

Progress in Soil Science

Jianming Xu
Donald L. Sparks *Editors*

Molecular Environmental Soil Science



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Progress in Soil Science

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Editors

Molecular Environmental Soil Science

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Preface

Chemical, biological, physical, and geological processes operate together to support life at the Earth's surface for sustainability. Advances on the frontiers of knowledge on this subject matter require scientists to cross disciplines and scales to integrate understanding of the processes ranging in scale from the environmental mineral-organism-humus-water-air interfaces to the impact on the globe and humankind. However, there are great knowledge gaps on how and to what extent the processes, especially in the rhizosphere, are affected by the interfacial interactions among environmental nanoparticles, mineral colloids, humus, water, and organisms (flora, fauna, and roots), at the molecular level. Therefore, an international symposium on the above-mentioned subject area was proposed and held in Zhejiang University, Hangzhou, China, on October 10–14, 2009 to explore the contribution of chemistry into this new field. The conference provided a forum for the exchange of information, interactions, and collaboration among soil chemists, mineralogists, microbiologists, and physicists with allied scientists including pure chemists, mineralogists, biologists, environmental scientists, ecologists, and eco-toxicologists to address the current state of the art on “Molecular Environmental Soil Science” which is fundamental to understanding and regulating soil processes at the molecular level.

The International Symposium of Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone (ISMESS2009) was the first international conference focused on the above-mentioned subject area with special significance for understanding environmental pollution and global change processes. The conference was cosponsored by the International Union of Soil Sciences (IUSS) and the International Union of Pure and Applied Chemistry (IUPAC). Drs. J.M. Xu (China), P.M. Huang (Canada), A. Violante (Italy), H.H. Cheng (USA), J. Berthelin (France), J.M. Zhou (China), K. Wada (Japan), R.F. Shen (China), R.G. Burns (Australia), and W. E. H. Blum (Austria) served in the Symposium Organizing Committee. The conference attracted 266 delegates from 21 countries in the world including Australia, Austria, Belgium, Brazil, Canada, China, D.P.R. Korea, Egypt, France, Iran, Italy, Kenya, New Zealand, Pakistan, R.O. Korea, Russia, South Africa, Spain, the UK, USA, and Vietnam. The theme of ISMESS2009 was “Biophysico-Chemical

Processes in Soil Environments at the Molecular Level and the Impact on the Globe and Humankind.” The conference program was divided into the following five sessions: (1) The Role of Mineral Colloids in Carbon Turnover and Sequestration and the Impact on Climate Change; (2) Biogeochemical Interfacial Reactions and the Transformation, Transport, and Fate of Vital and Toxic Elements; (3) Anthropogenic Organics, Crop Protection, and Ecotoxicology; (4) Environmental Nanoparticles: Distribution, Formation, Transformation, Structural and Surface Chemistry, and Biogeochemical and Ecological Impacts; and (5) Environmental Processes and Ecosystem Health. There were 2 IUPAC plenary lectures, 18 invited speakers, 29 oral presentations, and 56 posters. Dr. D. L. Sparks from University of Delaware, USA, presented one plenary lecture entitled “Advances in the Use of Synchrotron Radiation to Elucidate Environmental Interfacial Reaction Processes and Mechanisms in the Earth’s Critical Zone.” Dr. G. M. Gadd from University of Dundee, UK, presented another plenary lecture entitled “Microbial Role in Global Biogeochemical Cycling of Metals and Metalloids at the Interfaces in the Earth’s Critical Zone.”

The 15 chapters in this book are mainly the papers from the plenary and invited speakers of ISMESS2009. They address the current state of the art on chemical-biological-physical-geological processes and the interfacial interactions at the molecular level. The book presents a variety of issues on the fundamental processes and interactions among nanoparticles, soil minerals, native and anthropogenic organic compounds/pollutants, and microorganisms and their impacts on the globe and humankind. This book is divided into four parts.

Part 1 addresses current research into fundamental processes in the soil-microbial ecosystem. The latest research is presented on a wide range of soil-based microbial processes, including organic pollutant degradation and the role of exocellular enzymes in soil processes. Other work addresses the structure and biological activity and environmental fate of both natural Bt proteins and those produced by genetically modified plants.

In Part 2, the latest research findings concerning the fundamentals of elemental and mineral transformations and metal cycling processes and reaction and transformation mechanisms of metals and metalloids are discussed. In addition, new mechanisms to account for the interaction between heavy metals and variable charge surfaces, and ion diffusion/adsorption as affected by microbes, biomolecules, and the electrostatic field from surface charges are presented. Advances in the use of synchrotron radiation to elucidate these various environmental interfacial reaction processes and mechanisms are also reviewed in depth.

Part 3 presents some of the latest developments in the field of surface charge chemistry and ion diffusion/adsorption by soil. The effects of “ageing” on the retention, bioreactive chemical transformations and transport in soil are reviewed extensively. Further work is presented on the sorption characteristics of pharmaceuticals and hydrophobic organic chemicals in the environment and the role of black carbon in the adsorption of organics from aqueous solutions.

Finally, Part 4 is concerned with soil fertility and soil quality as affected by agricultural management and microbial activities. This is a broad field and the focus here is on subsoil acidification, including causes and solutions, use of microbial indicators in soil quality evaluation and, finally, the impacts of agricultural management practices on soil properties.

These chapters address current knowledge gaps and provide future research directions at the molecular level. We believe that the publication of this ISMESS2009 special book will promote in-depth studies in molecular environmental soil science and the book will provide an invaluable reference for research scientists, professors, graduates, and consultants working in soil, agricultural, microbial, biological, ecological and environmental sciences.

We wish to extend our special thanks to the many sponsors including Organization for the Prohibition of Chemical Weapons (OPCW), National Natural Science Foundation of China (NSFC), Soil Science Society of China (SSSC), Zhejiang University, and Zhejiang Provincial Key Laboratory of Subtropical Soils and Plant Nutrition.

In addition to this book, a book of proceedings composed of extended abstracts that were subject to peer review by external referees, by International Scientific Committee members of the symposium, and by the editors of the proceedings was published by Zhejiang University Press and Springer. Volunteered papers presented at ISMESS2009 and accepted after rigorous external review were also published as a special issue by the *Journal of Soils and Sediments*. The book of proceedings and the special issue serve as companion volumes of this IUSS- and IUPAC-sponsored book published by Springer-Verlag.

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Part I
Soil Microbial Processes

Chapter 1

The Sorption Behavior and Bioavailability of Persistent Organic Pollutants (POPs) in Soils

Jianming Xu, Tahir Hayat, and Na Ding

Abstract Persistent organic pollutants (POPs) pose a threat to the environment because of their potential for long-range atmospheric transport, bioaccumulation and toxicity. The POPs behave dynamically in the environment according to their different processes e.g. volatilization, sorption, desorption and transportation. Environmental variables like temperature, soil pH and moisture have serious effects on POPs behavior in soil. Organic as well as inorganic compounds may react with the xenobiotics and play an important role in their transformation in soil. Manganese and iron oxides and clay minerals (e.g. smectites containing Fe(III)) had well-documented properties to promote the oxidation of a number of organic pollutants. Organic matter is considered the most important factor limiting the availability and mobility of POPs in soil and a substantial percentage of the organic contaminants applied to a soil might become associated with soil humic fraction. Organic pollutants strongly adsorbed to carbonaceous sorbents such as black carbon. In particular, activated charcoal (AC) had a strong adsorptive capacity due to its high specific surface area. Adsorption to activated charcoal could render hazardous organic pollutants in soils and sediments less available to organisms and hindered their dispersal into unaffected environment. Some studies also showed that some sorbents from natural organic materials, such as peat, soybean stalk and pine needle under superheated temperature/pressure conditions, significantly affected the sorption of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils. Natural materials significantly decreased the extractability and bioavailability of POPs from contaminated soils. Organic matter also plays a vital role in controlling the contamination of POPs in soil. The rhizosphere effect is showing promising to control POPs contamination in the soil environment. This review evaluated the work on the environmental behavior and bioavailability of POPs in soils as affected by various environmental variables.

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Keywords Persistent organic pollutants • Polychlorinated biphenyls • Polycyclic aromatic hydrocarbons • Pentachlorophenol • Sorption • Desorption • Bioavailability • Organic matter

1.1 Introduction

The term persistent organic pollutants (POPs) refers to the organic chemical compounds that persist and bio-accumulate in the environment through the food web, and are a risk to human and environmental health. People may be exposed to POPs in occupational settings through the inhalation of contaminated workplace air and dermal contact or with wood products treated with the chemicals. Also, general population exposure may occur through contact with contaminated environmental media, particularly in the vicinity of wood treatment facilities and hazardous wastes sites. In addition, some other important routes of exposure seem to be the inhalation of contaminated air, ingestion of contaminated ground water used as a source of drinking water, ingestion of contaminated food, and dermal contact with soils or products treated with the chemicals. POPs are highly dangerous because they are highly toxic, persistent, lasting for years or even decades before degrading into less dangerous forms. They may evaporate and travel long distances through air and water and accumulate in living fatty tissues. These properties make them, arguably, the most problematic chemicals that natural systems can be exposed to. POPs can be divided into three main categories: (1) pesticides e.g. DDT, (2) industrial chemicals e.g. polychlorinated biphenyls (PCBs) & polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), and (3) unintentional by-products e.g. dioxins, furans.

POPs keep accumulating through the food web as one animal eats another, so that the highest levels are found in predator animals at the top level of the food web. Research from numerous countries has demonstrated that measurable quantities of POPs are present in human adipose tissue, blood and breast milk, because they are soluble in fats and are not easily broken down in the body (<http://www.epa.ie/whatwedo/resource/hazardous/pops>). POPs are of environmental concern because of their potential for long-range atmospheric transport, bioaccumulation and toxicity (Klecka et al. 2000). They display high affinities for soils where they can persist over years to decades. Persistence of organic pollutants in soils has been attributed to sequestration mechanisms including intra-organic matter and intra-particle diffusion of the parent compounds and transformation products; contaminant humification to soil organic matter (SOM); low aqueous solubility; and/or microbial recalcitrance (Northcott and Jones 2000). Quite a number of organic pollutants exist in soil environment and these comprise a very significant source of pollution. We can not review all POPs in this article. Instead we emphasize only some organic pollutants and their entry into the environment through industrial and agricultural processes or as unintentional by-products such as polychlorinated biphenyls (PCBs), pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs).

The commercial production of PCBs began in 1930. Industrial manufacturing of PCBs was based on the chlorination of biphenyl in the presence of suitable catalysts. Over one million tons of PCBs have been produced in industrialized countries. The commercial use of PCBs began in 1965 in China, most commercially used PCBs were PCB₃ and PCB₅. In 1972, the production and use of PCBs were banned by law in Switzerland, UK and USA. Now, only the congeners with low degrees of chlorination can be sold and used as dielectrics in closed systems (WHO 1979). After that, many countries restricted the sale of PCBs. PCBs were also listed as priority pollutants by US Environmental Protection Agencies (USEPA) since the 1970s (Hu and Wang 1998; Keith and Telliard 1979). By the end of 1974, most factories stopped the production of PCBs and in the early 1980s, and the commercial production of PCBs was completely banned in China. Within this period of time, approximately 10⁷ kg PCBs were produced and most of the products, about 9,000 t, were used as dielectric fluid in electric capacitors, except that a small part were used as additives in paints. Most of the electric capacitors containing PCBs have been exhausted. Furthermore, some electric capacitors and transformers containing PCBs were imported into China without pre-notification from some developed countries from 1950 to 1970 or even later. Although the commercial production of PCBs has been banned for almost two decades, improper disposal of the PCBs containing appliances will cause and has caused serious pollution in many parts of the world. It is worth mentioning that PCBs can also be used in many industrial processes such as chloranil and dicloran production. Therefore, PCBs will enter the environment when they are produced and used. PCBs entering the environment will go into the global cycling of materials and energy. These PCBs become major pollution sources in soil and water and ultimately through food cycle enter in the human body and become a serious cause of diseases such as liver cancer and biliary track. PCBs also have been shown to mimic the action of estrogen in breast cancer cells and can enhance breast carcinogenesis. Due to toxic effect as well as classified as persistent organic pollutants the production of PCBs was banned by the United States Congress in 1979 and by Stockholm Convention on Persistent Organic Pollutants in 2001.

Pentachlorophenol (PCP) is a synthetic chlorinated phenol that was first produced in the 1930s. It can be found in two forms: PCP itself or as the sodium salt of PCP, which dissolves easily in water. In the past, it has been used as a herbicide, insecticide, fungicide, algaecide, disinfectant and as an ingredient in antifouling paint. Some applications were in agricultural seeds (for nonfood uses), leather, and masonry, wood preservation, and cooling tower water, rope and paper mill systems. PCP can be produced by the chlorination of phenol in the presence of catalysts (anhydrous aluminum or ferric chloride) and a temperature of up to approximately 191°C. However this process was incomplete and resulted in the production of commercial grade PCP of between 84 and 90% purity. During the process several contaminants including other polychlorinated phenols, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans were also produced, which are more toxic than the original PCP. After entering into soils, PCP could be irreversibly bound to soil particles (Chen et al. 2004).

PAHs are ubiquitous environmental pollutants, with well-documented toxic, mutagenic, and carcinogenic properties. PAHs can be formed naturally by low-temperature and high-pressure reactions of natural organic matter. These compounds are produced by natural processes, including forest and grass fires, volcanoes, and seepage of oil into the environment. However, the majority of PAHs are released from a wide variety of anthropogenic sources, including petroleum spills, incomplete combustion of fossil fuels in electric power generation, refuse incineration, home heating, internal combustion engines, as well as the production of coke, carbon black, coal tar and asphalt (Eisler 1987; Burgess et al. 2003). The petroleum industry is an important source of PAHs, especially in the vicinity of petroleum refinery facilities. Waste water and soil in these areas are often characterized by PAHs concentration 100 times higher than in other areas (Douben 2003). PAHs are found in air, soil, vegetation, water and ice (Holoubek et al. 2000). PAHs are also found in remote areas far from the emission sources (e.g. the arctic) (Sehili and Lammel 2007). Sediments in aquatic environment function as a reservoir for PAHs (Ankley et al. 1994). PAHs are highly hydrophobic compounds, with physicochemical properties that generally favor association with particulate matter. These compounds are usually associated with airborne particulate matter (Fox and Olive 1979; Legzdins et al. 1995; Oda et al. 1998), soil (Chen et al. 2004; Lors and Mossmann 2005; Lampi et al. 2006), sediments in the water column (Lampi et al. 2001, 2006; Kilemade et al. 2004; Olajire et al. 2005), as well as organic surface films in urban environments (Gingrich et al. 2001; Butt et al. 2004).

1.2 General Behavior of POPs

In recent decades, a vast number of POPs have been produced and used worldwide (<http://www.greenpeace.org/international/campaigns/toxics/toxic-hotspots/what-are-persistent-organic-pop>). Many are still in production and are used in everyday products. POPs behave dynamically in the environment according to their nature of action as they volatilize in the air and cause pollution. These chemicals have become widespread environmental pollutants. POPs contaminated areas close to sites where they were released into the environment from industry and agriculture. However, volatile and semi-volatile POPs also contaminated regions remote from their source, because they could be transported for thousands of kilometers via air currents. POPs might also be transported for long distances by rivers, ocean currents and as contaminants in wildlife. Their sorption and desorption processes were very important in order to understand their toxicity levels. PCBs have a high degree of physical and chemical stability under normal conditions. They are very resistant to acids, bases and oxidants. They are, in practice, fire resistant with rather high flash points. The liquid phase vapor pressures of PCBs at ambient temperature are not very high but the change of temperature affects them significantly (Dai et al. 1997). PCBs have low aqueous solubility and most of their values of K_{OW} are greater than 10^4 (Wan and Mackay 1986).

Environmental pollution with PCBs is caused by their release into the atmosphere via leakage and improper disposal in industry. Other pathways of dispersal into the environment include combustion of industrial and urban wastes and storage and dumping of wastes in landfill sites. Although the amount emitted by these ways is much less, however, they can enter the food chains (WHO 1979). PCBs volatilized into the atmosphere during their use and disposal and returned to the terrestrial and aquatic environment as dry material or precipitation deposition. In most areas of North America, PCBs in the soil mainly originated from the atmosphere. There were from 1×10^3 to 2×10^3 ton PCBs deposited on the soil from the atmosphere, especially in urban areas (Meng et al. 2001). Other than deposition, PCBs in soil derived from the use of sewage sludge as a fertilizer, leaching from landfill sites and the use of pesticides containing PCBs. They entered water mainly from discharge of industrial and urban wastes into rivers, lakes and ocean. When discharged into open water, the water soluble PCBs would concentrate onto dissolved particles, and then sinked into the sediment at different rates according to the particle size and accumulated there. The sinking rate of PCBs from the surface to deeper layers in the open ocean was relatively slower in tropical waters than in high latitude waters (WHO 1993). PCBs in sediments are the main source to enter in the food chains (Dai et al. 1997; WHO 1979).

Sorption is a phase distribution process that accumulates solutes at surfaces and interphases (i.e., adsorption) or from one phase to another (i.e., partitioning). This process affected the transport and reduced the chemical and biological reactivity of relatively hydrophobic organic chemicals (HOCs) such as PAHs and chlorinated aliphatic and aromatic compounds in surface aquatic and groundwater systems (Weilin et al. 2003). Sewage treatment could remove the solid combined PCBs, but it could not remove the dissolved fraction. It has been widely recognized that the ecotoxicity or biodegradability of POPs e.g. PAHs, PCP and PCBs in soils was controlled by the rate and extent of desorption from the solid phase. The sorption ability decreased with increasing residence time of the compounds in soil (Alexander 2000; Reid et al. 2000) and depended on the nature and quality of SOM. This was reflected by the wide variation of organic carbon water partition coefficient (KOC) ranging up to three orders of magnitude among different soils (Chiou et al. 1998; Krauss and Wilcke 2001).

Because of the high hydrophobicity of PCBs, their environmental behavior would significantly depend on sorption phenomena (Voice et al. 1983). PCBs in the aquatic environment were mainly adsorbed onto sediments and suspended particles and then transported to areas far away from the source of pollution. Due to the binding of PCBs, the concentration of PCBs in the sediment near estuaries was as high as $2\text{--}5 \times 10^3 \mu\text{g kg}^{-1}$ (Wang 1991; WHO 1993). In highly polluted waters, the concentration of PCBs was several times higher than their solubility due to the interaction between PCBs and solid particles in water (Dai et al. 1997; WHO 1979).

PCBs in water could not be hydrolyzed and their retention period in water was very short because of their high hydrophobicity and chemical stability. PCBs could not be decomposed chemically other than by photolysis. However, biological

degradation was important in decreasing PCBs. When PCBs entered food chains, the congeners with low chlorination would be biodegraded stepwise hence they could be totally decomposed in this way (Dai et al. 1997; Wang 1991; WHO 1979).

1.3 Sorption Behavior of POPs in Soil

Soils and sediments are heterogeneous organic and inorganic materials. The heterogeneity has an impact on the linearity of the sorption isotherm and the sorption mechanism. Soil particles can be divided into three size-classes: first, the exposed inorganic minerals, which had little impact on the sorption of HOCs; second, the amorphous organic matter, which included humic and fulvic acids; third, the condensed organic matter, the existence of which was proven by X-ray diffraction spectra (Piatt and Brusseau 1998). Sorption of HOCs by condensed soil organic matter (SOM) appeared to be energetically more favorable and more nonlinear than that by amorphous SOM, most likely because of the more heterogeneous composition and less polar character of condensed organic matter (Weber and Huang 1996; Chiou et al. 1979). The change in the composition of organic matter resulted in a decrease or increase of the relative amounts of oxygen-containing functional groups. High amounts of oxygen containing functional groups might result in an increase in the polarity of organic polymers composed of natural organic matter, and thus in a lower affinity for nonionic compounds, and thereby decreased the sorption capacity. Therefore, a relationship existed between the elemental composition and the partition coefficient.

Organic carbon content and particle size had a significant impact on the sorption of PCBs. Chiou et al. (1983) found that the sorption mechanisms of HOCs like PAHs and PCBs were different between coarse particles and fine particles. The sorption coefficient of PCBs was inversely proportional to their solubility. When Aroclors transported to the soil, they would be fractionated by soil similarly to chromatography and they had a poor mobility (Chu et al. 1995; McGinley et al. 1993). The distributed coefficients changed with time (Girvin and Scott 1997). Different kinds of soil had different abilities to adsorb POPs.

He et al. (2006a) studied the sorption isotherms of PCP in ten different soils with various physico-chemical properties. They also investigated the sorption-desorption hysteresis phenomena and its possible mechanism. They applied a Freundlich and Langmuir-derived dual mode model (DMM) to study the sorption onto and into fractal sorbents (Fig. 1.1). They produced typical sorption isotherms of PCP on soil spanning two orders of magnitude in concentration. The isotherms showed an inflection point which was solute dependent within the solution concentration of 0–5 mg L⁻¹. Both DMM and Freundlich model had a good fit to sorption data, but the DMM model appeared to be superior according to the actual R² values. Examples of fits of the DMM and Freundlich models to the full isotherms of soil 2, 6, and 10 were shown in Fig. 1.2. With the increase of soil pH, the nonlinearity of the isotherms gradually disappeared (Fig. 1.2). In this experiment, He et al.

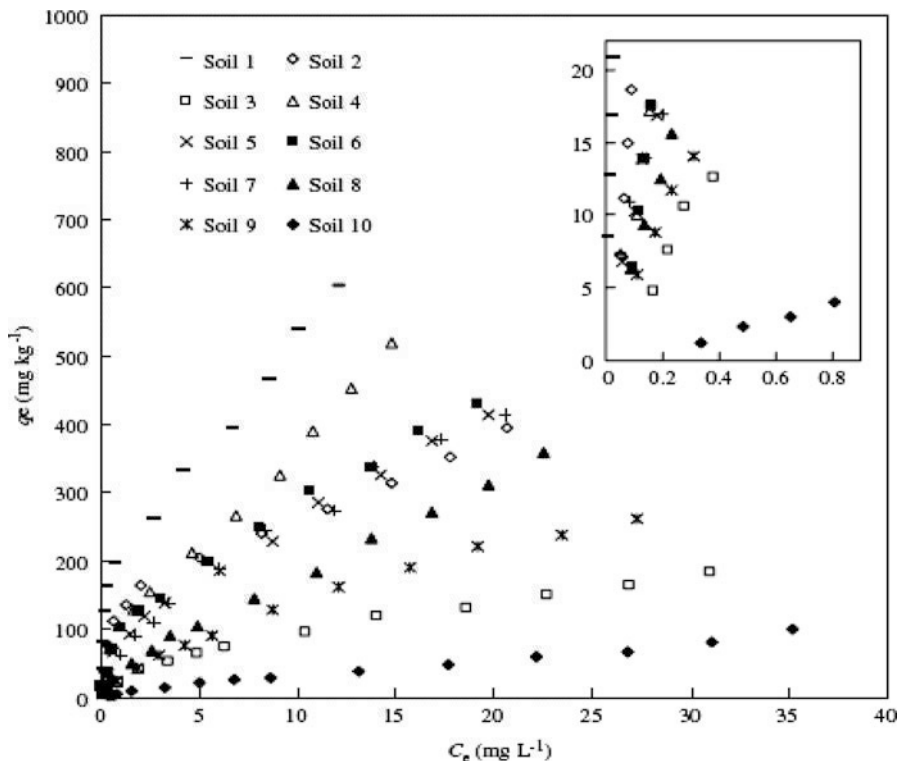


Fig. 1.1 Sorption isotherms of pentachlorophenol (PCP) on 10 soils. q_e is the amount of PCP sorbed per mass of soils, C_e is the equilibrium PCP concentration. The *symbols* denote experimental data points (He et al. 2006a)

(2006a) reported that total nitrogen in soils might contribute in these processes. Correlations of stepwise regression equations confirmed that pH, soil organic carbon and fractions of organic carbon, and particle size distribution were the main factors responsible for the sorption and desorption hysteresis (Table 1.1). These factors acted in concert in influencing the fate of PCP sorption-desorption in soil.

The retention of HOCs in the soil-water system was strongly correlated with soil organic matter (SOM) content, and the soil mineral fractions played a comparatively minor role except in the absence of SOM (Xing and Pignatello 1997; Xia and Ball 1999). He et al. (2006b) reported that the presence of SOM showed a significant positive effect on the sorption of PCPs in six soils. By removing 80% of the organic carbon from soil with H_2O_2 , sorption of PCP decreased by an average of 50%. They reported the hysteresis index (HI) for pentachlorophenol sorption on the six soils at five representative concentrations before and after treatment of soil with H_2O_2 . Figure 1.3 showed that the value of HI generally decreased after treatment with H_2O_2 , especially in soils 1, 2, 4 and 5. In soil 4, PCP desorption was completely reversible (zero or negative HI value indicated that sorption-desorption hysteresis

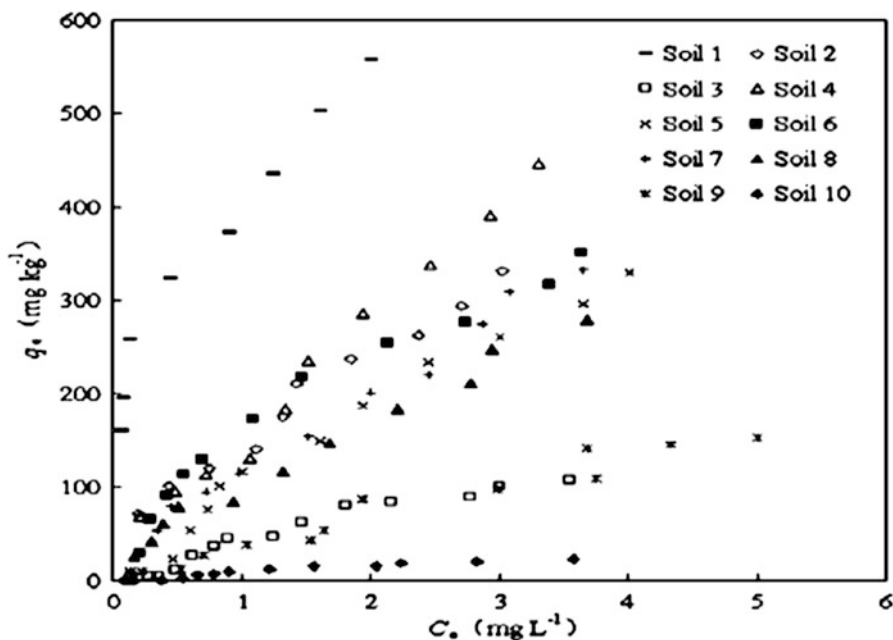


Fig. 1.2 Single-dilution desorption isotherms of pentachlorophenol (PCP) on 10 soils. q_e is the amount of PCP sorbed per mass of soils, C_e is the equilibrium PCP concentration. The symbols denote experimental data points (He et al. 2006a)

was statistically insignificant). These results also indicated that the H_2O_2 treatment had great effects on the TOC and pH values of different soils. However, soils 3 and 6 showed unexpected increases in the value of HI with the majority of concentrations of PCP tested. This might happen due to minor surface changes in clay and oxide minerals. He et al. (2006b) also reported that the removal extent of TOC was low. Thus the increment of HI was possibly related to the change of pH value.

The impact of clay minerals and DOM on the competitive sorption-desorption of PAHs was studied by Hwang and Cutright (2002). They reported that the amount of desorbed pyrene was similar in subsoil where SOM had been chemically removed compared to bulk soil. However, when clay minerals were removed, a significant amount of pyrene was desorbed. For instance, 3.97 and 12.76 $mg\ kg^{-1}$ pyrene was desorbed when it was added at the rate of 3 and 15 $mg\ L^{-1}$, respectively. These values indicated that in the clay-depleted subsoil containing SOM the amount of pyrene desorbed was 1.5 (3 $mg\ L^{-1}$) to 3.4 (15 $mg\ L^{-1}$) times greater than the bulk soil. The contribution of clay minerals to phenanthrene (PHE) desorption was more significant at lower initial concentrations. Desorbed amounts of PHE increased by 3.2 (3 $mg\ L^{-1}$) to 1.7 (15 $mg\ L^{-1}$) times in clay depleted soil, desorption of pyrene decreased by 26.7 and 64.8% at 3 and 15 $mg\ L^{-1}$, respectively, when only clay minerals were present as sorbent. They also reported that the clay mineral contribution to PHE sorption was 2.6% greater than SOM when the level of added

Table 1.1 Stepwise regression models for predicting parameters of PCP sorption on soils based on soil properties (He et al. 2006a)

Stepwise regression models ^a	R^2	F value ^b	T value and R^2 of the partial regression coefficient		
			T value ^b	R^2	
$Y_1 = 261.791 - 21.810X_1 - 56.379X_2 + 3.009X_3 + 30.523X_5$	0.939	19.406**	X_1	2.553*	0.566
			X_2	5.482**	0.857
			X_3	4.593**	0.808
			X_5	2.717*	0.596
$Y_2 = 14.960 - 1.722X_1 - 0.102X_6 - 0.004X_8 + 0.059X_{10}$	0.843	6.685*	X_1	3.987**	0.760
			X_6	2.864**	0.621
			X_8	3.250*	0.679
			X_{10}	1.984	0.441
$Y_3 = 62.296 - 12.416X_1 + 0.431X_7 - 0.012X_8 + 0.362X_{10}$	0.897	10.844*	X_1	6.139**	0.884
			X_7	3.808**	0.743
			X_8	2.280	0.510
			X_{10}	2.591*	0.573
$Y_4 = 62.311 - 5.349X_1 - 13.623X_2 + 0.464X_3 + 0.398X_9$	0.901	11.284*	X_1	3.465*	0.706
			X_2	5.320**	0.850
			X_3	3.601*	0.723
			X_9	2.208	0.494
			X_{10}	2.591*	0.573
$Y_5 = 4.102 - 0.295X_1 - 0.459X_2 + 0.039X_4$	0.960	47.884**	X_1	9.487	0.937
			X_2	6.070	0.859
			X_4	4.028	0.729
			X_{10}	2.591*	0.573
$Y_6 = 1.288 - 0.623X_2 + 0.078X_4$	0.856	20.760**	X_2	6.259	0.674
			X_4	6.165	0.845

^a Y_1 , S^0 , mgkg^{-1} ; Y_2 , b , L mg^{-1} ; Y_3 , K_D , L kg^{-1} ; Y_4 , $(S_0b)/K_D$; Y_5 , $\text{Log}K_{oc}$, L kg^{-1} ; Y_6 , HI ($T=20^\circ\text{C}$, $C_e=0.8 \text{ mg L}^{-1}$); X_1 , pH ; X_2 , TN , g kg^{-1} ; X_3 , CEC , cmol (+) kg^{-1} ; X_4 , TOC , g kg^{-1} ; X_5 , FA-C , g kg^{-1} ; X_6 , HA-C , g kg^{-1} ; X_7 , Humin-C , g kg^{-1} ; X_8 , C_{mic} , mgkg^{-1} ; X_9 , clay content, %; X_{10} , the silt content, %.

^b *Correlation is significant at 0.05 probability level; **correlation is significant at 0.01 probability level.

PHE was 3 mg L^{-1} at a clay concentration of 12.22%. Therefore, the desorption resistant fraction was attributed to the PAHs binding to the clay minerals. The PAHs bound on the SOM surface were easily desorbed due to relatively weak binding forces compared to PAHs bound to clay minerals. Therefore the PAHs desorption in soil containing SOM was greater than in subsoil or bulk soil containing clay minerals.

From the above discussion it could be concluded that the dynamic behavior of POPs sorption was the main risk for global contamination. The dynamic behavior of POPs sorption in the environment was directly related to the types of minerals and organic matter present in the soil. The sorption ability decreased with increasing residence time of the compounds in soil and depended on the nature and quality of the SOM. Soil texture also played a significant role in sorption-desorption reactions of POPs in soil. For example, the presence of clay had a pronounced positive effect on the availability of POPs in soil with low content of organic matter.

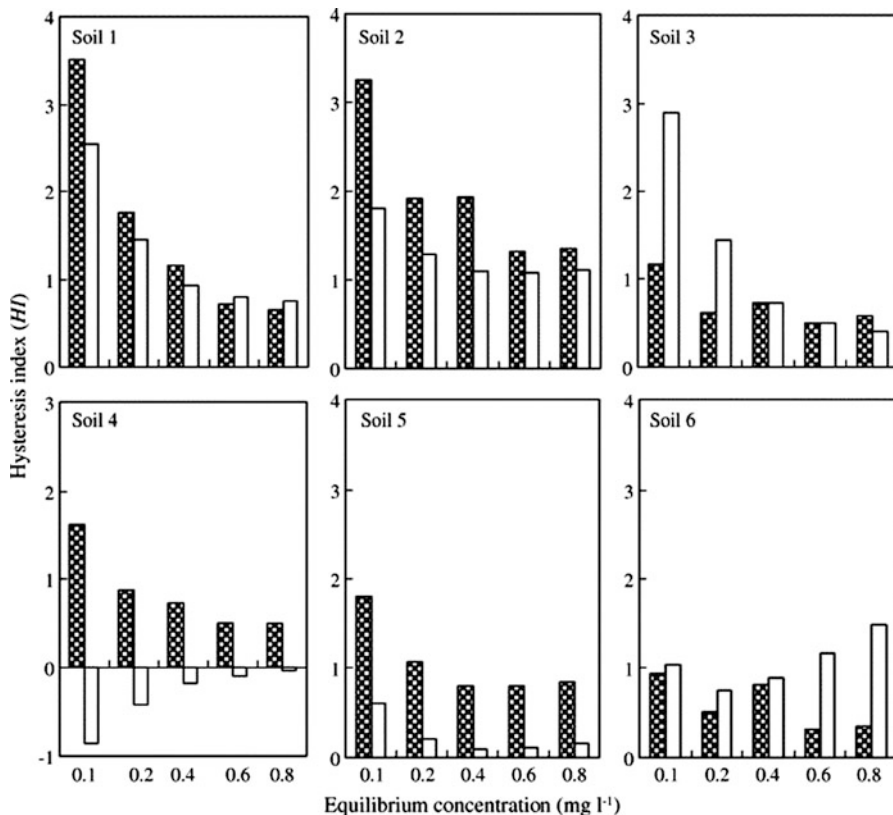


Fig. 1.3 Hysteresis index (HI) for pentachlorophenol sorption on six soils at five representative concentrations before and after removal of the organic carbon by H_2O_2 . Symbols: (■) before H_2O_2 – treatment; (□) after H_2O_2 – treatment (He et al. 2006b)

1.4 POPs Bioavailability in the Presence of Organic Matter

Organic matter is a very important factor that can limit the availability and mobility of POPs in soil (Northcott and Jones 2000). A substantial percentage ranging from 20 to 90% of the total organic contaminant applied to a soil might become associated with the humic fraction (Xie et al. 1997; Burauel and Fuhr 2000). Humic substances have been traditionally divided into three operationally defined fractions: (i) fulvic acid, (ii) humic acid (HA), and (iii) humin which is defined as that fraction which is insoluble in an aqueous solution at any pH (Kohl and Rice 1998). According to Fabio and Alessandro (2001), microcosms that received humic substance (HS) at 1.5% showed a higher persistence of specialized bacteria and yields of PCB biodegradation and dechlorination products about 150 and 100%, larger, respectively, than those in HS-free microcosms. Therefore, humic substances and similar materials might enhance PCB bioavailability and biodegradation during

soil bioremediation. Kastner and Mahro (1996) also reported that the presence of the solid organic matrix of compost seemed to be essential for the enhanced degradation of PAHs in soil.

PCBs binding to humus in the soil environment and the adsorption of PCBs have been related to soil organic matter content. The toxicity of Aroclor 1254 decreased in the presence of organic matter (Strek and Weber 1982a). Moza et al. (1979) speculated that PCBs in soil were metabolized to phenols which polymerized to form bound residues. However, it was more commonly accepted that these xenobiotics were bound to humic substances through charge-transfer complexing, electrostatic attractions, and hydrophobic bonding (Strek and Weber 1982b). Adsorption increased as the number of chlorine atoms in the PCB molecule increased and was influenced by the position of the chlorine substituent on the biphenyl ring. The 2,4-monochloro isomers and 3,4-dichlorobiphenyl were more likely to bind to organic matter than other biphenyls (Bollag and Loll 1983).

Organic pollutants strongly adsorbed to carbonaceous sorbents such as black carbon (Bucheli and Gustafsson 2000; Cornelissen et al. 2006; Koelmans et al. 2006; Ghosh 2007). In particular, activated charcoal had a strong adsorptive capacity due to its high specific surface area (Cornelissen et al. 2005). Adsorption to activated charcoal could render hazardous organic pollutants in soils and sediments less available to organisms (Burgess et al. 2009) and hindered their dispersal into unaffected environments. Tomaszewski et al. (2007) added 3.2% carbon or reactivated carbon to contaminated sediment (containing up to 252 mg DDT kg⁻¹) and thereby reduced aqueous equilibrium concentrations by up to 83%. In a study by Vasilyeva et al. (2001), the addition of 1% activated carbon to a TNT-contaminated soil (2,000 mg kg⁻¹) reduced the concentrations of extractable TNT and its metabolites by 89% within 120 days. The accelerated removal was attributed to reduced toxicity of the contaminants leading to enhanced microbial degradation.

Pan et al. (2007) also studied the effect of organic matter fractions on sorption of phenanthrene, naphthalene and o-xylene. They adopted humic acid and de-ashed humin using batch equilibration techniques. Aliphatic-rich de-ashed humin exhibited the highest sorption capacity for HOCs while mineral associated humin had the strongest nonlinearity. Aliphatic components of SOM contributed greatly to sorption of HOCs in soil and sediments.

Wen et al. (2009) studied the immobilization of pentachlorophenol in soils amended with 2.0% char, humic acid (HA) or peat. The extractability of PCP was significantly decreased (Fig. 1.4). Desorption kinetics indicated that the amendments could lead to strong binding and slow desorption of PCP in soils. The results of both physicochemical and biological tests suggested that the amendments reduced PCP bioavailability quickly and implied that addition of carbonaceous materials, especially char, was a potentially attractive in-situ remediation method for sequestration of PCP in contaminated soil.

Weber et al. (2006) proposed in-situ remediation methods to reduce the bioavailability of organic pollutants in soils. The organic contaminants were partitioned to carbonaceous sorbents that were mixed with soil to enhance the natural process of contaminant stabilization. They developed engineered sorbents from natural

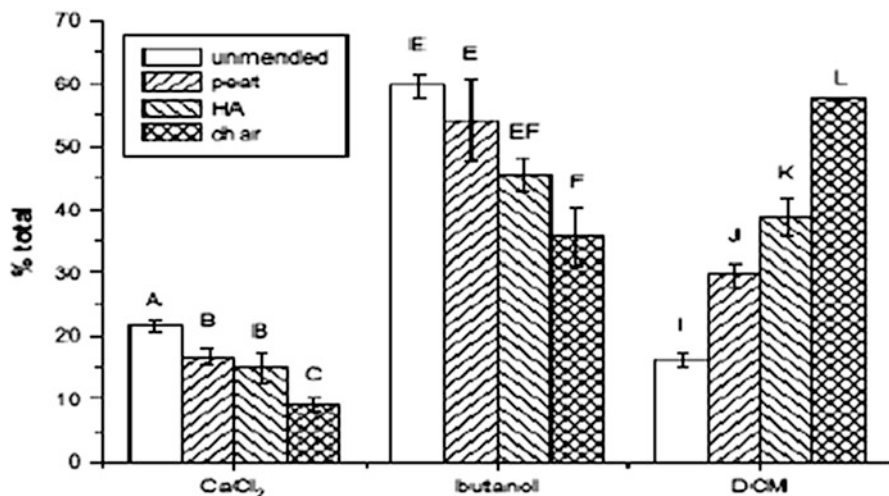


Fig. 1.4 Extractable fractions of PCP in soil amended with carbonaceous materials for 250 days using CaCl₂, butanol and DCM as extractants. Error bars represent one standard deviation. Bars with same letter or letters imply no significant difference ($P < 0.05$) (Wen et al. 2009)

organic materials, such as peat, soybean stalk and pine needles under conditions of superheated temperature and high pressure, for sorption of PAHs in contaminated soils. Both natural and engineered natural materials significantly decreased the extractability and bioavailability of PAHs from contaminated soils (Tang and Weber 2006; Weber et al. 2006; Tang et al. 2007). Addition of active carbon to sediments increased the desorption of PCBs and PAHs (Zimmerman et al. 2004). The bioavailability and bioaccumulation of PCBs were reduced markedly by activated carbon amendment in both laboratory (Millward et al. 2005) and field (Cho et al. 2007) tests. This clearly demonstrated the effectiveness of amendments for immobilization of hydrophobic organic contaminants in soils and sediments.

Rhizosphere technology is one of the emerging techniques to control POPs activity in soil. This technology has been applied to bioremediate POPs through plant growth in order to accelerate degradation rates. The presence of plants had positive effects upon the degradation of a wide range of organic compounds (Hayat et al. 2011; Ma et al. 2010). These included the degradation of simple phenolics, aliphatic hydrocarbons, trichloroethylene, polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatics and insecticides. He et al. (2005) reported that the effect of root proximity (i.e. the distance from the root surface) was important in the removal of PCPs. The rhizosphere environment enhanced the ability of soil microorganisms to remove POPs, in addition to enhancing phosphatase and urease activity which were active in the degradation of PCPs in the rhizosphere of ryegrass. As a result, the corresponding degradation gradients of PCP occurred (Fig. 1.5). He et al. (2009) demonstrated that the rhizosphere gradient effect of ryegrass (*Lolium perenne* L.) on the first two principal components of phospholipids fatty acids

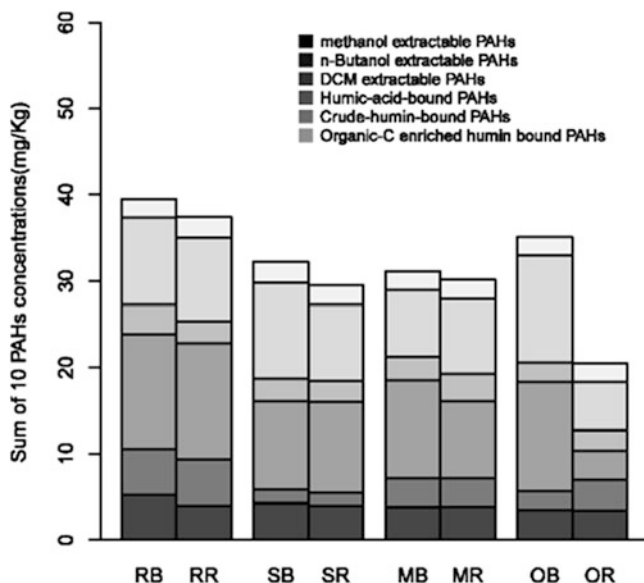


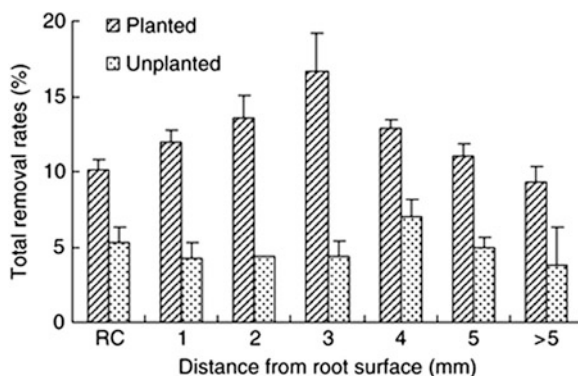
Fig. 1.6 Total concentration of PAHs in rhizosphere and bulk soils based on sequential extraction. *RR* rhizosphere soil of rape, *RB* bulk soil of rape, *SR* rhizosphere soil of soybean, *SB* bulk soil of soybean, *MR* rhizosphere soil of maize, *MB* bulk soil of maize, *OR* rhizosphere soil of oat, *OB* bulk soil of oat (Ma et al. 2010)

13.5 mg kg⁻¹ under rape. Comparison of profiles among the plant species showed that profiles of sequential extraction were relatively similar between bulk and rhizosphere soils under the same plant species. However, the concentration of PAHs fractions were significantly lower than in the corresponding bulk soil, including the DCM extractable PAHs in the rhizosphere of maize, methanol extractable PAHs in the rhizosphere of rape, and crude humin-bound PAHs in the rhizosphere of soybeans and oat.

Ding et al. (2009) reported that rhizoremediation played a vital role in the degradation of PCBs in contaminated soils. They measured the degradation of Aroclor 1242 in the rhizosphere of ryegrass in specially designed rhizobox in which they measured Aroclor 1242 at the millimeter scale in the near and far rhizosphere. The total removal rates of Aroclor 1242 in planted soils were much higher than in unplanted soils (Fig. 1.7). Ryegrass removal rates were affected by the proximity to the root. The degradation of Aroclor 1242 near the rhizosphere was higher than in the root compartment and far rhizosphere. However, there were no significant differences in the removal rates with increasing distances from the central compartment.

It can be concluded that organic matter present in soil or came through plant in the form of root exudates has significant interactions with POPs activity in soil. Natural organic matter plays an important role in controlling the movement as well

Fig. 1.7 Aroclor 1242 total removal rates (%) in various sampling zones as a function of proximity to ryegrass roots grown in the soil treated with 8.0 mg kg^{-1} of Aroclor 1242. Bars are the SE of means of three replicates. RC, root compartment (Ding et al. 2009)



as the bioavailability of POPs. Rhizosphere effect can also play a vital role in the remediation of POPs in the soil because roots release significant amounts of organic compounds in the form of root exudates which directly affect POPs bioavailability as well as microbial activity in the rhizosphere, thus increase the degradation of the POPs in rhizosphere vicinity.

1.5 Environmental Factors Affecting Transport, Sorption and Bioavailability of POPs

POPs undergo long range atmospheric transport and reach remote regions where they have never been produced or used. This process could happen as a simple emission-transport-deposition event or following a series of “hops” by deposition onto a surface and subsequent emission (Wania and Mackay 1996). In general, the capacity of an environmental compartment to retain and release chemicals, which depended on several processes, was widely variable both spatially and temporally. The distribution of POPs based on the environmental compartments depended on their properties and on the capacity of the exchange surfaces (vegetation, soil, water) to retain them (Mackay 2001). Therefore, the effects of possible future climatic changes, which can imply, for example, the acceleration of desertification, changes in land use, the reduction of glacier surfaces, can significantly influence global POPs cycling (e.g. Dalla Valle et al. 2004; Macdonald et al. 2005).

The transport distance and the number of air-surface exchange episodes depended on the type of surface (soil, water, vegetation, etc.) and on the physical-chemical properties of the given chemical. According to this principle, persistent chemicals with high volatility would be transported long distances followed by deposition in distant areas (e.g. arctic regions), while those with lower vapor pressure would be deposited preferentially in areas closer to the emission source. Many other mechanisms and factors were able to influence the distribution of POPs in the atmosphere: the capacity of the environmental compartments to accumulate

or to degrade POPs; the atmospheric circulation patterns; the spatial and temporal distribution of primary sources and the kinetic of the air-surface exchange. POPs in air could be degraded by photo-degradation and via reactions with hydroxyl radicals, both depending, to a certain extent, on the solar radiation intensity (Dalla Valle et al. 2007) and other reactive agents.

Temperature had a significant effect on the microbial growth and physiological activity including uptake and enzymatic dehalogenation of PCB congeners. The influence of temperature was multifaceted, which included changes in the adsorption and desorption kinetics of PCBs from soil particles. pH affected the equilibrium between PCBs that were dissolved and those that were adsorbed to organic matter and thus influenced the bioavailability of PCBs in soil (Jota and Hassett 1991). Temperature was one of the main factors which influenced the global distribution of POPs, even if several other processes played an important role. Processes directly depending on temperature were: emission rates from primary and secondary sources, the gas-particle partitioning of POPs in air, reaction rates (biodegradation, photolysis and oxidation in air), and the air-surface exchange (Halsall et al. 1999). The degradation rates, for example, were estimated to increase by a factor of two to three for every 10 °C increment (Lammel et al. 2001; Macdonald et al. 2005). In addition, important atmospheric depletion mechanisms for organic contaminants were photochemical degradation and the degradation initiated by the hydroxyl radicals, whose concentration was related to solar activity and cloud cover (Mandalakis et al. 2003). Recently, an attempt to estimate the spatial and temporal variability of POPs distribution has been made for the oceans (Jurado et al. 2004), surface soils (Dalla Valle et al. 2005) and vegetation (Dalla Valle et al. 2004). The spatial variability of this capacity depended on the combination of several factors e.g. organic carbon content (in soil or within plant leaves), green biomass, or more generally the ecosystem type. Those factors even could vary markedly within a limited space (e.g. along a mountain slope), thus influencing POPs distribution according to their properties (Grimalt et al. 2004; Van Droodge et al. 2004; Daly and Wania 2005). The temporal variability was mainly dependant on temperature (e.g. Hornbuckle and Eisenreich 1996; Halsall et al. 1999), therefore showing daily and seasonal oscillations, but also on biomass trends and biogeochemical cycles (e.g. phytoplankton cycles; Dachs et al. 2002), which could be seasonal or exhibiting a long term trend, and on soil use and properties. Another complication was given by the wide range of physical-chemical properties of the different classes of chemicals. Other climate related variables such as the frequency of storm surges, precipitation, the seasonality and the intensity of the atmospheric events, could influence the fate of POPs in the environment. Increased precipitation, for example, could cause an increase of POPs deposition onto the soil. More frequent storm surges might enhance the mobilization of chemicals stored in the soil compartment, which could be transported by land runoffs, making them available to aquatic organisms.

The degradation of POPs might be further limited by a number of environmental parameters, such as temperature, pH, presence of oxygen, nutrients, moisture and salinity. Soil and ground water temperatures varied regionally and seasonally. Optimizing these variables in-situ would enhance and maintain bioavailability of

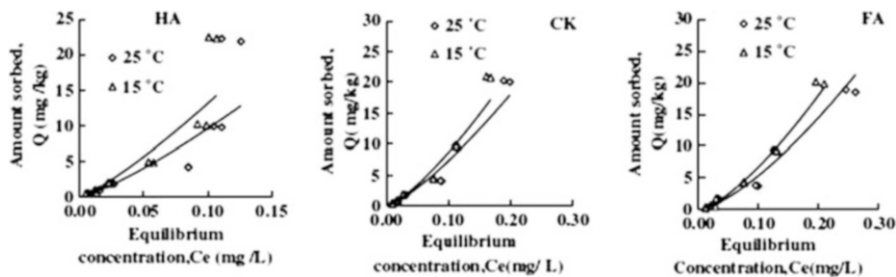


Fig. 1.8 Sorption isotherms for phenanthrene (PHE) in soils at different temperature levels (Ping et al. 2006)

POPs. Most biodegradation studies have been performed at temperatures from 20°C and 30°C. Only a limited number of studies have illustrated the biodegradation of PAHs at low temperatures and they generally agreed that PAHs biodegradation rates and efficiencies were lower at lower temperatures (Eriksson et al. 1999; Phillips et al. 2000; Yuan et al. 2000). However, some studies have shown that a decrease in temperature did not affect PAHs biodegradation (Whyte et al. 1997; Mohammed et al. 1998).

Moisture levels determined the oxygen content, redox potential, and type of microflora of a soil. The amount of water in soil then had a profound effect on the interactions between humus and POPs. When soils were flooded and, therefore, became anaerobic, dinitroanilines and nitrobenzenes were converted to anilines, which could react with humus (Moza et al. 1979). Inorganic minerals also had some interactions with the POPs and played an important role in the transformation of POPs. Manganese and iron oxides and some clay minerals promoted the oxidation of a number of organic pollutants (Mortland and Halloran 1976; Pizzigallo et al. 1995).

Ping et al. (2006) reported that the sorption of phenanthrene along with environmental factors such as pH and temperature also affected exogenous humic acids (Figs. 1.8 and 1.9). Humic acid and fulvic acid from the same source had different effects on the adsorption of phenanthrene. Adsorption of phenanthrene was higher in soil treated with fulvic acid compared to humic acid. Added humic substances influenced the adsorption of phenanthrene, which was also affected by environmental conditions. Exogenous humic substances played an important role in the regulation of soil PAHs mobility under appropriate conditions leading to a decrease in PAHs pollutant diffusion.

Ghosh et al. (2001) investigated the kinetics and thermodynamics of PAHs desorption from sediment. They demonstrated that desorption of PAHs associated with clay/silt particles was faster at room temperature and was characterized by low desorption activation energies, whereas desorption of PAHs associated with coal-derived material at room temperature was much slower and was characterized by high desorption activation energies. Particles derived from coal in the sediment, which contained the majority of PAHs, were in the state of non-equilibrium even after decades of aging in the field due to their extremely slow diffusion through

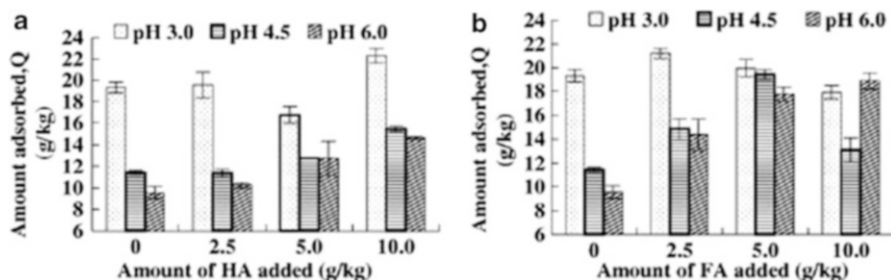


Fig. 1.9 Adsorption of PHE under different pH conditions (Ping et al. 2006)

the polymeric coal-derived materials. Internal non-equilibrium conditions slowed down the long-term desorption from the coal-derived materials. To strongly bond PAHs on coal-derived materials high activation energy required for desorption and relatively unavailable at ambient temperatures. PAHs associated with media having large activation energies might thus comprise the unavailable PAHs fraction in sediments, and these PAHs might pose less environmental risk than PAHs in clay and silt fractions (Luthy et al. 2000).

The potential capacity of soil abiotic components (e.g. oxides, clay minerals, humic substances) to promote the transformation of aromatic molecules, was unexplored for POPs characterised by a very low water solubility. Taking into account that the adsorption process represented the first fundamental step of the oxidation reaction, the interaction between the inorganic catalyst and the POPs could be studied by mixing and grinding the two reactants in solid phase. This method called “mechanochemical” was well known in environmental fields and has attracted attention in relation to the degradation of organo-chlorides (Loiselle et al. 1997; Nasser et al. 2000; Mio et al. 2002). The treatment provoked a solid-state transformation at the mineral surface without any deformation of the structure. The solid contact of the modified surface with the POPs induced the production of free radicals, which were very active in subsequent oxidative coupling reactions. Thus, the “mechanochemical” procedure could start the reaction between the POPs and the minerals without any interference from the organic solvents required to solubilise non-polar compounds. Mechanochemical treatments of soils contaminated with organochlorides molecules were conducted by grinding using a ball mill with different dechlorinating reagents (Loiselle et al. 1997; Mio et al. 2002). Few authors provided information on the mechanochemical technique applied to oxidative reactions. Some researchers (Nasser et al. 2000; Shin et al. 2000) successfully tested the degradation of herbicides such as 2,4-D and atrazine using very gentle grinding of manganese oxides with herbicides together. The authors advocated that the grinding of a reactive mineral in the presence of adsorbed organic molecules could operate as a surface alteration of the mineral structure producing structural defects (Pizzigallo et al., 2004). These defects might produce chemical activation, which promoted the breaking of chemical bonds and consequently the degradation