leach is higher among the least chlorinated congeners (i.e. PCB 28).

*Table 2***.** The average log K_d values for target PCBs.

Compound	log Kd L1	Log Kd L2	log Kd L3	log Kd L4	log Kd L6	log Kd L7	log Kd L8	Kow [65]
PCB-28	5.47±0.01	5.72±0.03	5.57±0.13	5.63±0.15	4.25±0.06	3.83±0.01	3.34±0.11	5.67
PCB-52	5.71±0.01	6.03±0.05	5.92±0.02	4.53±0.14	4.20±0.11	3.76±0.01	3.22±0.12	5.84
PCB-66	5.79±0.03	5.98±0.05	5.88±0.02	4.54±0.13	4.19±0.09	3.80±0.01	3.25±0.10	6.20
PCB-101	5.92±0.01	6.19±0.06	6.08±0.02	4.55±0.13	4.19±0.10	3.75±0.01	3.24±0.11	6.38
PCB-105	5.92±0.02	6.18±0.06	6.13±0.06	4.59±0.12	4.17±0.09	3.73±0.00	3.25±0.11	6.65
PCB-118	5.78±0.01	6.01±0.06	5.92±0.03	4.39±0.12	4.16±0.09	3.71±0.00	3.21±0.10	6.74
PCB-138	5.78±0.02	6.01±0.07	5.92±0.02	4.39±0.12	4.16±0.10	3.71±0.02	3.21±0.08	6.83
PCB-153	5.84±0.04	6.00±0.09	5.94±0.06	4.45±0.12	4.16±0.11	3.72±0.00	3.22±0.07	6.72
PCB-156	6.62±0.01	6.76±0.07	6.70±0.01	5.10±0.13	4.73±0.08	4.43±0.01	3.93±0.07	7.18
PCB-180	5.91±0.08	6.03±0.09	5.98±0.01	4.52±0.12	4.15±0.10	3.71±0.02	3.20±0.07	7.21
PCB-187	6.05±0.02	6.25±0.09	6.14±0.03	4.49±0.12	4.14±0.10	3.68±0.02	3.20±0.07	7.17
Average initial pH	3.32±0.01	4.17±0.06	5.19±0.08	6.11±0.03	7.28±0.12	8.22±0.05	9.31±0.06	
Average final pH	3.95±0.01	4.16±0.03	4.79±0.04	5.28±0.03	6.33±0.01	7.20±0.01	8.05±0.35	
TOC (mg/L)	57.7	67.2±33.7	65.0±19.4	92.8±51.5	80.9±23.4	133.0±19.8	465.0±115.3	

Note. The L5 batch experiment was not included in Table 1 since it used clean OECD soil at pH 7.

3.1.2 Variation of leachability of indicator PCBs with DOC

In order to elucidate the influence of dissolved organic carbon on leachability of different PCBs, the concentrations of different PCBs were plotted as function both of pH and TOC. The results are shown in Figures 1A for PCB 28 and PCB 52 and in Figure 1B for PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180 respectively. The concentration of PCB 28 and PCB 52 varied from 38.2±1.0 ng/L for PCB 28 and 7.9±0.1 ng/L for PCB 52 in the experiment with the initial pH of 3.3±0.0 to 5160±1240 ng/L for PCB 28 and 2530±720 ng/L for PCB 52 respectively in the experiment with the initial pH of pH 9.3±0.1, while the total organic carbon was increasing from 57.7 mg/L (single replicate only) at initial pH of 3.3 ±0.0 to 465 ±115 mg/L at pH 9.3±0.1 (Figure 1A). Although showing the same trend, due to their lower initial concentrations in the soil and due to their hydrophobicity, the concentrations of PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180 in leachates were lower comparing with the above mentioned concentrations of PCB 28 and PCB 52. The concentration pattern of penthachlorinated indicator PCBs (PCB 101 and PCB 118) was somewhat similarly. While the concentration of PCB 101 in leachates increased from 1.1±0.0 ng/L at pH of 3.3±0.0 to 508±130 ng/L at pH 9.3±0.1, the concentration of PCB 118 in leachates increased from 1.2 ± 0.0 ng/L (pH 3.3 ±0.0) to 409±98 ng/L (pH 9.3±0.1). Also the hexachlorinated indicator PCBs (PCB 138 and PCB 153) showed a similar concentration pattern. The cconcentration of PCB 138 in leachates varied from 0.54 ±0.0 ng/L the initial pH of 3.3 ±0.0 to 201 ± 35.8 ng/L at pH 9.3±0.1, while the concentration of PCB 153 varied from 0.36 ± 0.0 ng/L (pH 3.3 ±0.0) to 153±24 ng/L (pH 9.31±0.06) (Figure 1B).

The concentration of heptachlorinated PCB 180 increased from 0.23±0.0 ng/L in the experiment with the initial pH of 3.3 ±0.0 ng/L to 120 ±19.8 ng/L in the experiment with the initial pH 9.3±0.1 while the total organic carbon was increasing from 57.7 mg/L (single replicate only) at initial pH of 3.3 ±0.0 to 465 ±115 mg/L at pH 9.3±0.1 (Figure 1B).

3.1.3 The variation of leachability of ortho-PCBs with DOC

In order to investigate the influence of molecular structure of selected ortho-PCBs on their leachability the ratio of concentrations of mono-ortho to di-ortho PCBs (PCB 66 to PCB 52 and PCB 105 to PCB 101) and the ratio of concentrations of di-ortho to tri-ortho PCBs (PCB 156 to PCB 153 and PCB 180 to PCB 187) were plotted vs. pH and TOC (see figure 2). The ratio of concentrations of mono-ortho to di-ortho PCBs varied from 0.89±0.0 for PCB 66 to PCB 52 ratio and from 0.63 ± 0.0 for PCB 105 to PCB 101 ratio (pH 3.3±0.0) to 0.99±0.1 for PCB 66 to PCB 52 ratio and to 0.62 ± 0.0 for PCB 105 to PCB 101 ratio respectively (pH 9.3±0.1), showing no clearly influence of the ortho-chlorine bonds substitution through pH effects on the leachability of PCB 52. Also the ratio of concentrations of PCB 156 (mono-ortho) to PCB 153 (di-ortho) varied from 0.10±0.0 at pH 3.3±0.0 to 0.12 ± 0.0 at pH 9.3±0.1 without any clearly trend showing no clearly influence of the ortho-chlorine bonds substitution through pH effects on the leachability of PCB 153. The absence of planarity effects was also observed by Koelmans et al. 2009 [66] in a sorption study of PCB to charcoal for the hexachlorobiphenyl congener couples

138/156 and 156/169, since the compounds in this homologue group might be too bulky to enable preferential adsorption of the planar congeners. Nevertheless, the ratio of concentrations of heptachlorobiphenyl congeners PCB 180 (di-ortho) to PCB 187 (tri-ortho) increased from 3.12 ± 0.48 at pH 3.32±0.01 to 4.27±1.09 at pH 4.17±0.06 and afterwards decreased to 2.23±0.05 at pH 9.31±0.06 clearly showing the influence of the ortho-chlorine bonds through pH effects on the leachability of PCB 187. In order to elucidate the molecular-level interactions controlling the sorption of organic compounds in soils, Zhu et al. [67] suggested that the π-donor solutes interact with π-acceptor sites in soil organic matter (SOM), including aromatic rings with multiple carboxyl groups, aromatic amines, or heteroaromatic amines. The π-acceptor ability of such aromatic moieties would increase with protonation and therefore is expected to appear at low pH values. This behavior could not be attributed to pH-dependent alteration of the hydrophobic character of humic substances, π-H-bonding, interaction with mineral surfaces, interaction with black carbons, solute co-planarity, or pH effects on solute activity coefficient. The above mentioned study [67] found that the apparent distribution coefficients (K_d) of PCB 52 (non-coplanar) and PCB 77 (co-planar) were slightly affected by the low pH of the leachate. The K_d-value of PCB 77 was greater influence than the K_d-value of its isomer PCB 52, a result that cannot be predicted just based on differences in log K_{ow} values. This could be due to the comparative difficulty of PCB 52 to achieve a coplanar ring conformation due to steric effects of the ortho-chlorines. Therefore we suggested that the decreased ratio of concentrations of PCB 180 (di-ortho) to PCB 187 (tri-ortho) at pH 3.3±0.0 of the leachate (Figure 2) might be cause by the impossibility of PCB 187 to achieve a coplanar ring conformation due to steric effects of the ortho-chlorines. Preferential sorption of coplanar molecules (PAHs, chlorobenzenes, and mono-*ortho*-substituted PCBs) relative to non-coplanar compounds has been observed by Jonker et al [68], and its cause is still unclear. However, to articulate this effect with surety we need to express more pairs of PCBs congeners.

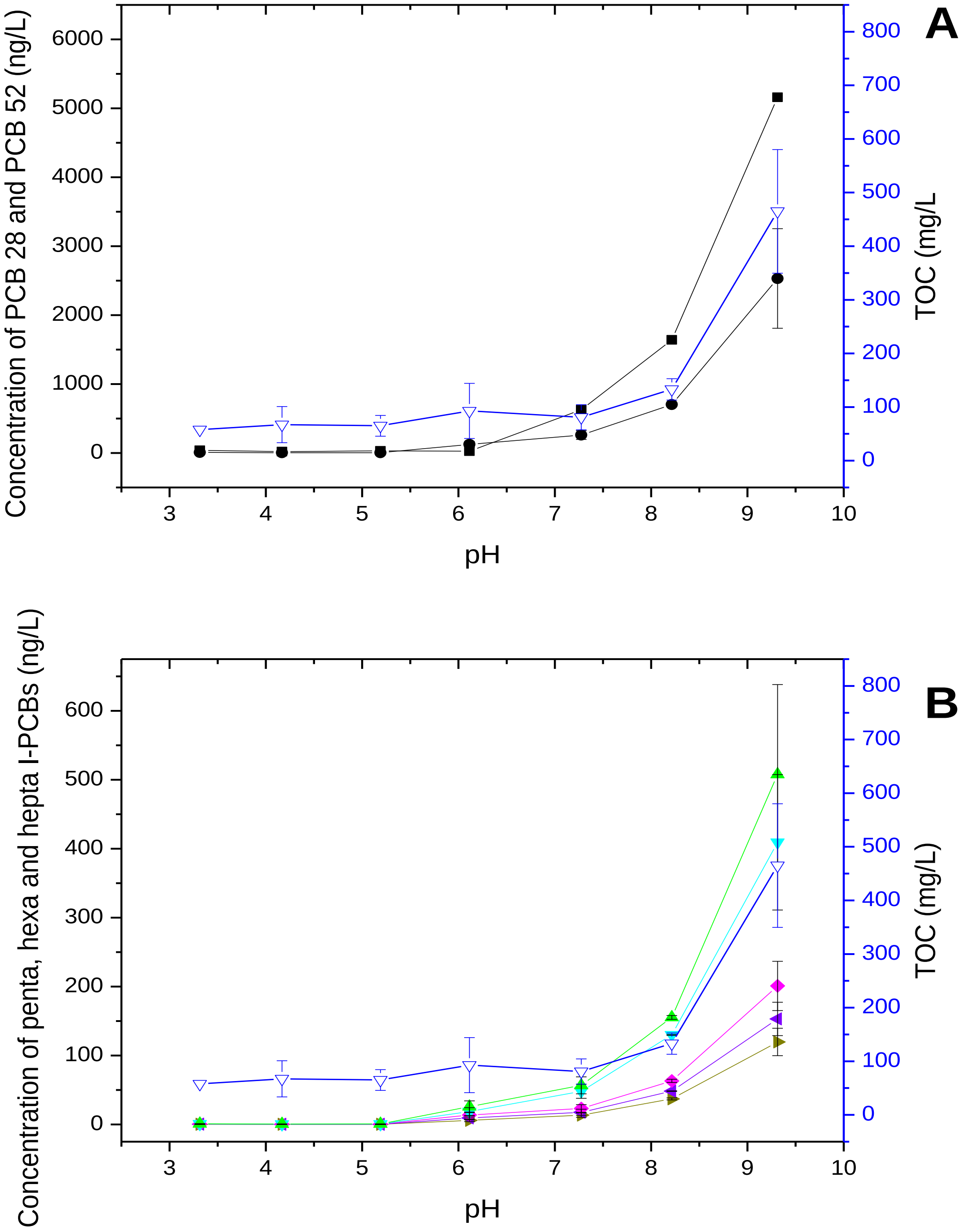


*Figure 7***.** Change in concentration of PCB 28 (■) and PCB 52 (●) and total organic carbon (▼) vs. pH (A). Change in concentration of PCB 101(▲), PCB 118(▼), PCB 138 (◆), PCB 153 (◀) and PCB 180 (▶) respectively and total organic carbon (▼) vs. pH (B).

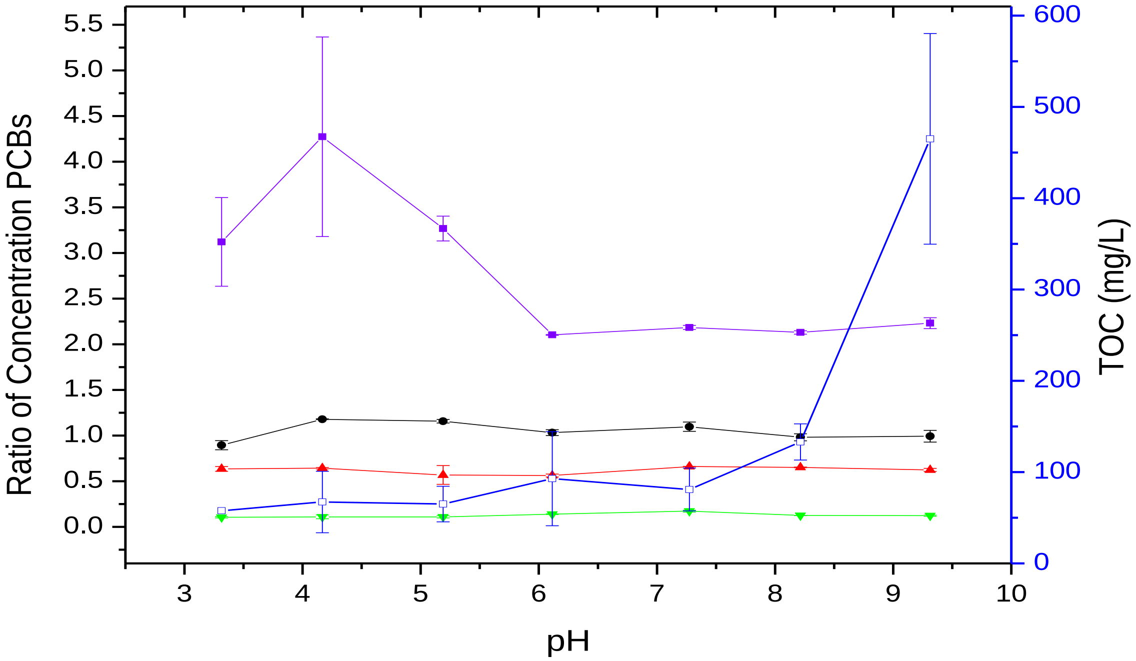


Figure 8. Change in ratios of concentration of PCB 66 to PCB 52 (●), PCB 105 to PCB 101 (▲), PCB 156 to PCB 153 (▼) and PCB 180 to PCB 187 (■) respectively and total organic carbon (□) vs. pH.

3.2 FTIR RESULTS

DOM including humic acid and fulvic acid has been demonstrated to be an important factor influencing the interfacial behaviors of hydrophobic organic contaminants (HOCs). FTIR has been used extensively for this purpose. It facilitates us to accommodate the information of DOM's functional and structural properties [69]. For interpretation of FTIR spectra in the current study, two extreme sample spectra at pH 3 (sample L1R1) and pH 9 (sample L8R1) respectively, are shown in figure 9. All the spectra are given in the Appendix 1.

A very strong and broad band at pH 3 around 3400 cm^{-1} is attributed to the overlap of O-H stretching of carboxylic acid, phenol and carbohydrates. The broadness of band is resulted from the inter-molecular and intra-molecular hydrogen bond interactions of COOH [70]. As the pH increases, the intensity and broadness of the band is decreased substantially as shown in spectra at pH 9. This change is due to the loss of hydrogen bonding at higher pH where more of the DOM is humic rather that fulvic acid. A shoulder peak at approximately 3270 cm^{-1} at pH 3 may because of amide N-H functional group. But as the pH increases to 9, the intensity of N-H (functional group) bands at 3350 cm-1 and 3180 cm-1 has increased prominently [71]. The reason might be that at higher pH humic acid increased and fulvic acid decreased. Similarly, the intensity and broadness of C-H aliphatic alkane bands 2925 cm^{-1} and 2860 cm^{-1} at lower pH (i.e. 3) are increased to 2943 cm^{-1} at higher pH (i.e. 9) [72].

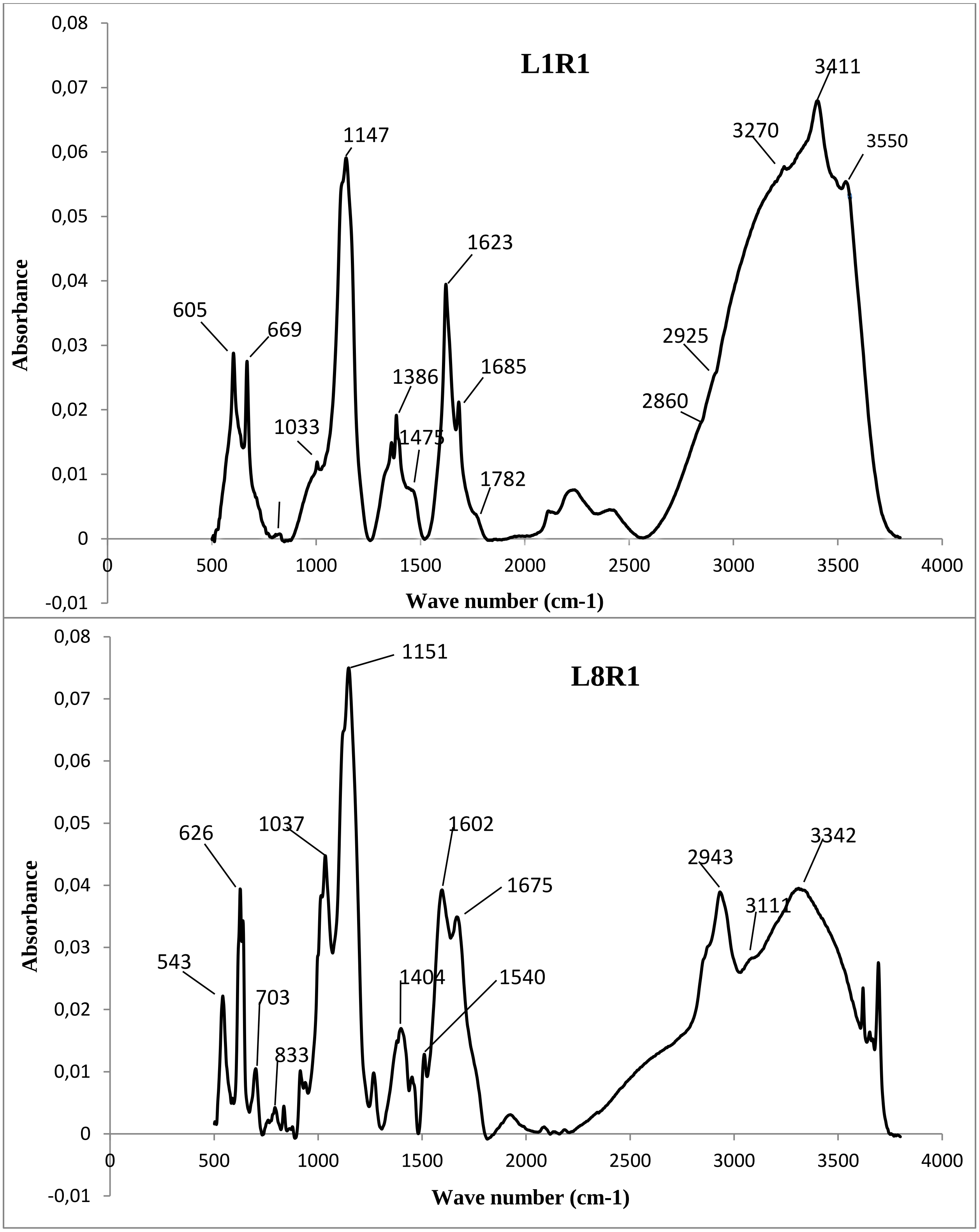


Figure 9. FTIR spectra of extreme samples (L1R1 & L8R1), showing Wavenumber (cm-1) on the ordinate and Absorbance on the abscissa.

Moreover, a band at 1782 cm^{-1} is resultant from carbonyl stretching of the protonated carboxylic acid function group at lower pH (i.e. 3) [73] but this peak disappeared as pH is increased from 3 to 9 because of the de-protonation of the carboxyl group [74]. Meanwhile, the absorption band around 1685 to 1623 cm-1 at pH 3 can be attributed to the aromatic C=C and de-protonated asymmetric carboxyl stretching The peak position slightly shifted from 1685 and 1623 cm-1 to 1675 and 1602 cm-1 at pH 8 and 9 (basic pH). The shift toward lower wavenumbers is attributed to de-protonation of carboxyl group and the release of intra- molecular hydrogen bonds between the keto group and the neighboring carboxyl group of DOM [74]. On the other hand, the symmetric stretching of de-protonated carboxyl group is appeared as a broad band around 1400 cm^{-1} [73]. Similarly, a small band of secondary amines/amide appeared at approximately 1540 cm-1 as pH is increased from acidic (i.e. 3) to Basic (i.e. 9) range [75]. Hay and Myneni (2007) reported that addition of base to the humic substances increases the absorbance around 1540 cm^{-1} which is a strong indication of de-protonation of carboxyl functional group [76]. A sharp peak at 1384 cm^{-1} that is more prominent from pH 4 to 8, may probably comes from nitrate [77] and/or C-H deformation of CH3 group [78]. The intensity of the peak increases as the pH increases from 3 to 6 and then again decreases from pH 7 to 9.

Furthermore, C-O stretching of phenol and/or O-H deformation of –COOH and/or C-O stretching of ester [78] and/or saturated C-N stretching are probably responsible for the intense band at approximately 1150 cm^{-1}. This band looks independent of pH change. Moreover, band at approximately 1035cm-1 is attributed to the C-O stretching of alcohol, ethers [78] and/or polysaccharides [79]. Intensity of band is varied with the variation of pH from 3 to 9. Hence, normal height peaks in the range of 600-800 cm-1 may be the characteristics of C-H stretching, C-Cl stretching and/or by the substitution at benzene ring [75]. Two sharp peaks at approximately 833 cm-1 and 703 cm-1 appeared at higher pH (7 to 9) are most likely N-H vibration of amine/amides groups [79].

These soil samples have more carboxylate and aliphatic components in DOM, as shown by the relative strength of carboxylic C=O stretch regions and the C-H stretching bands (just below the 3000 cm-1).

3.3 MULTIVARIATE DATA ANALYSIS RESULTS:

3.3.1 Preprocessing

Spectra from the FTIR instrument is shown in Figure 10A, where spectral region was set for the subsequent analysis (white background). Finally, base line correction and area normalization was done with in limit on all spectra. All this processing affected the properties of spectra that can be seen apparently in Figure 10B, that’s why all spectra were treated in the same way of processing.

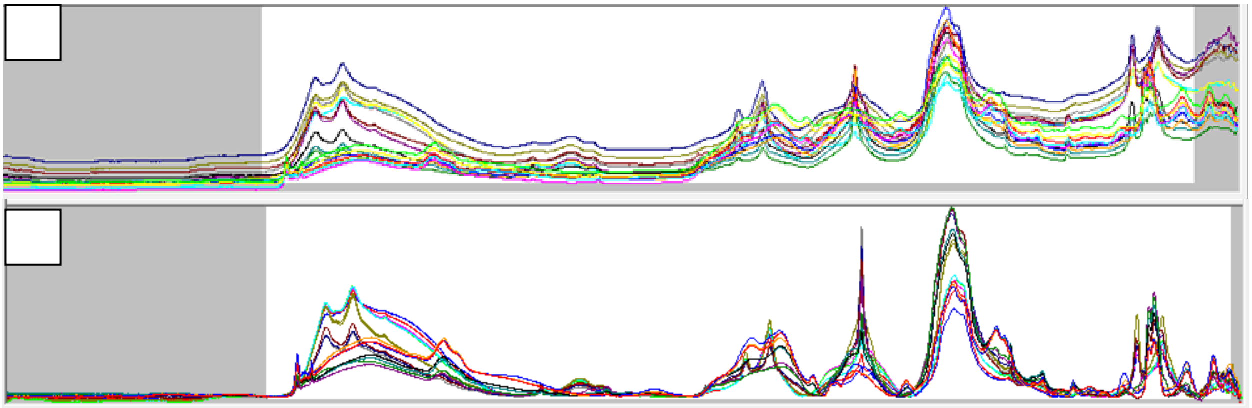


Figure 10. FTIR spectra before (A) and after (B) base line correction and Area Normalization

3.3.2 PCA modeling:

Processed spectra were converted into Matlab format after preprocessing because in SIMCA modelling, only this format is readable. Finally, PCA model was created by using Standard Normal Variate (SNV) spectral filter. PCA was generally used to explore the groupings and trends present in the data which can then be understood by quantifying the significance of variables in loadings plot. The sample scores and variable loadings for first two significant principal components (PC1 & PC2) of PCA are given in figure 1 & 2, respectively.

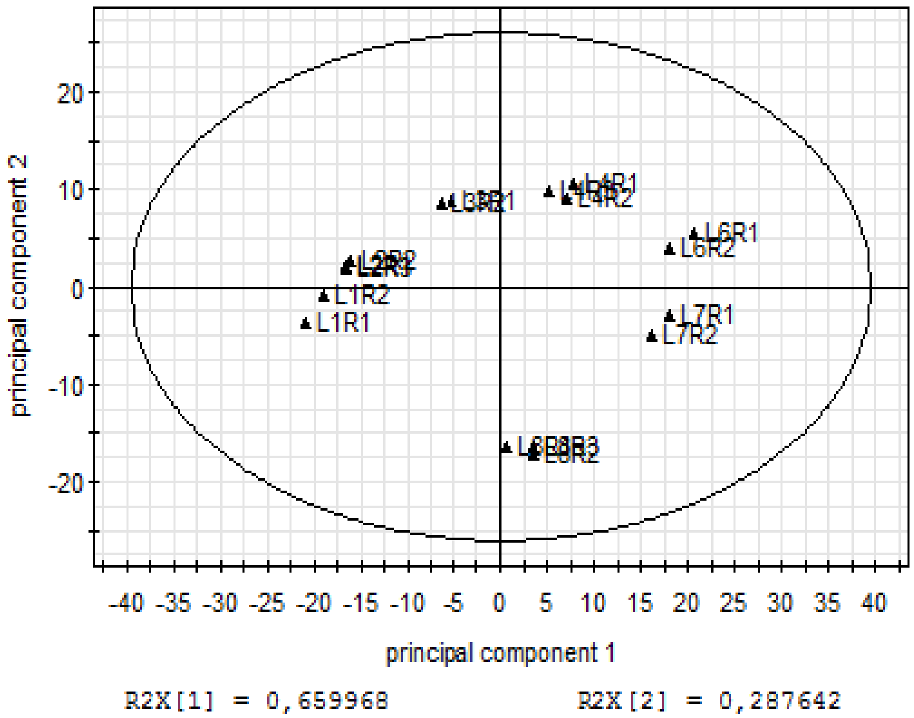


Figure 11. PCA scores plot, showing PC1 on the ordinate and PC2 on the abscissa

PC1 is explaining almost 66% of the variance in the samples and PC2 explains 28.7% of the total variation in the data X. PC3 is not shown here, elucidates 3.2% of variance. Moreover, Q2 for sum of all three components is 0.97 which is the indication of good model. All related parameters of PCA model are given in Appendix 2.

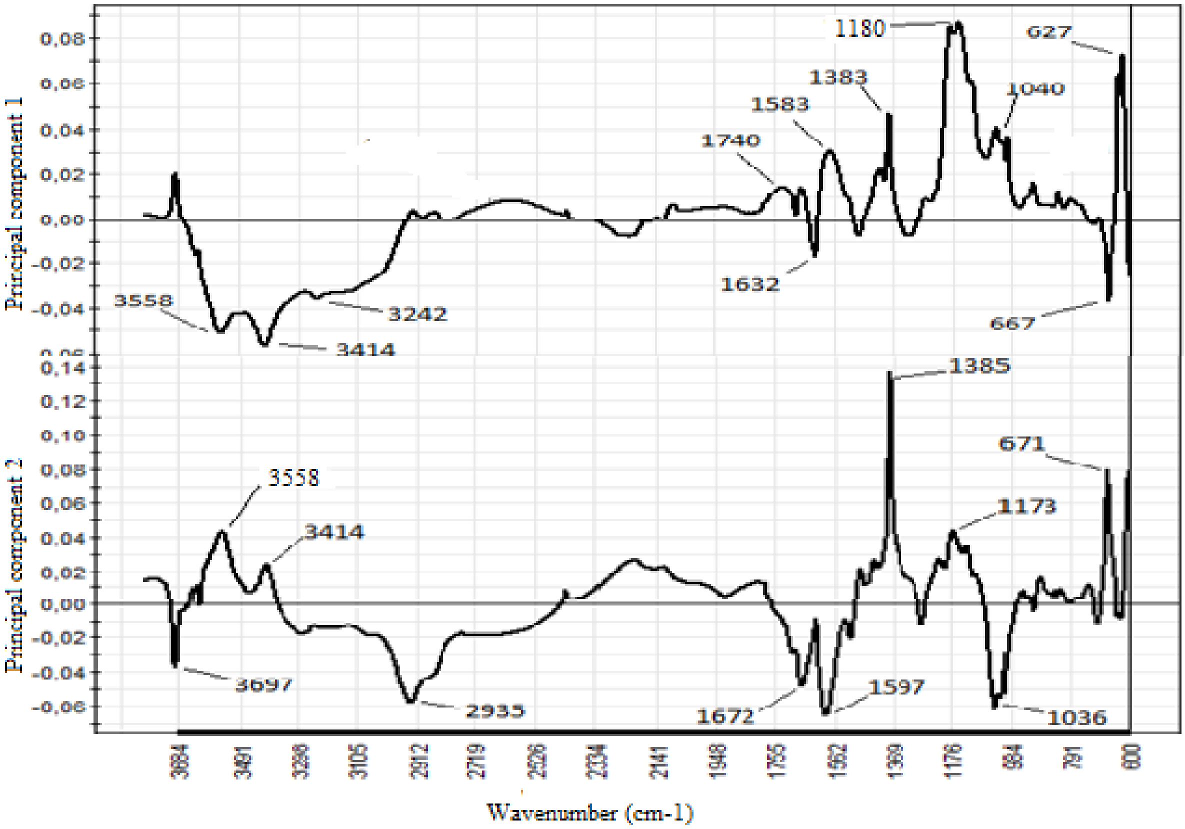


Figure 12. PCA Loadings plot for PC1 (upper) and PC2 (lower) along Wavenumber (cm-1) on the ordinate

Loadings for PC1 (Figure 12) are describing the reasons for samples separation in scores plot (Figure 11). We may say that negative peaks in PC1 loadings are responsible for those samples that have negative values (L1, L2, L3 and their replicates or duplicates) along PC1 in scores plot. So, it can be concluded that negative peaks are liable for separation at low pH (3-5). Similarly, samples L4, L6, L7 and L8 might be influenced and separated by positive peaks in PC1 of loadings plot. Hence, Positive peaks may responsible for separation at higher pH (6-9). Influence of the peak on the samples can be related to the peak intensity. Peaks at 3414, 3558, 3242 and 667 cm-1 are the most intense in the negative peaks while from positive peaks, 1180, 1383, 1040 and 1583 cm-1 are the most intense and influential peaks. Hence in PC2, peaks at 1036, 1597and 2935 cm-1 are most responsible peaks for separation at pH 3.3±0.0, 8.2±0.1 and 9.3±0.1 while at pH (4-7) sample L2, L3, L4 and L6 might be more influenced by peaks at 1385, 671, 1173 and/or 3558 cm-1.

3.3.3 OPLS modelling:

OPLS model was created by using K_d values of all the PCBs (28, 52, 101, 118, 138, 153, 180, 66, 187, 105 and 156) as y variables. All parameters of this model are provided in Appendix 2. Score plot of OPLS model is showing the samples distance and separation along PC1 and orthogonal component 1 in Figure 3.

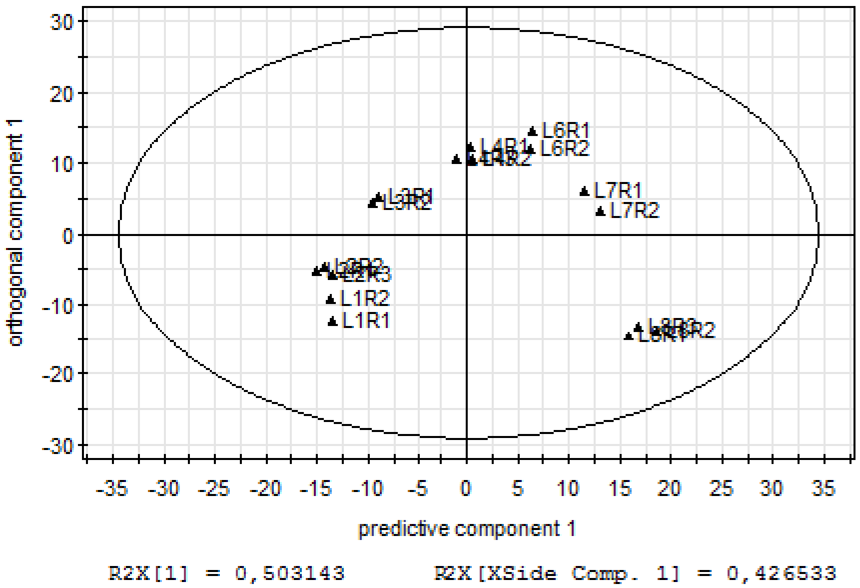


Figure 13. OPLS scores plot, showing Predictive component 1 on the ordinate and orthogonal component 1on the abscissa

Predictive component 1 is describing 50% variation in the data that can be correlated to y. Although PC1 variance was reasonable but on the other hand orthogonal component 1 is also elaborating 42% of variance which might have some useful and interesting information. That is why; orthogonal component 1 will also be studied.

The loadings plot for PC1 in Figure 4 is describing all bands (peaks) in relation with IR spectra of two extreme samples (L1R1 & L8R1) at extreme pH points. This figure illustrates the effect of functional groups (in form of spectral bands) on samples separation at different pH. Discovery of similarities and dissimilarities in spectra of different samples can be helpful to assign the major functional groups that cause separation in the scores plot (in Figure 13). Peak intensity and nature (positive or negative) in loading plot helps more to understand and explain the relationship.

Peaks at 3558 and 3414 cm-1 are the most intense on the negative side of PC1 loadings but the intensity of absorbance is significantly varying from pH 3 to 9. These peaks may attribute to O-H stretching and/or N-H stretching as cited in FTIR results. So, we may say that O-H and/or N-H functional groups are more influential at lower pH 3.3±0.0 (L1R1) than at higher pH 9.3±0.1 (L8R1). Similarly, peaks at 1155, 1591 and 1670 cm-1 are showing the largest positive contributions. These peaks may resulted from C-O stretching and/or O-H deformation, C=O and aromatic C=C stretching, respectively. Thus, we can conclude that these positive peaks may responsible for separation at higher pH. Peak at 1036 cm-1 shows the largest positive contribution, is resultant from the sample (L8R1) at higher pH while this peak is very weak (L1R1 spectra) at lower pH. This peak can be related to the C-O stretching of alcohol, ethers and/or polysaccharides. N-H stretching and C-H group are responsible for peaks at 1531 cm-1 and 2935 cm-1 respectively, in loadings plot. These peaks resulted at higher pH because they are not present in spectra at lower pH. Another difference is also observed in the region of 600-700 cm-1 where two sharp peaks are produced from two different samples. By above interpretation we may conclude that the detected functional groups might be responsible for separation of samples (L1R1 to L8R1) along PC1.

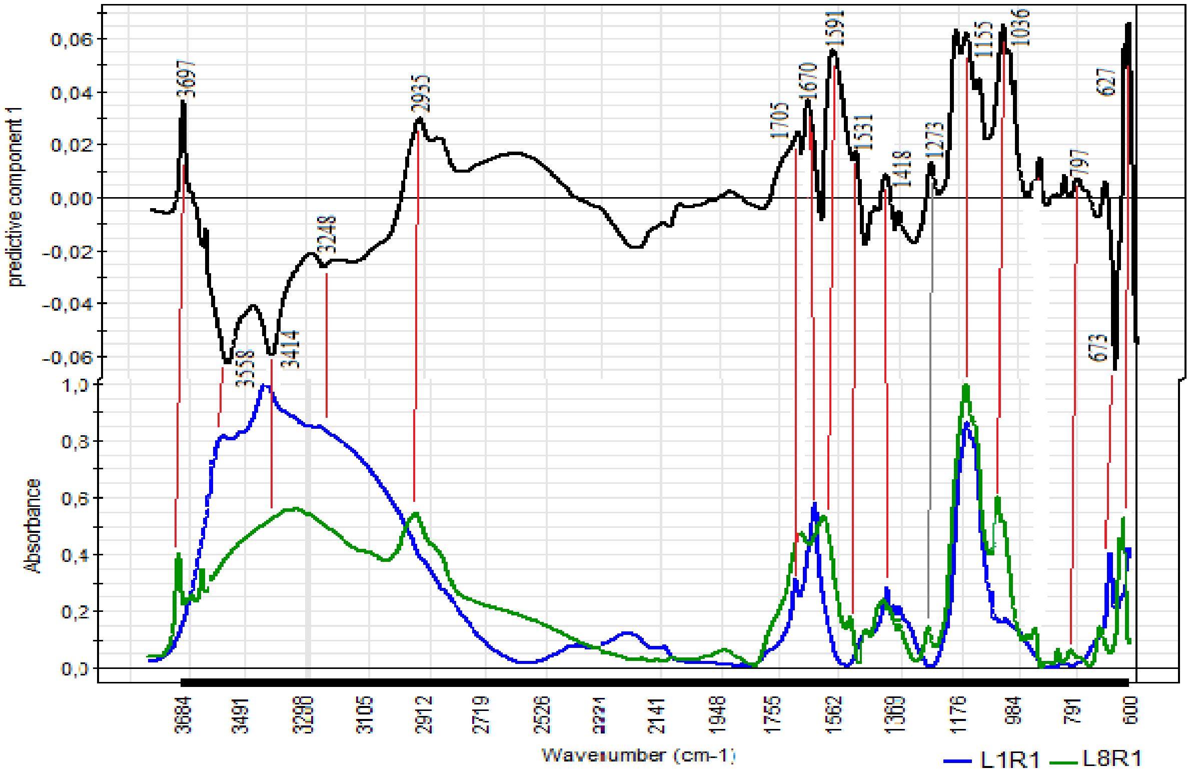


Figure 14. Co-relation of OPLS Loadings plot for PC1 (upper) and FTIR spectra (lower) of L1R1 (blue) and L8R1 (green)

Loading plot for orthogonal component 1 and IR spectra of L4R1 (pH 6) and L8R1 (pH 9) are correlated in Figure 5. L4R1 and L8R1 spectra were choosen to interpret because they are looking the most separated samples in orthogonal component in the scores plot (Figure 3). Peaks at 1385 cm^{-1} and 1167 cm^{-1} have the highest effect from positive side. A sharp peak at 1385cm^{-1} may resulted from sample L4R1 at pH 6 because L8R1at pH 9 does not show this sharp peak but only a broad band. This peak is attributed to nitrate and/or C-H deformation of CH3. Similarly broad band in the range of 1610 to 1678 cm^{-1} in negative side is most likely produced at pH 9. This band may attribute to C=O stretching and aromatic C=C stretching. All other bands have already discussed in PC1 section. By this correlation we may say that C-H deformation and peak at 1167 cm^{-1} are more influential at pH 5.2±0.1 to 8.2±0.1 (L3 to L7). Hence, C=O group, aromatic C=C and other influential functional groups (discussed earlier in PC1 explanation) could be more responsible for separation of samples L1, L2 and L8 at pH 3.3±0.0, 4.2±0.1 and 9.3±0.1 respectively.

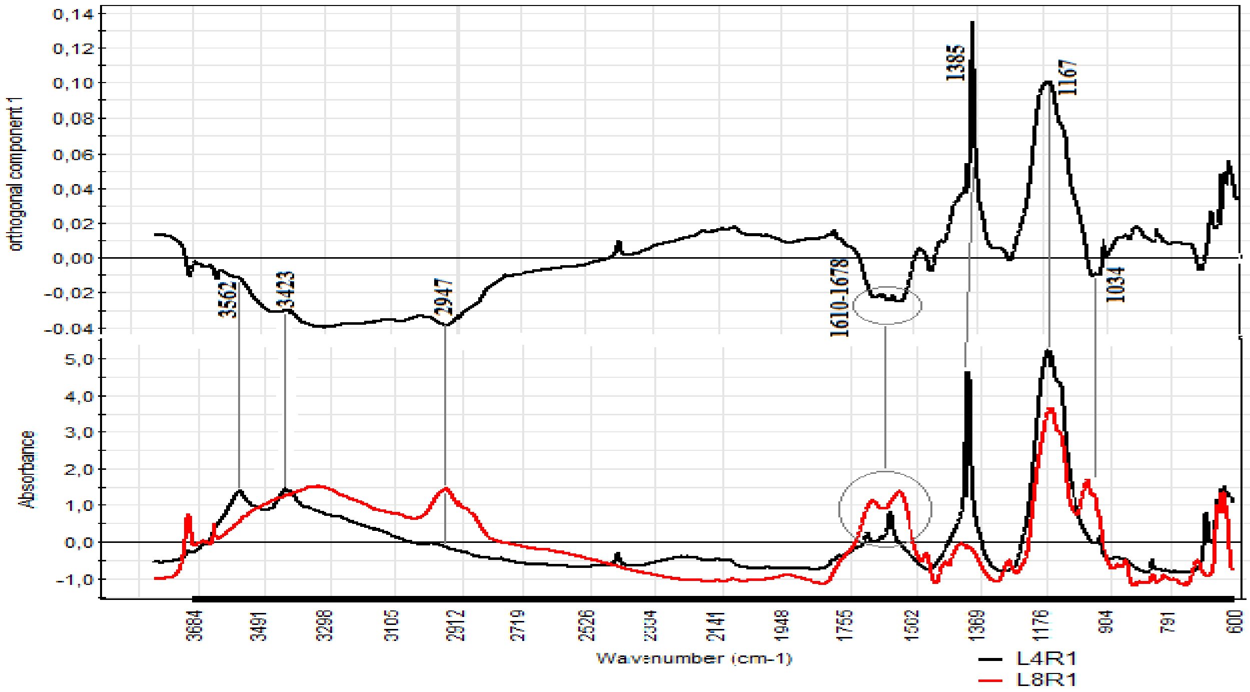


Figure 15. Co-relation of OPLS Loadings plot for orthogonal component (upper) and FTIR spectra (lower) of L4R1 (black) and L8R1 (red)

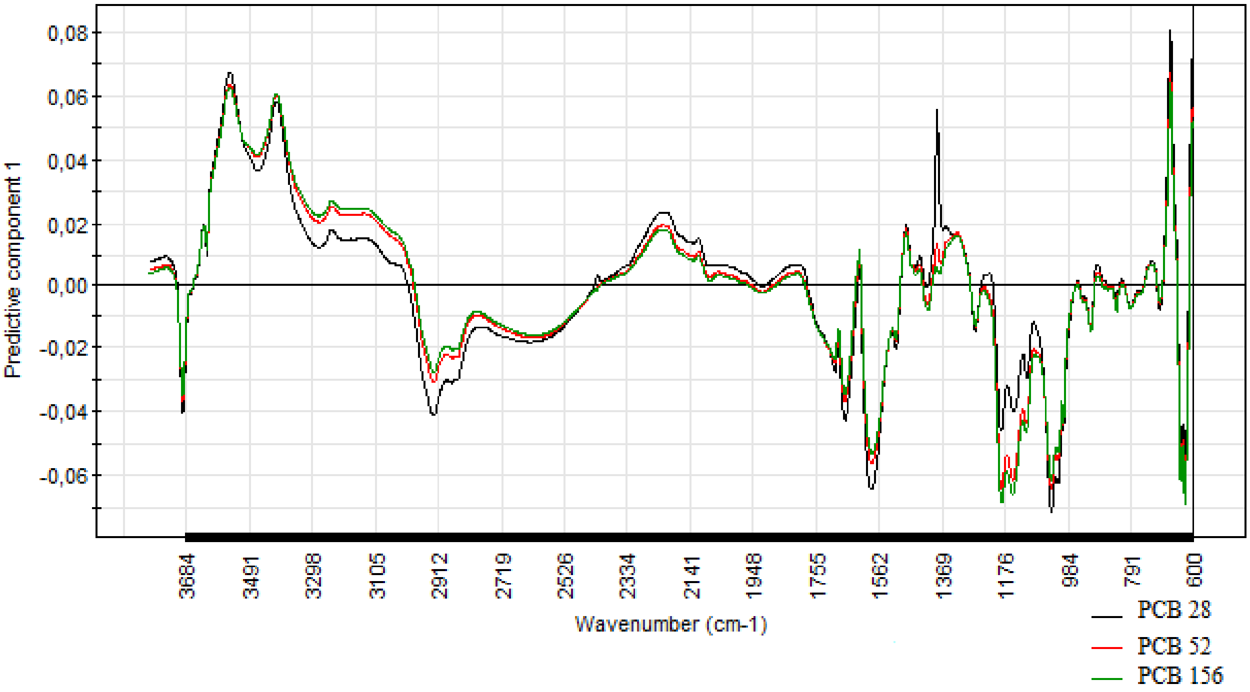
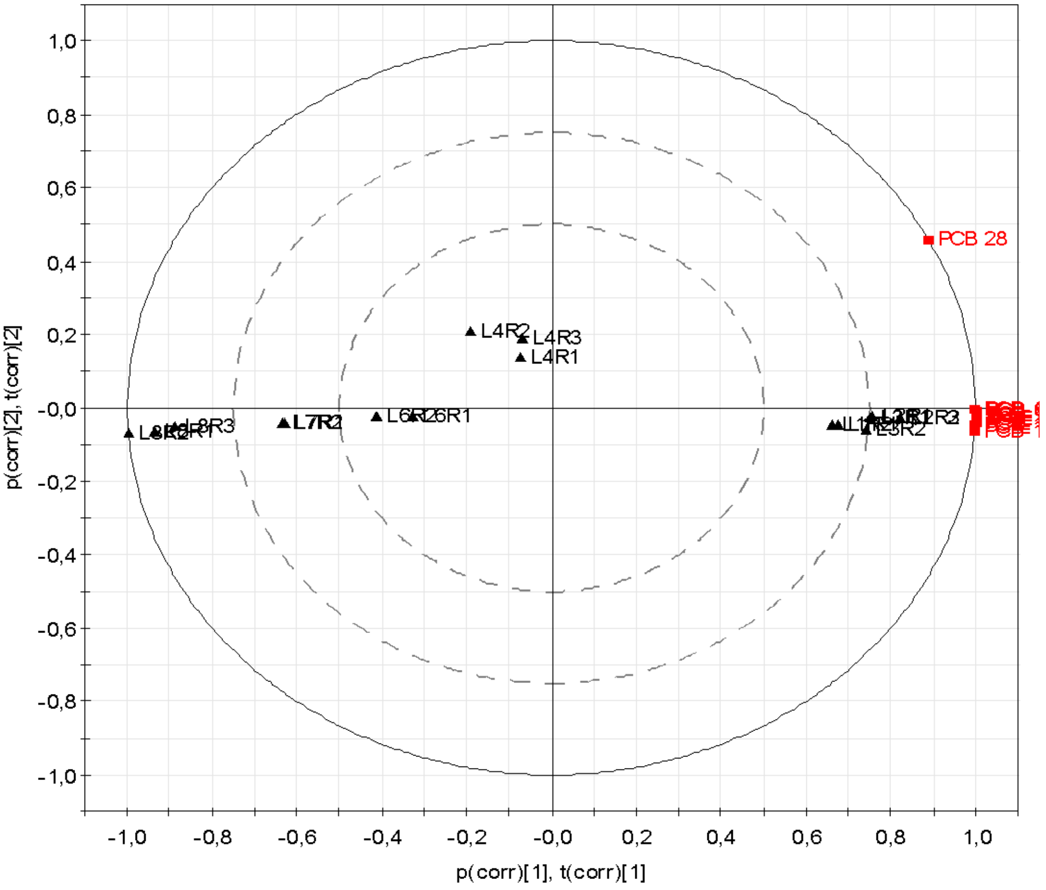


Figure 16: PC1 Loadings plot for response PCB 28, 52 and 156

An OPLS model is created by using one response (Only PCB 28 as Y-variable) at a time to observe the behavior of this specific response at different wavenumbers (cm^{-1}). Likewise, similar models are developed by using each response separately. All PCBs were behaving in the same pattern except PCB 28. So, PC1 loadings plot for three responses PCB 28, 52 and 156 with respect to wavenumbers (cm^{-1}) are shown in Figure 4. It can be seen that PCB 28 has some intensity differences from PCB 52 and 156. A strong and sharp peak at wavenumber 1385 cm^{-1} (nitrate group/C-H deformation of CH3) is looking the main difference in PCB 28 because PCB 52 and 156 show very week or negligible peaks at this wavenumber (cm^{-1}). Similarly, peak intensity differences are also observed in the ranges of 1150, 2900 and 3150cm-1. We may say that functional groups responsible for these peaks are mainly responsible for different behavior of PCB 28 from all other PCBs.

3.3.4 PCA-Y modelling:

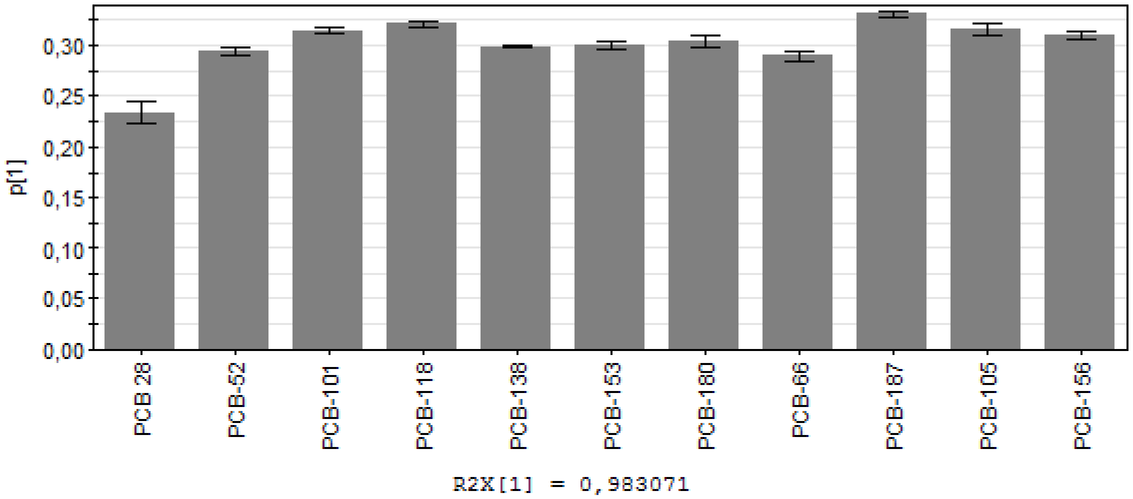
PCA-Y model is developed to observe the behavior and trend of samples with respect to Y responses. The sample scores and Y-variable loadings for PC1 and PC2 are plotted in Figure 5. By looking at biplot, we can differentiate clearly the trend among the samples with respect to PCBs (Y-variables). PC1 explains 98% of variance while PC2 does 1.5%. All other parameters of PCA-Y model is provided in Appendix 2. Furthermore, Figure 5 is showing that there is no abnormality and unusual trend in samples and responses along PC1 as all PCBs are behaving nearly same in all the samples at different pH. In addition, we can also observe that samples at lower pH (L1, L2 and L3) have higher k_d value of all PCBs (y-Responses) and low pH is more influential for PCBs k_d value (y-responses) than at higher pH. While in scores PC2, samples L4R1, L4R2 and L4R3 are separated from all other samples. It can also be observed that PCB 28 is laying a part from all other PCBs in loadings PC2. These samples (L4R1, L4R2 and L4R3) may have different pattern of PCBs where PCB 28 is more substantial. To find more information, we draw loadings plot.



SIMCA-P+ 12 - 2012-11-17 04:16:17 (UTC+1)

Figure 17. Bi-plot, score plot in black and loadings plot in red, showing PC1 on the ordinate and PC2 on the abscissa.

Column loadings plot for p1 (upper) and p2 (lower) is given in Figure 6. Loading plot for p1 is indicating that all PCBs are behaving more or less in the same way except PCB 28. PCB 28 has slightly less value that other. But column loading plot of p2 is indicating more interesting results. Here, again PCB 28 is behaving differently but in opposite manner. It seems that PCB 28 is the key congener that separates the samples along p2 as compared to other PCBs. If we looked at bi-plot, it is clear that only L4R1, L4R2 and L4R3 at pH 6.1±0.0 are separated by p2. So it can be concluded that L4R1, L4R2 and L4R3 are separating from other samples in p2 because of different pattern of PCB 28. This specific behavior of PCB 28 may because of less chlorination and slight solubility as compared to other PCBs congeners.



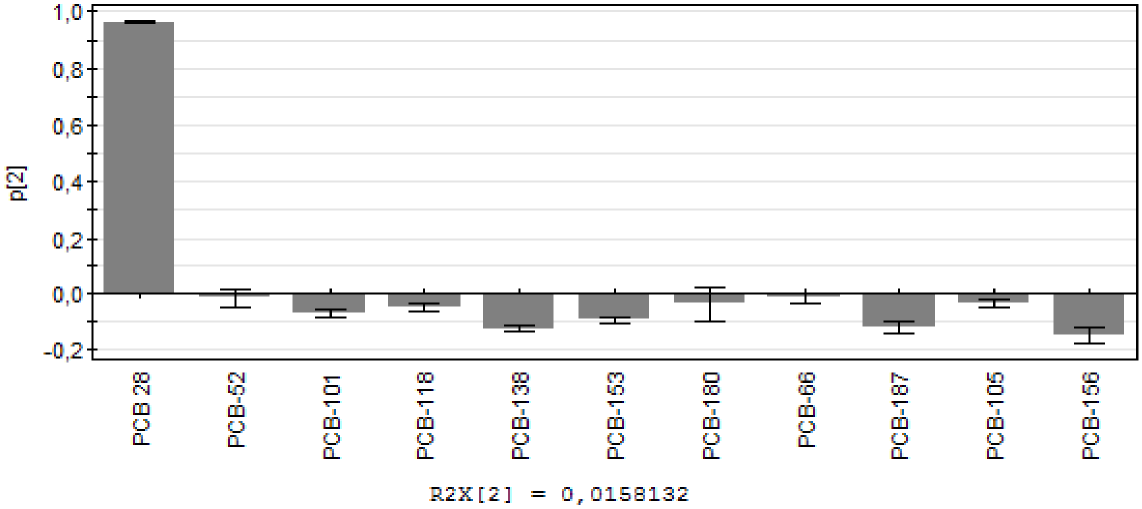


Figure 18. Column loadings plot for p1 (upper) and p2 (lower)

4. CONCLUSIONS:

The following conclusions were derived from the current study:

PCBs RESULTS:

- The concentration of all target PCBs increased with the increase of pH.
- The log K_d-values of all target PCBs decreased with the increase of pH.
- Kd-values of all PCBs were highly influenced by TOC except PCB 28 which was least influenced by TOC.
- Least chlorinated congeners (PCB 28 and PCB 52) showed more tendencies to leach as compared to higher chlorinated congeners.
- Ratio of concentrations of PCB 180 (di-ortho) to PCB 187 (tri-ortho) showed the influence of the ortho-chlorine bonds through pH effects on the leachability of PCB 187, while all other PCBs ratio did not prove any clear influence.
- Batch leaching method could be widely used to explain the mechanisms controlling the leaching.

FTIR RESULTS:

- The procedure used for characterization of DOM by FTIR gave satisfactory results and it did not require complicated and extensive sample preparation.
- Rapid, cheaper and non-destructive analysis by FTIR spectroscopy offered such a method that can complement already existing procedures.
- Characterization of DOM showed more contribution of carboxylate and aliphatic components in the samples.

MVDA RESULTS:

- In the modelling part, PCA model explained the differences in DOM with pH.
- An OPLS model was developed that correlated quantitative results of PCBs with DOM characterization. Obtained results from this model were satisfactory.
- PCX-Y model confirmed the different behaviour of PCB 28 from all other PCBs.

From the above analysis, it must be emphasized that more lower chlorinated PCBs should also be included to study the behaviour of leachability associated with TOC. It could provide evidence of different behaviour of least chlorinated PCBs from high chlorinated PCBs and effect of TOC. Moreover, dissolved organic matter (DOM) acts as a transport agent increasing the mobility and risk of spread of contaminants and characterization of the organic material will be of crucial importance for the interaction of organic contaminants and DOM. Meanwhile, comparison of different types of dissolved organic matters (DOM) will also help to understand the adsorption and mobility of hydrophobic organic contaminants at different pH.

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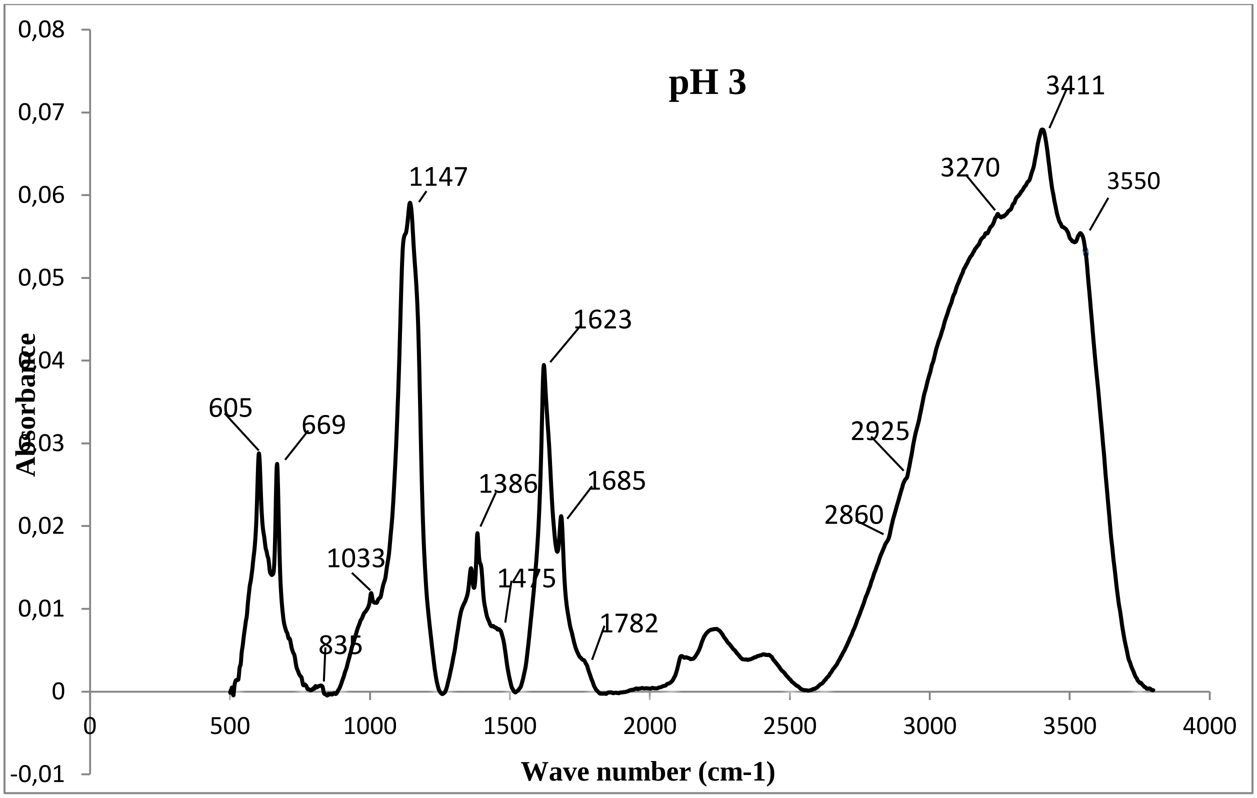
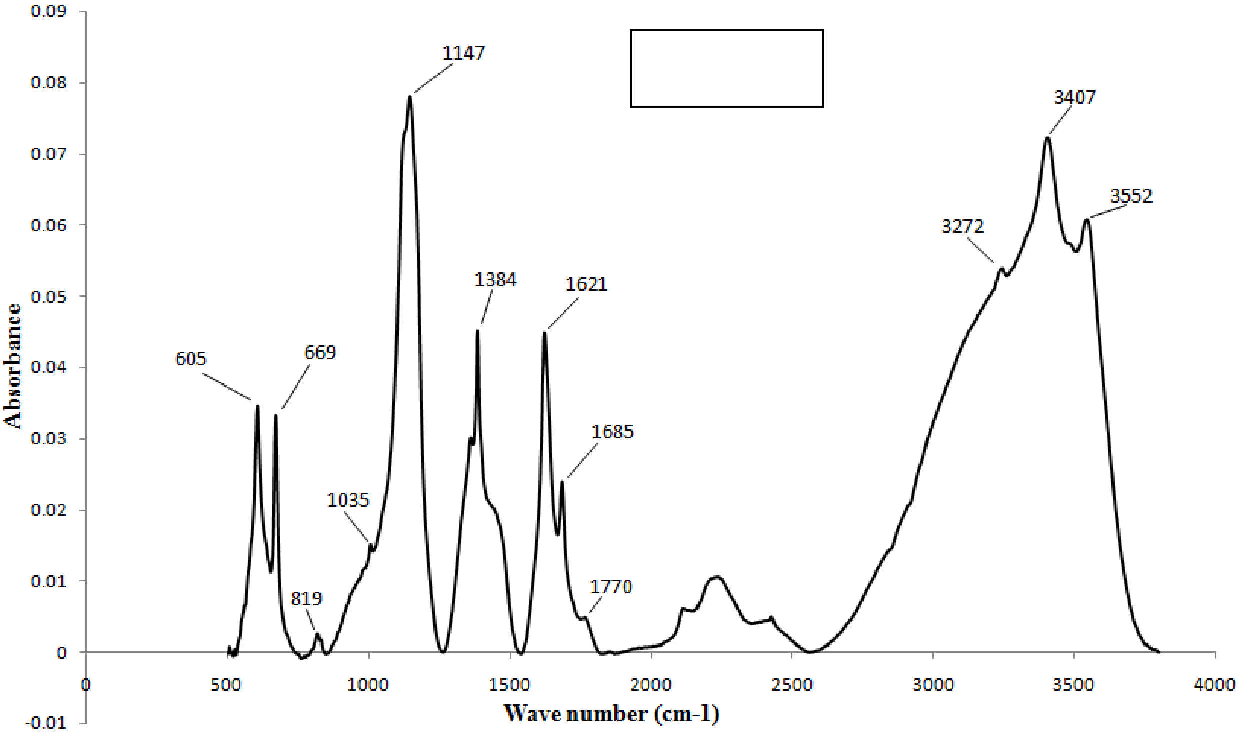
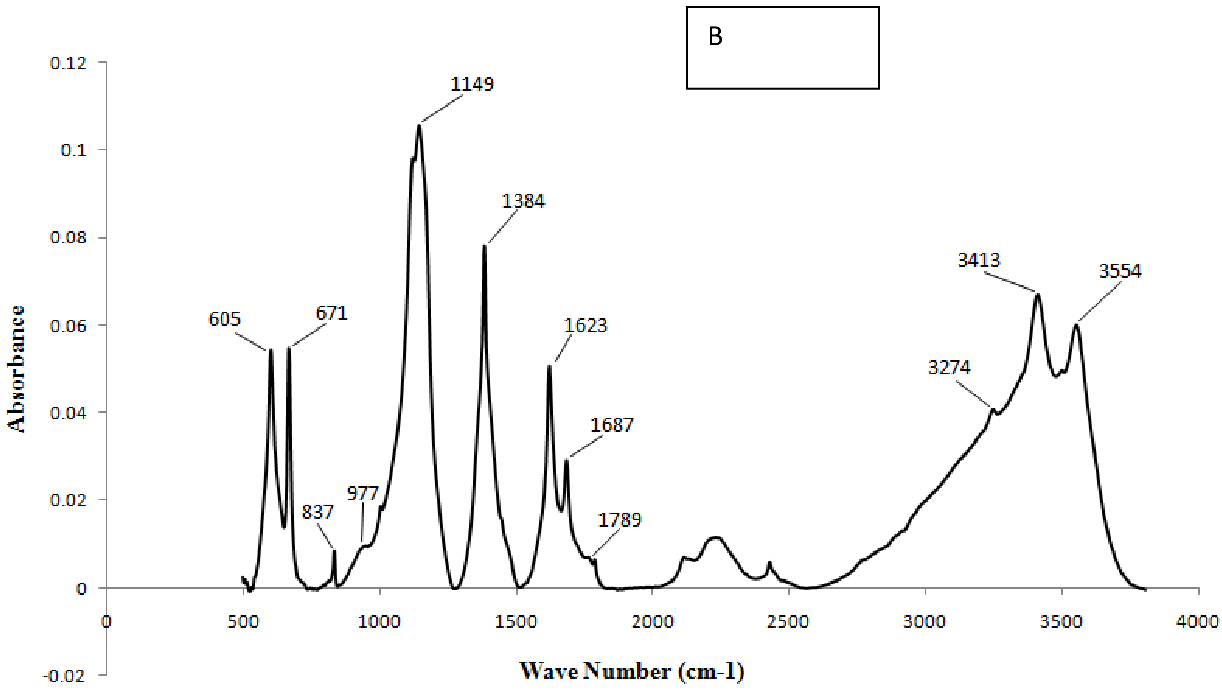
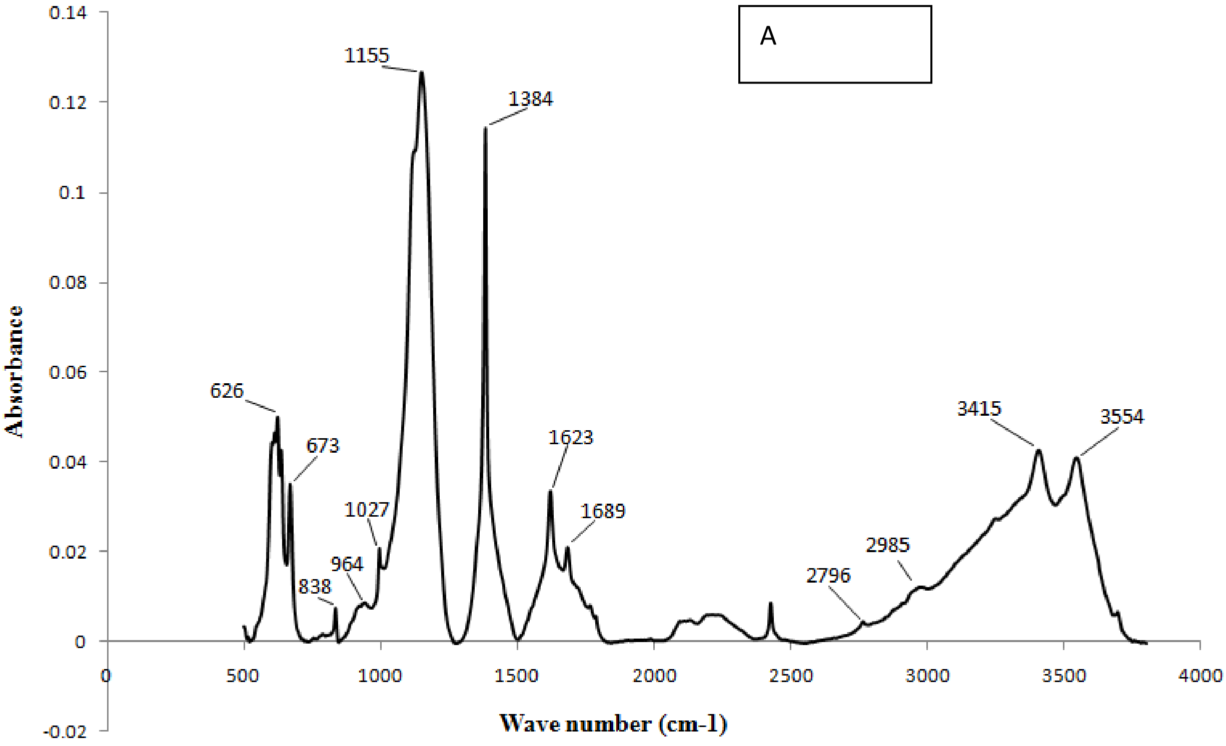
APPENDIX 1

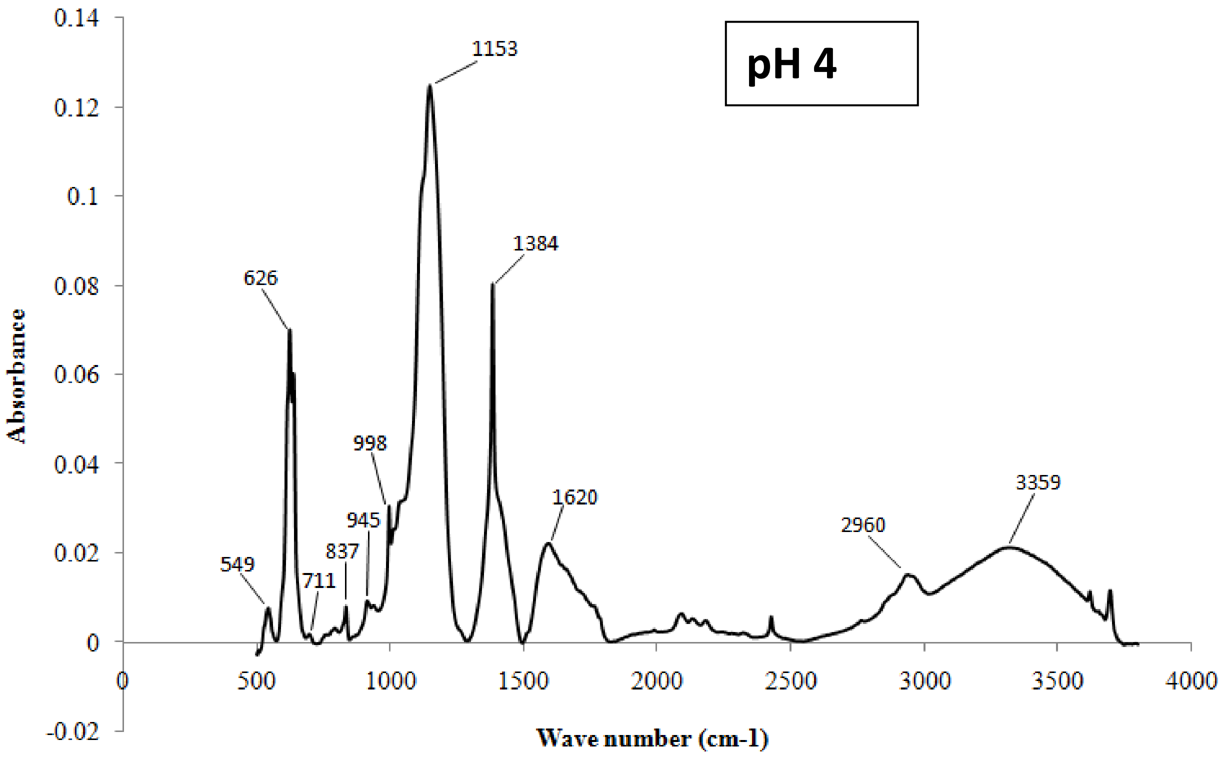
FTIR Spectra:

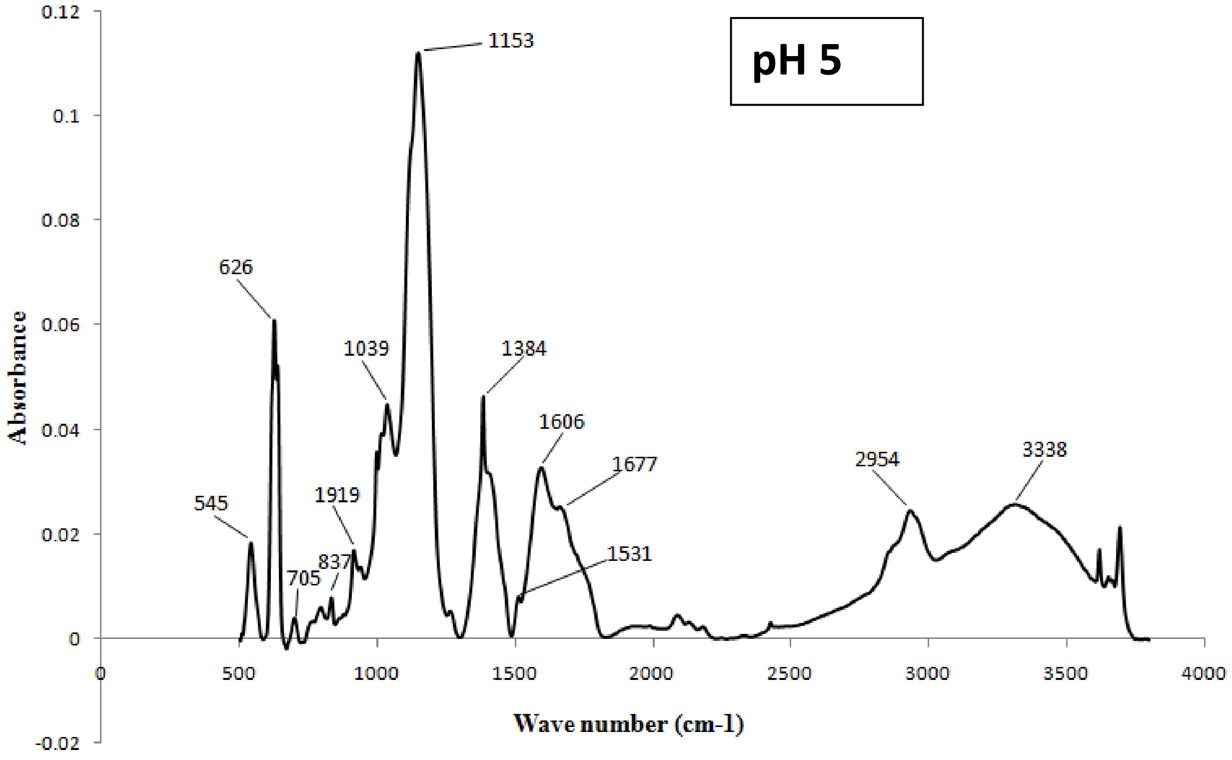





B
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
605
671
837
977
1149
1384
1623
1687
1789
3274
3413
3554
0
500
1000
1500
2000
2500
3000
3500
4000
Wave Number (cm-1)

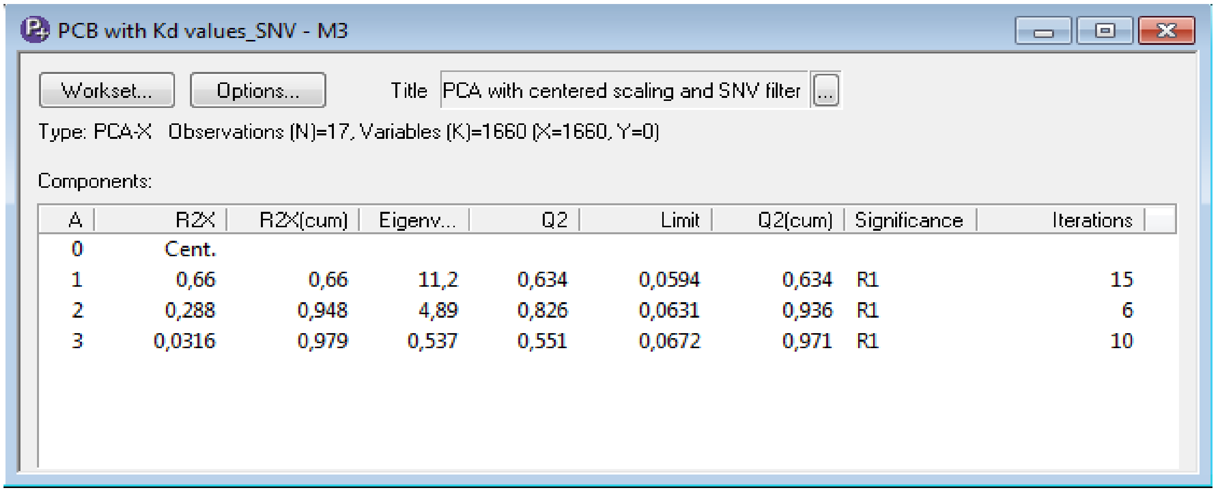

A
Absorbance
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
626
673
838
964
1027
1155
1384
1623
1689
2796
2985
3415
3554
0
500
1000
1500
2000
2500
3000
3500
4000
Wave number (cm-1)


pH 4
Absorbance
Wave number (cm-1)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
0
500
1000
1500
2000
2500
3000
3500
4000
1153
1384
626
998
945
837
549
711
1620
2960
3359


pH 5
Absorbance
Wave number (cm-1)
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
0
500
1000
1500
2000
2500
3000
3500
4000
1153
626
1039
1384
1606
1677
545
1919
837
705
1531
2954
3338

APPENDIX 2

PCA-X MODEL PARAMETERS:



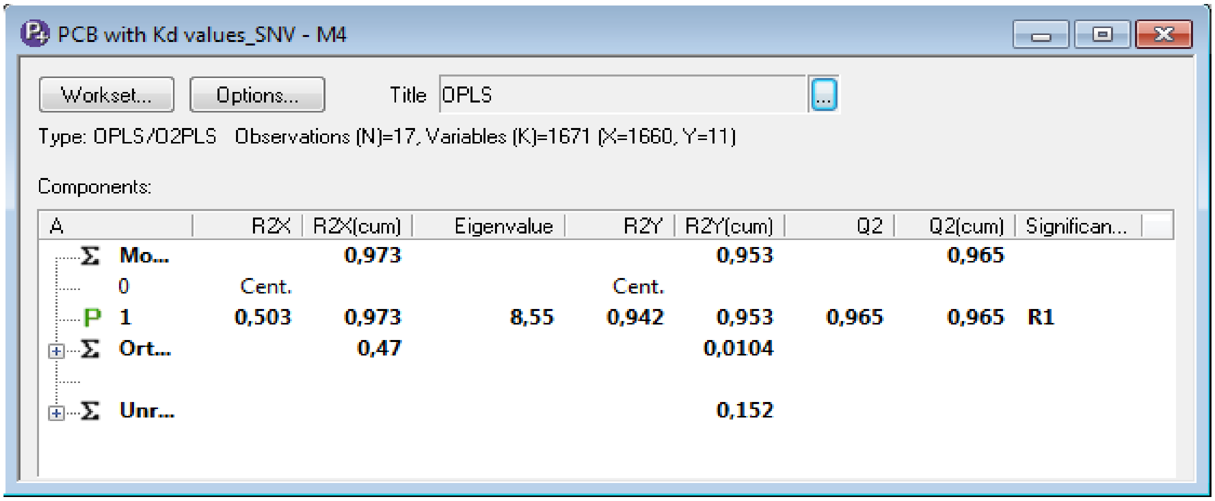
Title PCA with centered scaling and SNV filter

Type: PCA-X Observations (N)=17, Variables (K)=1660 (X=1660, Y=0)

Components:

A	R2X	R2X(cum)	Eigenv...	Q2	Limit	Q2(cum)	Significance	Iterations
0	Cent.							
1	0,66	0,66	11,2	0,634	0,0594	0,634	R1	15
2	0,288	0,948	4,89	0,826	0,0631	0,936	R1	6
3	0,0316	0,979	0,537	0,551	0,0672	0,971	R1	10

OPLS MODEL PARAMETERS:



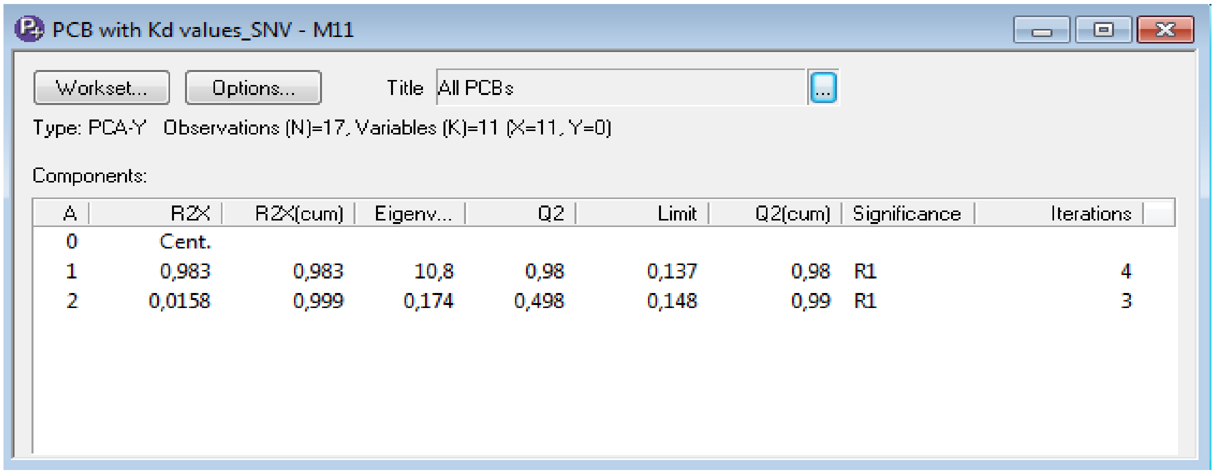
Title OPLS

Type: OPLS/O2PLS Observations (N)=17, Variables (K)=1671 (X=1660, Y=11)

Components:

A	R2X	R2X(cum)	Eigenvalue	R2Y	R2Y(cum)	Q2	Q2(cum)	Significan...
Σ Mo...		**0,973**			**0,953**		**0,965**	
0	Cent.			Cent.				
P 1	**0,503**	**0,973**	**8,55**	**0,942**	**0,953**	**0,965**	**0,965**	**R1**
Σ Ort...		**0,47**			**0,0104**			
Σ Unr...					**0,152**			

PCA-Y MODEL PARAMETERS:



Title All PCBs

Type: PCA-Y Observations (N)=17, Variables (K)=11 (X=11, Y=0)

Components:

A	R2X	R2X(cum)	Eigenv...	Q2	Limit	Q2(cum)	Significance	Iterations
0	Cent.							
1	0,983	0,983	10,8	0,98	0,137	0,98	R1	4
2	0,0158	0,999	0,174	0,498	0,148	0,99	R1	3