Research Advances in Remediation of PCBs Contaminated Soils

Longfei Xia [1, 2, 3, 4, a]

[1]Shaanxi Provincial Land Engineering Construction Group Co., Ltd, Xi'an 710075, China;

[2]Institute of Land Engineering & Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd, Xi'an 710075, China;

[3]Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Land and Resources, Xi'an 710075, China;

[4]Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi'an 710075, China.

[a]summerdragonfly@163.com

Abstract

This paper emphatically described behaviors of PCBs in soil environment and their hazards to mankind, and revealed laws of the movement and transformation of PCBs in soil. As a review, it had summarized and compared technologies for remediation of PCBs-contaminated soil in recent years. In the end the paper presented the prospect for the research on soil PCBs pollution.

Keywords

Soil, PCBs, progress.

1. Introduction

With the rapid development of industrial and agricultural production, toxic chemical pollutants had entered the living environment of people through various channels, especially persistent organic pollutants [1]. This problem had led to increasingly serious environmental pollution and had become a major environmental safety issue to be solved [2-4].

2. Environmental Behavior of PCBs in Soil Environment

Polychlorinated biphenyls (PCBs), as typical environmental estrogens, are a group of chlorinated aromatic compounds composed of 209 congeners that have potential carcinogenic biological effects. Its toxicity mainly depended on the amount of Cl and the position of Cl on the benzene ring. The lower the number of substitutions of the Cl atom, the less toxic, and the more volatile and water soluble. PCBs were a typical type of persistent organic pollutants (POPs). It accumulated, concentrated and amplified into the animal body and human body through the biological chain. Animal experiments had shown that PCBs had induced effects on the lesions of the skin, liver, gastrointestinal system, nervous system, reproductive system, immune system and even cancer. The acute toxicity of PCBs was very low, but human were exposed to low doses of the environment for long periods of time may cause chloroacne, other deficiencies or hyperplasia, endocrine disorders, hepatotoxicity, reproductive system toxicity and carcinogenesis [5]. In industrialized countries, social public hazards had already been formed. For example, rice bran oil in the northern part of Japan's Kyushu Prefecture was the most serious in 1968. 1,600 persons were poisoned by rice bran oil contaminated with PCBs, including 22 deaths; in 1979, Taiwan also repeated similar events. The distribution of PCBs was extremely widespread. There were many reports on the contamination of PCBs in the soil and sediment. In soils that were not directly contaminated, they were usually several mg/kg to several tens of μg/kg. PCBs could be up to a dozen mg/kg in industrial contaminated areas and up to 510 mg/kg in the soil near factories producing electrical components in Japan. In China's Tibet, the PCBs content in uncontaminated soil was 0.625~3.501 g/kg, and in Shenyang it was detected at 6~15 μg/kg [6]. More studies had shown that a certain amount of polychlorinated biphenyls could be detected in polar animals such as polar bears, livers of Weddell seals, and eggs of South Polar skua and penguins [7]. The ubiquity of PCBs in the environment could also explain their chemical and biological stability. The research on the bioactivity of polychlorinated biphenyls estrogens had focused on the structural effect relationship. However, there was still lack of sufficient evidence on the mechanism of its estrogenic activity, biological effects at low doses, and response to humans [8].

After PCBs pollutants entered the soil environment, they were affected by the natural environment and their composition would change significantly. First of all, different compounds in PCBs had different volatility at room temperature. Replacing PCBs from 1 Cl to 10 Cl, the volatility differed by 6 orders of magnitude [9]. In the air, the more volatile PCBs tended to migrate with the airflow. Second, different PCBs had different water solubility. Adsorption capacity of PCBs in the same family could also vary greatly due to the different Cl substitution positions. The PCBs that entered the soil would be lost along with the flow, such as rainfall and irrigation, at different rates according to their different solubility in water and different adsorption performance, resulting in significant differences in their composition and source of pollution. PCBs entering the environment were also affected by other factors in the natural environment. Although the photolysis of PCBs was very small, various microorganisms in nature had a certain influence on the degradation of PCBs. Various organisms also had different effects on the migration of PCBs [6].

3. PCBs Contaminated Soil Repair Technology

Due to the huge potential hazards of PCBs, PCBs contaminated soil repair technology had increasingly attracted worldwide attention. Current research methods could be roughly divided into: bioremediation, chemical remediation and physical engineering measures. PCBs had a strong hydrophobicity, which greatly affected its bioavailability and also affected the biodegradation efficiency. Therefore, it was necessary to increase the solubility of PCBs in hydrophobic environments first by using surfactants. The solubilizing effect of the surfactant enhanced the soil elution rate of the PCBs, thereby improving the remediation effect. At the same time, surfactants could promote the photolysis of PCBs, which could provide H atoms for photolysis reaction and promote the Cl-reaction of PCBs while reducing side reactions. Therefore, the use of surfactants could be used as a pretreatment for PCBs contaminated soil. Fabio Fava team studies had shown that humus could increase the bioavailability of soil PCBs under laboratory conditions and contribute to the biodegradation of PCBs [10]. Singer AC team reused PCBs degrading bacteria and surfactant for 34 times in more than 18 weeks, eventually partially degrading PCBs in soil [11].

3.1 Bioremediation

PCBs was a class of stable compounds that were generally not readily biodegradable, especially high Cl-substituted isomers. Under the predominant species and other suitable environmental conditions, the biodegradation of PCBs could not only occur but also increase the rate greatly. Biodegradation of PCBs had been carried out in the laboratory. It was also a research hotspot in recent years. PCBs with Cl number <5 under laboratory conditions had been shown to be oxidized by several microorganisms to inorganic substances. PCBs with high Cl substitution ($Cl>4$) were generally considered to be persistent under aerobic conditions. The more Cl substitutions, the more difficult it was for aerobic degradation of chlorobenzenes. But there are exceptions. Alcaligenes Y42, Pseudomonad SP. LB400 and Alcaligenes eutrophus H850, Alcaligenes SP. JB1 had been shown to degrade 4-6Cl substitutions [12]. The first and most important step in the biodegradation process of PCBs was anaerobic reduction of Cl. Rhee believed that the reductive Cl removal reaction mainly depended on the substitution form of Cl instead of the substitution position [13]. However, there were also reports that reductive ablitation occurs only at certain substitution sites, which may be related to their respective dominant bacteria and reaction conditions. The de-Cl reaction time under anaerobic conditions was generally long, and PCBs concentration, nutrient concentration, and other substances such as surfactants also affected the Cl-rate of PCBs [14]. Temperature could not only reduced the reduction time, but also had a certain influence on the Cl removal method and the degree of Cl removal. Theoretically, PCBs might be completely degraded into CO_2, H_2O, and chlorides through an anaerobic-aerobic combination treatment. For the first time in the laboratory, Fish used two stages of anaerobic and aerobic operation in series. After two days, Aroclor 1242 degraded 81% and Aroclor 1254 degraded 35% [15]. The actual environment was an open complex environment. Biotransformation of PCBs was slow due to light, temperature, bacterial species, pH, chemical substances, and other physical processes. It was almost negligible compared to other conversion processes. Therefore, the pollution of PCBs was difficult to eliminate fundamentally, and its pollution would have a long-term impact on the entire ecological environment.

PCBs in the natural environment, the most suitable treatment method that could be used at present was land biological treatment. Because the soil was called "a natural medium for microorganisms." The soil had the most suitable environment for microbial life. It degraded PCBs into environmentally acceptable substances such as CO_2 and H_2O. Compared with other methods such as landfill, incineration or soil washing, the method of land biological treatment had the characteristics of small environmental damage, economical efficiency, and was therefore a widely used treatment method. At present, there were many researches on the biodegradation of polychlorinated biphenyls in soil water environment. Scholars such as Brown [16], Bedard [17] and others had reported biodegradation through a large number of experimental and theoretical studies. PCBs in the soil environment could be degraded by indigenous microorganisms to a level where the concentration could no longer be reduced. Subsequently, the degradation rate of PCBs in the soil became very slow, and the degradation almost stopped, even though the best biodegradability conditions were maintained. At this time, polychlorinated biphenyls that remain in the soil had a greatly reduced permeability and diffusibility, and there was little possibility of re-diffusion to the outside of soil particles. It was almost impossible to contact microorganisms in the external water environment. Therefore, the risk of harm to the groundwater environment and human health was also greatly reduced. At present, there were models for predicting the biodegradation process. The "two-phase model" proposed by Scow [18] and the mathematical model established by Liu Ling comprehensively consider the reversible adsorption/desorption process, diffusion process, irreversible soil shielding reaction process, and the biodegradation process outside the soil particles. Through these models, they could quantitatively point out the end point of land biological treatment and predict the law of its degradation process [19].

Phytoremediation had been considered as a more effective technique for removing or degrading different pollutants in soil. However, there were some limitations for the hydrophobic organic molecules PCBs, mainly due to their insoluble water and low biological activity. Campanella BF studies had shown that plants could be used to increase the activity of bacteria in the soil and that phytoremediation offered new possibilities for reducing the risk of PCBs. But at the same time, they also pointed out that phytoremediation technology had limitations in removing PCBs from soil [20].

3.2 Chemical Remediation

Due to the biological unavailability of PCBs, chemical remediation had an irreplaceable position in the treatment of PCBs contaminated soil, mainly concentrated on heat treatment and photodegradation.

The pyrolysis method was a high-temperature destruction method. Such methods include: incineration pyrolysis, arc pyrolysis, ultrasonic radiation, plasma arc, molten lead, molten aluminum and so on. Combining various methods, the degradation rate of pyrolysis treatment of PCBs can reach above 99%. The incineration method had a wide range of treatment, especially for high concentration flammable pollutants. The other methods were basically applicable to the treatment of low-concentration pollutants. However, the cost of pyrolysis treatment was generally higher, and only the ultrasonic method had a lower cost and was more suitable for civilian use. Due to the small amount of PCBs in contaminated soils, there were few reports on direct treatment of PCBs in soil by pyrolysis.

Photolysis was mainly UV degradation. Although the physical and chemical properties of PCBs were stable and resistant to biodegradation, they were sensitive to ultraviolet light under certain conditions. Hutzinger pointed out that the factors affecting the UV absorption band of biphenyl and its halogenated compounds were as follows: the nature of the substituents; the substitution position of the substituents on the phenyl ring; the number of substituents; the degree of substitution of the ortho position on the phenyl ring. Bunce and Ruzo's study found that the photosensitivity of biphenyls substituted with Cl atoms on the benzene ring to generate PCBs was stronger than PCBs with meta and para positions substituted by Cl atoms [21, 22]. Sawhney further observed that PCBs with high Cl content were more prone to photolysis and faster reaction than low content of PCBs in PCB photoreaction [23]. Thereafter, the use of surfactants to elute PCBs in contaminated soils and then photodissolve the PCB contaminants in the eluent was a new method of treating soil contaminated by PCBs. In 1992, Hawarl reported that photodegradation of Aerorol 1254 in contaminated soil in alkaline 2-propanol with phenothiazine (a photosensitizer) can lead to effective Cl removal [24]. From a socioeconomic point of view, the use of a 100 kw photodegradation system to treat soil at a treatment efficiency of 1 m^3/d cost approximately \$120 to \$250 per cubic meter [25], which had a greater development prospect than other methods. Thus, foreign light degradation technology had matured. However, in 1996, China began to study the degradation mechanism of PCBs in n-hexane [26], and the overall level was weak. Research in this area needs to be strengthened.

3.3 Physical Engineering Measures

The physical engineering measures were mainly to transfer pollutants through landfills, topsoil, and land and other engineering methods. This law cannot fundamentally solve the problem of pollution of PCBs in the environment. It was only a temporary measure based on the different roles of the land.

4. Conclusion

PCBs were typical of persistent organic pollutants, and they were extremely widely distributed, which posed a huge potential hazard to the environment. The toxicological mechanisms, structural activity relationships, and pollution control techniques of PCBs had increasingly become the focus of research. Soil had become an important gathering place for PCBs. PCBs had little migration ability in soil and were difficult to be bio-utilized and degraded under natural conditions. With the aid of PCB degrading bacteria and surfactants acclimated in areas contaminated by PCBs, the contaminated soil can be bioremedied through aerobic and anaerobic mechanisms. There were still some difficulties in the biodegradation of high Cl-substituted PCBs. Photodegradation of PCBs in soil by UV photolysis had a good effect of degradation, and had certain social and economic value. Therefore, it had certain potential for development. China's research in this area was relatively weak, and the pollution hazards of PCBs in soil had not attracted enough attention. We should strengthen research on PCBs pollution remediation technology and use more scientific and technological achievements to explore new approaches to governance.

References

[1] Yu Gang, Huang Jun, Zhang Pengyi. Persistent organic pollutants: one of the important global environment problems. Environmental Viewpoint,2001,(04): 37-39.

[2] Iwata H, Tanabe S, Sakai N. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol,1993, 27(06):1080-109.

[3] Hayteas D.L, Duffield DA. The determination by HPLC of PCB and p,p'-DDE residues in marine mammals stranded on the Oregon Coast, 1991-1995. Mar. Pollut. Bull, 1997, 34(10): 844-848.
[4] Schade G, Heinzow B. Organochlorine pesticides and polychlorinated biphenyls in human milk of mothers living in Northern Germany: Current extent of contamination, time trend from 1986 to 1997 and factors that influence the levels of contamination. Sci. Total. Environ, 1998, 215(1-2): 31-39.
[5] Starek A. Polychlorinated biphenyls — toxicology and health risk. Rocz Panstw Zakl Hig, 2001, 52 (3): 187 – 201.
[6] Chu Shaogang, Yang Chun, Xu Xiaobai. Polychlorinated biphenyl congener residues in sediment and soil from pollution area.. China Environment Science, 1995, (6): 199 – 203.
[7] Kurunthachalam Senthil Kumar, Kurunthachalam Kannan, et al. Polychlorinated dibenzo-p-dioxins, dibenzofurans and polychlorinated biphenyls in polar bear, penguin and south polar skua. Environmental pollution, 2002, (119): 151 – 161.
[8] Du Kejiu, Xu Xiaobai. Research progress of environmental estrogen . Chinese Science Bulletin, 2000, (11): 2241 – 2251.
[9] Crine JP. Hazards decontamination and replacement of PCBs. A Comprehensive Guide. New York and London Plenum Press,1986, 12.
[10] Fava F, Piccolo A. Effects of humic substances on the bioavailability and aerobic biodegradation of polychlorinated biphenyls in a model soil. Biotechnol. Bioeng., 2000, 77(2): 204 – 211.
[11] Singer AC, Gilbert ES, Luepromchai E, Crowley DE. Bioremediation of polychlorinated biphenyl-contaminated soil using carvone and surfactant-grown bacteria. Appl. Microbiol. Biotechnol., 2000, 54(6): 838 – 843.
[12] Bedard DL, Wagner RE, Brennan MJ, Haberl ML, Brown JFJr. Extensive Degradation of Aroclors and Environmentally transformed Polychlorinated Biphenyls by Alcaligenes eutrophus H850. Appl.Environ. Microbiol., 1987, 5: 1094- - 1102.
[13] Sokol RC, Kwon O-S, Bethoney CM, Rhee G-Y, Reductive Dechlorination of Polychlorinated Biphenyls in St. Lwarence River Sediments and Variations in Dechlorination Characteristics. Environ.Sci. Technol., 1994,28, 2054 – 2064.
[14] Abramowicz DA, Brennan MJ, VanDort HM, Galiagher EL. Factors influencing the rate of polychlorinated biphenyls dechlorination in Hudson River sediment. Environ.Sci.Technol., 1993, 27: 1125 – 1131.
[15] Fish KM, Principe JM. Biotransformations of Aroclor 1242 in Hudson River test tube Microcosm. Appl. Environ. Microbiol., 1994, 60: 4289 – 4296.
[16] Brown JF, Bedard DL, Brennan MJ, Carnakan JC, Feng H, Wagner RE. Polychlorinated biphenyl dechlorination in aquatic sediments. Science, 1987a, (236): 709 – 712.
[17] Bedard DL, Quensen JR. Microbial reduction dechlorination of polychlorinated biphenyls. Microbial Transformation and Degradation of Toxic Organic Chemicals. Wiley-Liss, Inc. 1995, 127 – 216.
[18] Scow KM, Simkins S, Alexander M. Kinetics of mineralization of compounds at low concentrations in soil. Appl. Environ. Microbiol., 1986, (51): 1028 – 1035.
[19] Liu Ling, Cui Guangbai, Hao Zhenchun. Study on biodegration of PCBs in soil-water-microbes system. Journal of Hydraulic Engineering, 2000, (6): 6 – 8.
[20] Campanella BF, Bock C, Schroder P. Phytoremediation to increase the degradation of PCBs and PCDD/Fs.Potencial and Limitations. Environ. Sci. Pollut. Res. Int., 2002, 9 (1): 73 – 85.
[21] Bunce NJ. Phytodechlorination of PCBs: current status. Chemosphere, 1982, 11: 701 – 714.
[22] Ruzo, LO., Zabik MJ., Schutz RD. Phytochemistry of bioactive compounds: phyto-products and kinetics of polychlorinated biphenyls. J. Agr. Food Chem., 1974, 22: 199 – 202.
[23] Sawhney BL. Chemistry and properties of PCBs in relation to environmental effects. PCBs and environment. CRC press, 1986, 47 – 64.

[24] Hawarl J, Demeter A, Samson R. Sensitized photolysis of polychlorobiphenyls in alkaline 2-propanol:dechlorination of Aroclor1254 in soil samples by solar radiation. Environ.Sci. & Technol., 1992, 26: 2022 – 2027.
[25] Wekhof A. Treatment of contaminated water, air, and soil with UV flashlamps. Environ.Progr., 1991,10: 241- 246.
[26] Miao XS, Chu SG, Xu XB. Photodegradation of 2, 2, 5, 5-tetrachlorobiphenyl in hexane. Bull. Environ. Contam. Toxicol., 1996, 56: 571- 574.