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Review

Volatile Organic Compounds (VOCs) in Soil: Transport Mechanisms, Monitoring, and Removal by Biochar-Modified Capping Layer

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Abstract: Volatile organic compounds (VOCs), as a primary pollutant in industrial-contaminated sites or polluted soils, cause severe damage to the soil. Therefore, a comprehensive understanding of the transport of VOCs in soil is imperative to develop effective detection means and removal methods. Among them, biochar possesses potential advantages in the adsorption of VOCs, serving as an effective method for removing VOCs from soil. This review provides an overview of the VOCs within soil, their transport mechanisms, monitoring technology, and removal approach. Firstly, the historical development of the VOC migration mechanism within the capping layer is described in detail. Secondly, the in situ monitoring techniques for VOCs are systematically summarized. Subsequently, one of the effective removal technologies, a capping layer for polluted sites, is simply introduced. Following this, the potential application of a biochar-modified capping layer for the removal of VOCs is comprehensively discussed. Finally, the major challenges in the field and present prospects are outlined. The objective of this study is to furnish researchers with a foundational understanding of VOCs, their relevant information, and their removal approach, inspiring environmental protection and soil pollution control.

Keywords: volatile organic compounds (VOCs); transportation; in situ monitoring techniques; capping layer; biochar

1. Introduction

As urbanization rapidly advances, industrial restructuring continues, and traditional industrial enterprises gradually transform, a substantial number of industrial legacy contamination sites have emerged within and around urban areas. Among the contaminants prevalent in these industrial pollution sites or polluted soils, organic compounds are a significant issue. Common organic pollutants include total petroleum hydrocarbons, chlorinated hydrocarbons, and aromatic compounds, which are frequently employed as raw materials, products, or intermediates and widely used in industries, such as the chemical, metallurgical, and petroleum-refining sectors [1]. Organic pollutants exhibit high mobility and persistence, with their introduction into the soil through processes, including volatilization, leaching, dripping, and leakage, during their production, transportation, and storage, leading to severe soil damage [2]. Environmental issues caused by industrial organic pollutants are rising worldwide. According to statistics, the United States has approximately 500,000–1,000,000 contaminated sites, Germany has 240,000 sites, the Netherlands has 120,000 sites, and Canada has 30,000 sites [3–6]. In summary, addressing the pollution issues associated with organic contamination sites is an urgent problem, as the assessment, control, and remediation of water and soil pollution have become immediate needs within the environmental protection sector of various countries.

Industrial organic pollutants come from a variety of sources and include a wide range of compounds. Most of these organic pollutants are volatile organic compounds (VOCs). VOCs are characterized by their volatility, toxicity, irritancy, teratogenicity, and carcinogenicity, making them significant contributors to atmospheric, aquatic, and soil pollution [7]. With their broad spectrum and high potential hazards, VOC pollution has become a widespread problem worldwide. Liu et al. [8] arranged 30 sampling points for sampling groundwater in Lanzhou, China, and 13 VOCs were detected in 29 of these sampling points, with dichloromethane and toluene having the highest detection rate of 73.3%, and benzene and xylene having 66.7% and 50% detection rates, respectively. This evidence underscores the severe ecological damage inflicted by VOCs, emphasizing the urgent need for measures to remediate sites contaminated by VOCs.

To effectively remove VOCs from soil, it is imperative to understand the migration patterns and mechanisms of VOCs within the soil. Specifically, the migration of VOCs in soil is primarily governed by complex interactions between the VOCs and the soil materials, mainly involving convection–diffusion [9]. And, so far, many convection–diffusion models have been developed to describe the transport of VOCs in soil. In addition, it is crucial to develop methods for monitoring VOCs in the soil matrix. This includes not only efficient in situ monitoring techniques but also data interpretation and analysis tools [10,11]. These approaches are essential to enhance the identification and quantification of VOCs. Deploying effective monitoring solutions can help provide a deeper understanding of VOC behavior across a range of soil types and environmental conditions. This understanding is critical to developing more effective soil remediation and pollution prevention measures.

Currently, the remediation technologies for VOC-contaminated sites mainly include thermal desorption, cement kiln co-disposal, advanced oxidation, and soil drenching and are dominated by the ex situ treatment method [12,13]. In practical applications, these remediation methods are not only costly but also carry a high risk of secondary contamination. Therefore, remediation should consider both soil and water synergies and develop in situ treatment technologies. Among them, soil vapor extraction (SVE) is one of the most used in situ treatment methods. It extracts gas-phase compounds in the soil zone, induces directed airflow in the soil, facilitates the conversion of pollutants to the gas phase, and transports VOCs to the surface [14–16]. For instance, the results of indoor soil column tests by Yin et al. [17] showed that the SVE technology can reduce the concentration of multicomponent VOCs in soil columns by up to 99.52%. Nevertheless, when SVE technology is applied in the field compared to indoor test results, its efficiency in removing VOCs can be greatly reduced due to limitations such as large site areas and poor permeability of contaminated soil [18]. Labianca et al. [19] reported from field tests that after four years of SVE treatment, the concentration of VOCs in organic pollution sites was reduced by only 73%, which is lower than the results observed by Yin et al. [17]. These findings suggest that while SVE technology can effectively reduce the VOC concentration in polluted sites, it may not eliminate these contaminants, leaving residual concentrations in the site soil. This poses a risk to the redevelopment and reuse of the polluted site. Therefore, to comprehensively address the issue of residual VOC pollution in organic contamination sites, employing a capping layer to control VOC emissions should be considered.

A capping layer serves as a crucial in situ remediation technique for preventing the leakage of VOCs from organic contamination sites [20]. In traditional urban solid waste landfills, the capping layer can effectively reduce rainwater infiltration and uncontrolled landfill gas emissions [21]. Randazzo et al. [22] investigated the emission reduction mechanism of soil cover on pollutant gases and found that microbial activity in the cover soil also reduces the emission of VOCs. Furthermore, to enhance the VOC emission reduction capabilities, the soil capping layer should be modified. There are numerous existing materials for modifying the capping layer, such as compost mixtures [23–25] and organic blends [26–28]. Among these, biochar is an economically and environmentally friendly "green material" that can be effectively tailored to address this issue. Biochar possesses attributes, such as porosity, high surface area, and strong ion-exchange capacity [29,30],

which offer potential benefits in soil carbon sequestration, greenhouse gas mitigation, VOC adsorption, soil modification, and environmental remediation [31,32]. Nevertheless, despite the considerable amount of research on the capping layer and its modification, there is a lack of systematic reviews of the research progress in this field.

In light of this, this paper presents a comprehensive review of the VOCs within soil, their transport mechanisms, monitoring technology, and removal approach. Firstly, the historical development of the theory of the migration of VOCs within the overburden is described in detail. Secondly, in-depth discussions are held on field monitoring techniques for VOCs, including gas chromatography–mass spectrometry (GC-MS) and laser spectroscopy. Subsequently, the removal technology, capping layer for contaminated sites, is simply introduced. Following this, the prospects of a biochar-modified capping layer for the removal of VOCs are discussed. Finally, the main challenges faced in the field are outlined, and future perspectives are presented. The purpose of this review is to help researchers gain a deeper understanding of the VOCs within soil, their transportation mechanism, their monitoring approach, and their efficacious removal technology. More importantly, this review aims to provide a reference for the development of biochar-modified soil capping layer technologies. It also provides new insights into the field of environmental protection and soil pollution control.

2. Mechanisms of VOC Transportation in Soil

The transport mechanisms of VOCs in unsaturated soils are mainly convection and diffusion [33]. In unsaturated soil, gas convection can be described by Darcy's law at low flow rates. That is, gas convection velocity is directly proportional to the total gas pressure gradient. Additionally, fluctuations in atmospheric pressure at the surface of the soil result in pressure differentials between the surface and the bottom, leading to convection. In terms of gas diffusion, it is a process of disorderly and random molecular movement. Specifically, gas molecules spontaneously migrate and propagate from areas of higher concentration to those of lower concentration. The historical development of gas diffusion transport theory is illustrated in Figure 1. In particular, Fick introduced Fick's law in 1855 to describe the relationship between the diffusion flux of gas components under steady-state conditions and the concentration gradient. In this theory, the molar flux is directly proportional to the product of the diffusion coefficient and the gradient of molar concentration. However, Fick's law only applies to diffusion in two-component gas systems [9]. In 1868, Maxwell described the energy transfer during the motion of different gas molecules from the kinetic theory of gases. He further developed the Maxwell gas diffusion equation, which views gas molecules as a molecular group with intermolecular repulsive forces, rather than as an elastic sphere with a fixed radius. The direction of the repulsive force between the molecular group passes through the center of mass, and the force magnitude depends on the distance from the center of mass [9]. Klinkenberg found that the gas permeability coefficient varies with pressure under non-isobaric conditions as the gas molecules exhibit slip. This phenomenon in soil science is known as the Klinkenberg effect [34]. Knudsen, in 1909, discovered through experimental studies that the Knudsen diffusion flux is proportional to the gas concentration gradient, leading to the Knudsen diffusion equation [35]. In 1983, Mason and Malinauskas introduced the Dusty Gas Model (DGM), which comprehensively considers both gas volume diffusion and Knudsen diffusion. It assumes the transport tube walls to be large molecules fixed in space (dust molecules with zero momentum). That is, the molar mass is much greater than the $n + 1$ component of the other gases [36].
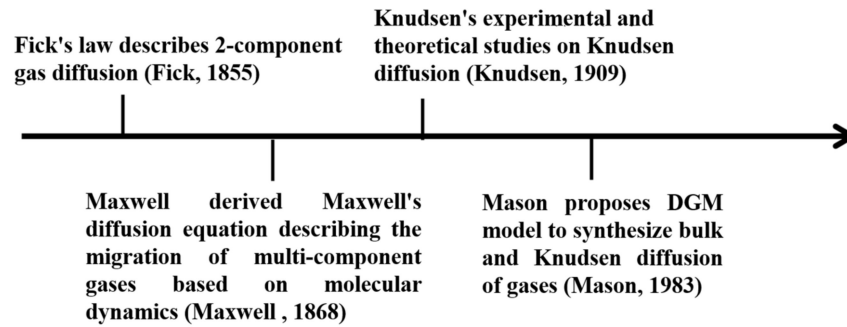
Figure 1. History of the development of the theory of diffusive transport of gases in porous media [9,33,35,36].

Furthermore, other models can also be employed to describe gas transport. Among them, the advection–dispersion model (ADM) is based on Fick's law to depict gas diffusion, and its advantage is the simplicity of the calculation process. However, the ADM model cannot account for the interactions between different gas components during the gas diffusion process. Additionally, when the permeability is low or when gas transport in the soil is dominated by diffusion, this model may produce deviations in gas flux predictions [37]. Compared to the ADM model, the Dusty Gas Model (DGM) can consider the interactions between different gas components and the relationship between the concentration of each gas component and the flow rate [38]. Molins et al. [39] investigated the effect of methane oxidation on multicomponent gas transport predicted by the DGM. They observed that gas transport at the top of the soil is primarily dominated by convection, while diffusion becomes the predominant mechanism at the bottom of the soil. However, it should be noted that the DGM only accounts for steady-state VOC gas transport, thereby showing some limitations. Furthermore, current theoretical research on the transport of landfill gases in the soil typically employs convection–diffusion models to describe gas diffusion [40–42]. Gas transport models established by Feng et al. [43] (Figure 2) investigated the coupling of methane oxidation and microbial growth. Qiu et al. [44] proposed a method for simultaneously measuring the gas diffusion coefficient and gas permeability coefficient in unsaturated soil gas transport based on the steady-state theoretical model of unsaturated soil gas migration. However, the above convective diffusion model ignores the molecular collisions during the diffusion of multicomponent gases, resulting in insufficient modeling accuracy.
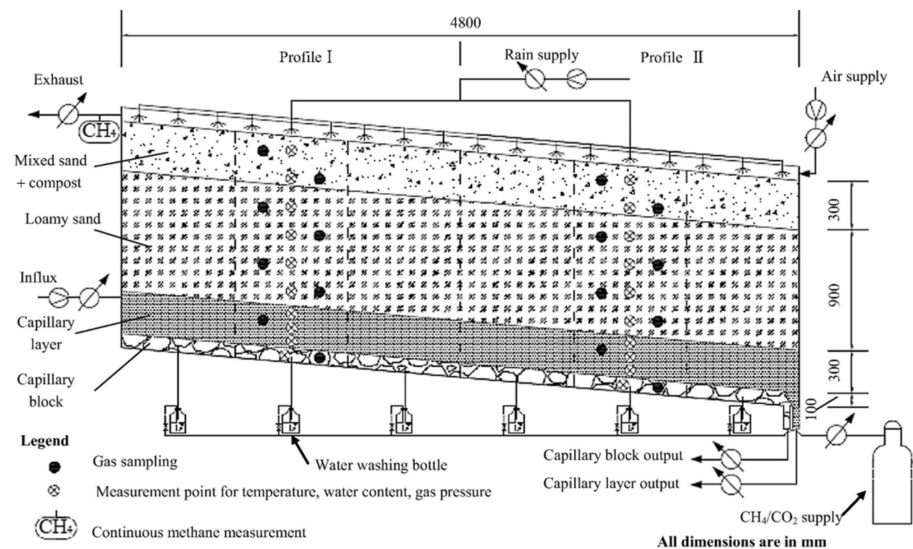

Figure 2. Experimental flume setup for validation of two-dimensional numerical simulations of methane oxidation [45].

In summary, the transport of VOCs in unsaturated soil is primarily governed by convection and diffusion. Meanwhile, there are numerous models available to describe the convection–diffusion behavior of VOCs in soil. However, VOCs consist of multiple components, and the prediction of gas fluxes using Fick's law is often inaccurate when permeability is low or when gas transport in the soil is dominated by diffusion. In addition, existing models for gas transport in unsaturated soil still have limitations. They do not consider the adsorption of gases by soil and often ignore the influence of gases that dissolve in water. For soils with significant adsorption capabilities, it is necessary to consider the adsorption of multicomponent VOCs in the soil, as well as gas dissolution in soils on the migration and release of gases within soil.

3. VOC In Situ Monitoring Technology

The environmental issues arising from polluted sites are becoming increasingly severe, posing a significant challenge to the ecosystem. Research indicates that noxious gases can be harmful to humans, even at low concentrations, causing damage to the nervous and respiratory systems. Certain toxic odorous gases, such as H_2S gas, can even lead to poisoning and the onset of cancer [46]. Therefore, the detection of the components of polluting gases in polluted sites holds significant importance.

Polluting gases come in a diverse range, which can generally be categorized into five groups: (1) sulfur-containing compounds, such as H_2S, SO_2, and thiols [47,48]; (2) nitrogen-containing compounds, including ammonia and amine substances [49]; (3) halogens and their derivatives, such as chlorine gas and halogenated hydrocarbons [50–52]; (4) hydrocarbons and aromatic hydrocarbons [53,54]; (5) oxygen-containing organic compounds, like alcohols, phenols, and aldehydes [55]. Dincer et al. [56] measured the concentrations of VOCs at a landfill site in Izmir, Turkey, where they identified a total of 48–53 VOCs, as depicted in Figure 3. Through multivariate linear regression analysis, they determined that aldehydes, ketones, and esters accounted for 96% of the contribution to the odorous gases. Furthermore, Ding et al. [57] performed experiments at a landfill site in Hangzhou, China, detecting up to 68 different odorous gases. Among all the compound types, NH_3 and H_2S represented 83.91%–93.94% and 4.47%–10.92% of the total concentrations, respectively.
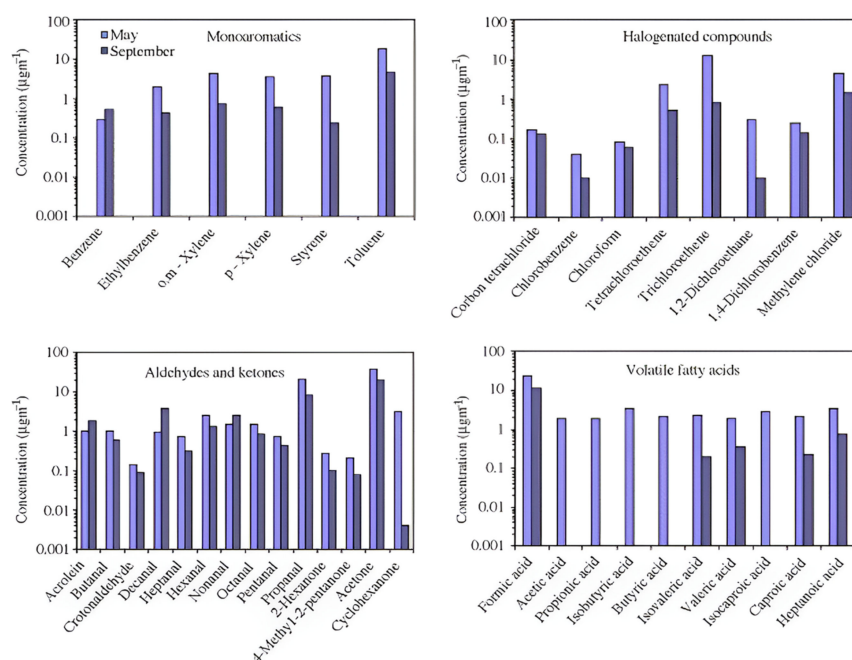

Figure 3. Concentration changes in VOCs (monoaromatic compounds, halogenated compounds, aldehydes and ketones, and volatile fatty acids) [56].

The detection techniques for toxic and hazardous pollutants at contaminated sites mainly include electrochemical sensors, gas chromatography, and laser spectroscopy [10,11,58]. Among these, the most widely employed method is gas chromatography–mass spectrometry [59–61]. Figure 4 presents a schematic diagram of gas chromatography–mass spectrometry, and the device facilitates the separation of air samples into the chromatograph without the need for pre-treatment. Additionally, a quantitative dilution function is added to the adjustable injection volume setting so that standard reference samples can be obtained at lower concentration levels. Additionally, when gas sample component concentrations are too low, they can be subjected to pre-concentration techniques. That is, gas samples are collected and processed using solid-phase extraction, solvent desorption, and thermal desorption and subsequently detected using instruments, such as gas chromatography and gas chromatography–mass spectrometry [62]. However, these detection methods often require complex sampling and pre-processing, and the analysis time is long, which cannot meet the requirements for rapid real-time monitoring. Additionally, electrochemical sensing methods are characterized by their small size and low cost. However, these techniques are susceptible to interference from substances with similar electrochemical properties. In addition, the detection and control of malodorous gases remain a huge challenge due to the complexity and low concentration of the pollutant gases and their susceptibility to weather conditions in open-air environments.
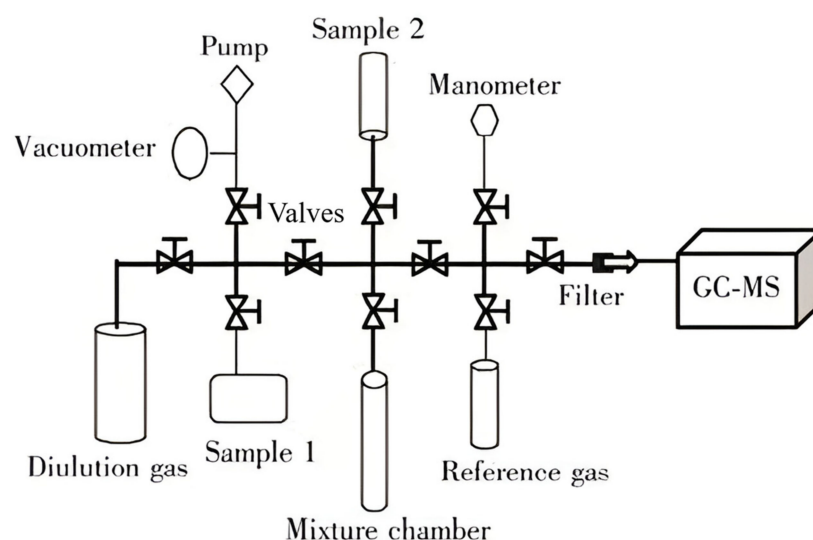

Figure 4. Schematic of direct injection device for gas chromatography–mass spectrometer [61].

Laser spectroscopy techniques currently include tunable diode laser absorption spectroscopy (TDLAS) and photoacoustic spectroscopy (PAS), which have been widely employed in atmospheric environmental monitoring, industrial pollution monitoring, medical diagnostics, scientific research, and other fields [63–65]. Among them, TDLAS combines with wavelength modulation, frequency modulation, and other techniques to greatly improve the signal-to-noise ratio, and the system sensitivity can reach the order of ppmv or even ppbv. As for PAS, it generates acoustic signals from the sample being detected through the photoacoustic effect and analyzes these acoustic signals to determine the composition and concentration of samples. Benefiting from this, PAS has found extensive applications in environmental monitoring, industrial process control and monitoring, medical diagnostics, and national defense hazardous material detection [66,67]. Laser spectroscopy techniques exploit the unique infrared absorption peaks of various target gases for measurements. They are known for their high precision, minimal interference, and real-time capabilities. These characteristics are advantageous for on-site, real-time, and rapid analysis of polluting gases, facilitating the identification of abnormal levels at waste storage/processing sites or compliance at emission sites. This enables timely alerts for taking appropriate measures [68–71]. However, a comprehensive VOC in situ detection technology based on

laser spectroscopy has not yet been developed, which hinders pollution risk control and management in organic-contaminated sites.

In brief, traditional soil site still faces challenges in effectively monitoring sites with a high concentration of VOCs. Modifying conventional capping layers to meet the demands of organic pollutant treatment can address these issues. However, research on VOC emission reduction remains scarce. Furthermore, there is a lack of in situ monitoring technologies for real-time assessment of VOC atmospheric concentrations at polluted sites, and research evaluating the VOC emission reduction efficiency of soil in organic-contaminated sites is also lacking.

4. Contaminated Site Capping Technology

The capping layer of contaminated sites is an important technology for the risk control of organic composite sites, and its service performance mainly depends on the impermeable materials and structural types. Its permeability coefficient is unable to reach or be lower than 10^{-9} m/s due to the influence of temperature, humidity, and other environmental factors [45,72]. Using modified materials to alter the soil pore structure to reduce the permeability of anti-seepage materials is a prominent research direction. Covering anti-seepage materials are prone to shrinkage and expansion due to wet–dry and freeze–thaw cycles, leading to the dominance of water and gas fracture flow and increasing the probability of capping layer failure [73]. Ng et al. [74] invented a three-layer cover structure that can be used for all climate conditions. It contains a clay layer, a gravel layer, and a pulverized soil layer sequentially from top to bottom and can effectively inhibit landfill gas release and rainwater infiltration. They also demonstrated that a 0.6 m thick compacted clay layer was effective in reducing gas release when the air pressure difference was less than 10 kPa and the water saturation was greater than 0.6. When any condition was unsatisfied, gas-dominant flow occurred in the compacted clay layer. This is an urgent problem and difficulty in promoting the application of modified bentonite-based impermeable materials in the capping layer. Additionally, the structural type of capping layer has developed from the traditional single-layer structure to the composite structure (such as capillary blocking capping layer), and the function has developed from seepage control to both seepage control and gas closure (blocking the soil gas escape and oxygen intrusion) [75,76]. Zhan et al. [76] analyzed the performance of a capillary capping layer (consisting of 1.3 m compacted loam and 0.3 m gravel) at a landfill site in northwestern China using numerical models and field test data. Their results are depicted in Figure 5, indicating that the capillary capping layer can effectively inhibit rainwater infiltration in wet conditions. Furthermore, due to its ability to store rainwater, it can effectively inhibit the release of landfill gas. However, the complex chemical environment and uneven settlement of contaminated sites can deteriorate the gas closure performance of capping layers. Therefore, improvements in the long-term performance of the capping layer are urgently needed, encompassing anti-seepage material modification, capping layer structural design, and maintenance measures.

In summary, pollution site capping can significantly reduce VOC concentrations. However, existing methods of capping layer designs are based on landfill closure technical standards and generally do not consider the adsorption effect on VOCs. There is a lack of research and development concerning barriers for VOCs like aromatic compounds and chlorinated hydrocarbons. Therefore, future research should further modify the capping layers, investigating their performance in reducing gaseous VOCs and assessing their long-term serviceability, thereby developing comprehensive risk control techniques for soil-contaminated areas.
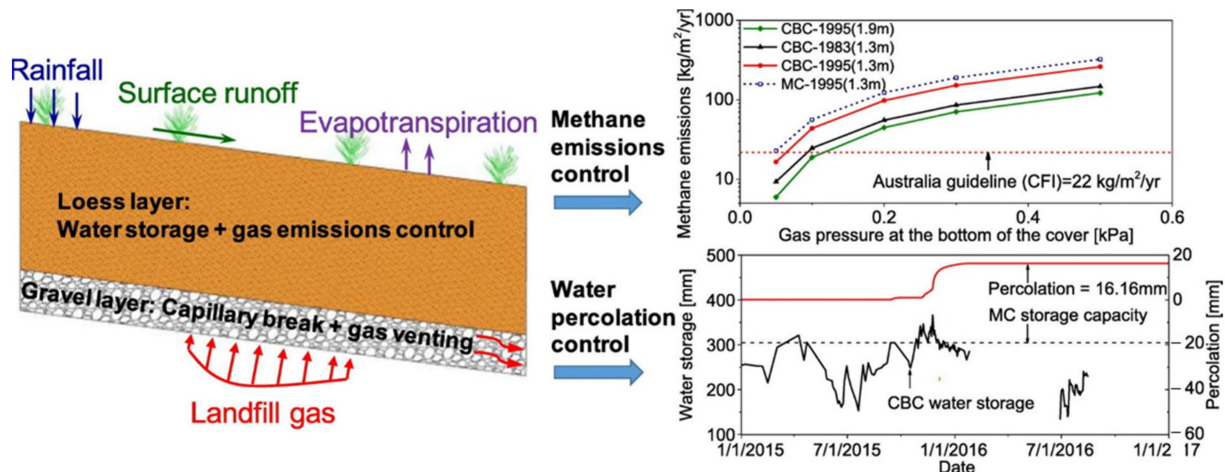
Figure 5. Schematic illustration of capillary capping layers and gas release/water storage [76].

5. Biochar-Modified Capping Layer of VOCs

Biochar is a solid, carbon-rich material formed by the pyrolysis of biomass materials, such as straw, wood, or other agricultural residues, under anaerobic or oxygen-limited conditions [77–79]. It is characterized by its loose and porous structure, well-developed pore network, high stability, and substantial surface area, making it an effective adsorbent for heavy metal pollutants and VOCs in underground soils (Figure 6) [80]. Biochar is derived from a wide range of feedstock materials and is produced at a relatively low cost (about one-sixth that of activated carbon) [81]. Therefore, biochar holds significant promise as an adsorbent for contaminated sites, and its application in environmental pollution control has attracted increasing attention from scholars [82–85].
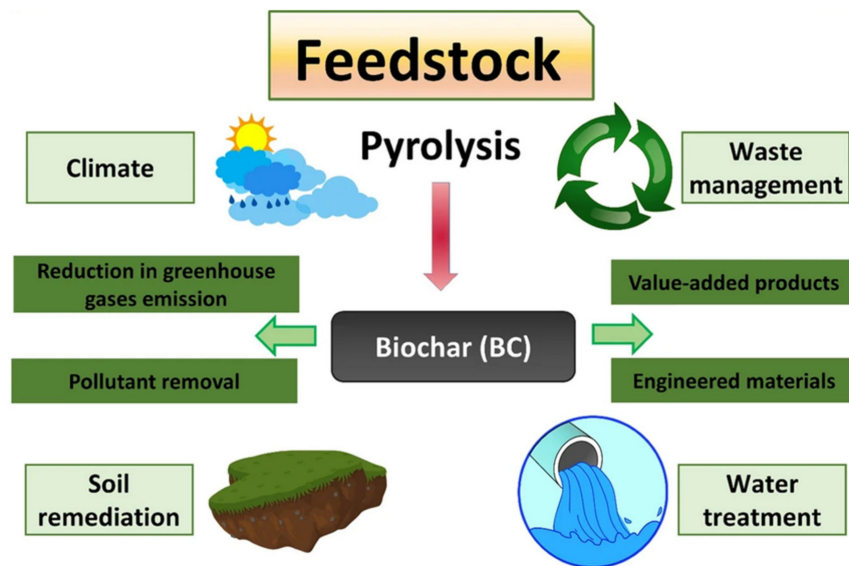

Figure 6. Application of biochar in environmental remediation [80].

In soil remediation and the management of organic-contaminated sites, biochar serves as a significant adsorbent for VOC pollutants [86,87]. The adsorption of organic pollutants by biochar is the result of physical or chemical interactions between the inherent characteristics of organic pollutants (molecular size, molecular charge, and hydrophobicity) and the physicochemical properties of biochar (surface area, pore structure, surface oxygen functional groups, and aromatic structure) [88,89]. Current research indicates that the adsorption process of organic pollutants by biochar involves interactions among the adsorbent, adsorbate, and solvent, with the main forces including π–π interactions, hydrogen

bonding, hydrophobic interactions induced by van der Waals forces, and electrostatic interactions [90,91]. As shown in Figure 7, Chun et al. [92] investigated the adsorption of nitrobenzene and benzene by wheat-straw-derived biochar prepared at temperatures ranging from 300 to 700 °C. They found that biochar exhibited a stronger affinity for polar organic compounds (nitrobenzene) than nonpolar organic compounds (benzene). This distinction is primarily attributed to the fact that polar functional groups on the biochar surface are more likely to generate nonspecific interactions with polar organic compounds. Zhang et al. [93] studied the adsorption behavior of simazine on corn straw biochar, as shown in Figure 8, and they observed that the adsorption capacity for organic pollutants increased with an increase in the specific surface area of biochar. In this context, the adsorption parameter $\log K_{oc}$ is positively correlated with the content of condensed aromatic carbon and negatively correlated with the content of aliphatic carbon. This observation indicates that the stronger aromaticity of biochar results in a stronger interaction with organic compounds. The aromaticity of biochar is a significant factor influencing its adsorption of organic pollutants. Zhu et al. [94] examined the adsorption behavior of pine wood biochar prepared at three different temperatures on sulfamethoxazole and sulfapyridine (Figure 9). Their study revealed that the adsorption affinity normalized according to the surface area was positively correlated with the graphitization degree of biochar. The increase in the surface graphite layer structure enhanced the π–π interactions.
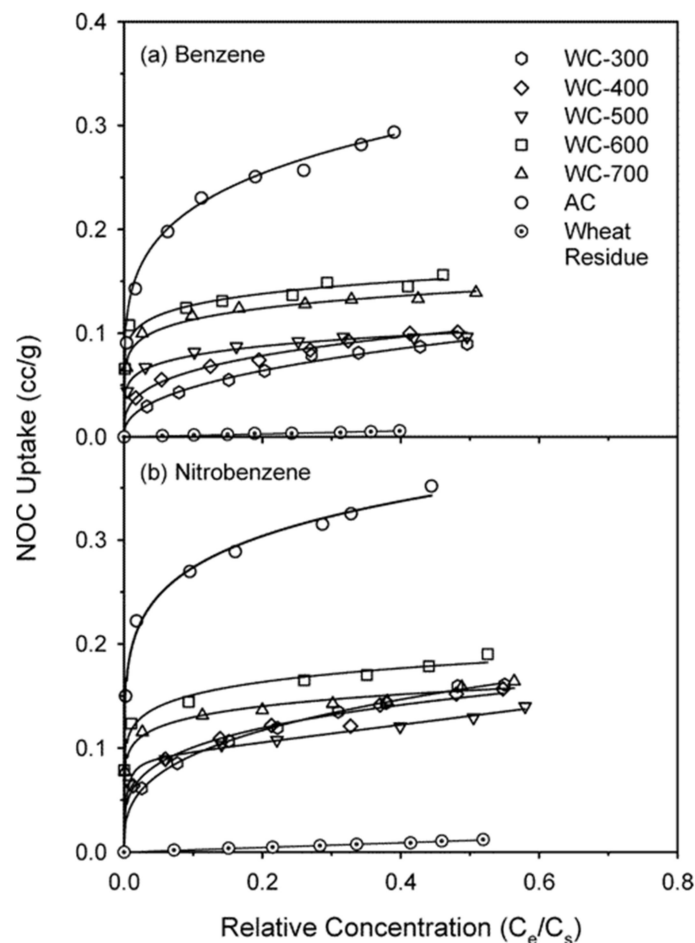

Figure 7. Adsorption efficiency of VOCs by biochar: adsorption of nitrobenzene (**a**) and benzene (**b**) by wheat straw biochar [92].
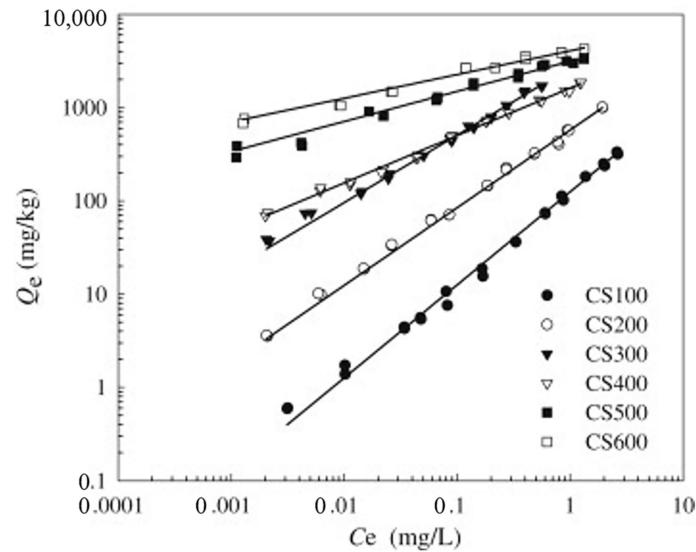
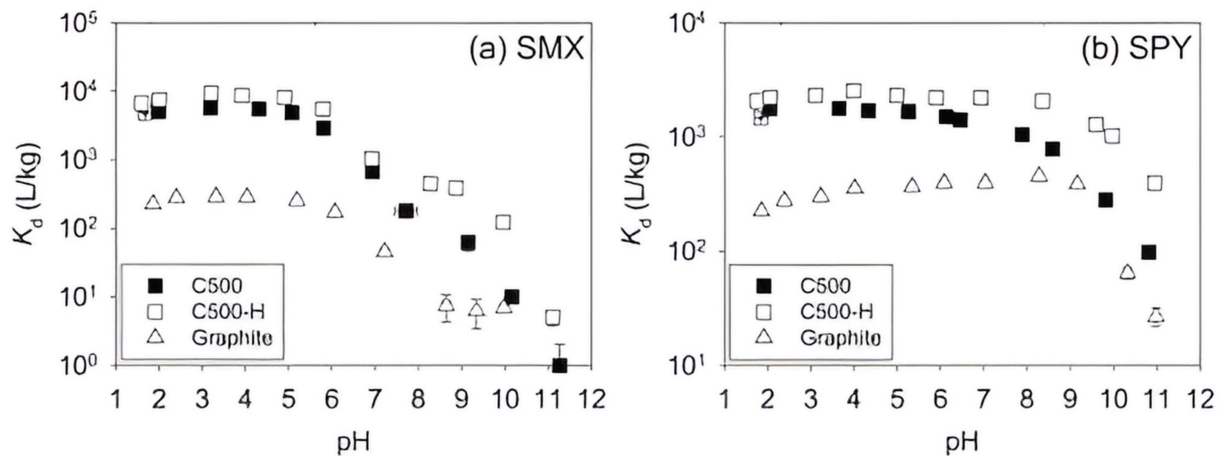**Figure 8.** Adsorption of simazine by corn stover biochar [93].

Figure 9. Adsorption efficiency of sulfamethoxazole and sulphapyridine by pine wood biochar [94].

Abundant research indicates that a biochar-modified capping layer is effective in reducing VOC emissions. For instance, Zhang et al. [95] evaluated the adsorption of three VOCs on 15 different biochars. The results demonstrated that the adsorption rate of VOCs on biochar ranged from 5.58 to 91.2 mg/g, with the adsorption capacity dependent on the surface area of biochar and non-carbonized organic content. Randazzo et al. [22] found that the key to removing VOCs from the capping layer lies in the microorganisms within the layer. Biochar serves as a reliable carrier for these microorganisms, and its substantial surface area makes it an ideal medium for adsorbing pollutants and facilitating further microbial decomposition. Qin et al. [96] reported that a capping layer modified with sewage sludge could remove up to 85% of VOCs, as shown in Figure 10. Zhou et al. [97] demonstrated that biochar can effectively adsorb VOCs due to its inherent carbon negativity and porosity. Specifically, a capping layer modified with waste wood biochar significantly reduced the release of VOCs in petroleum-contaminated sites (Figure 11). Kumar et al. [98] conducted experimental research showing that biochar's maximum removal rate for toluene can reach 65.5 mg/g (Figure 12). Moreover, the pyrolysis temperature and raw material type of biochar have a significant impact on its porosity and surface area, further influencing its adsorption efficiency for various types of aromatic compounds and halogenated hydrocarbons. Rajabi et al. [99] investigated the adsorption and competitive adsorption behavior of biochar for various aromatic and non-aromatic VOCs. The results indicated that when biochar was used for the adsorption of single aromatic VOCs, its adsorption rate was

relatively high, ranging from 51 to 110 mg/g. When biochar simultaneously adsorbed multiple VOCs, the adsorption rate for individual VOCs was slightly lower, but the overall adsorption rate still ranged from 50 to 109 mg/g.
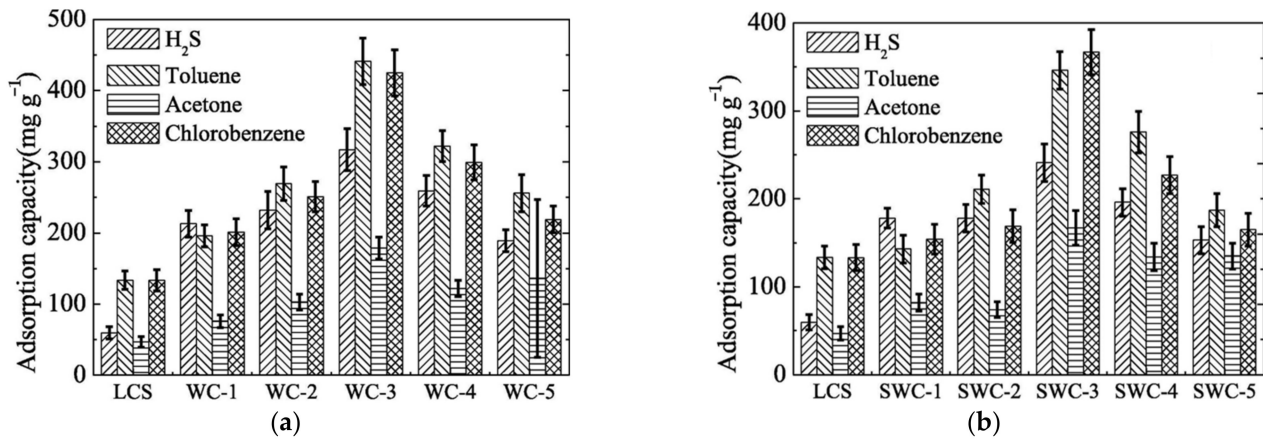

Figure 10. Adsorption capacity of different types of biochar to VOCs: (**a**) landfill cover soil (LCS), waste-char (WC), (**b**) WC modified by sewage sludge [96].
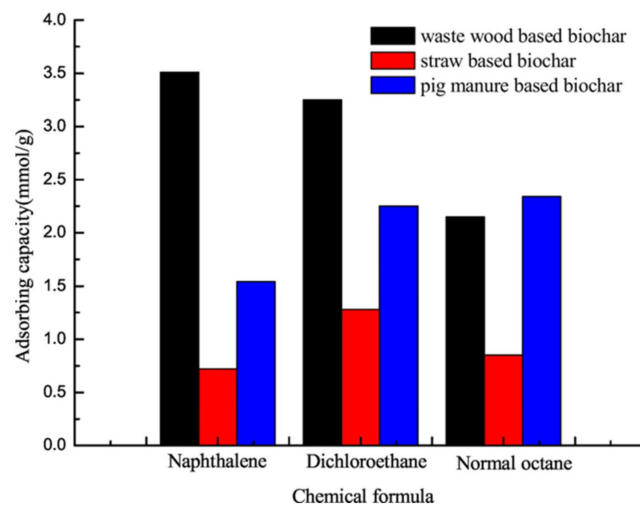

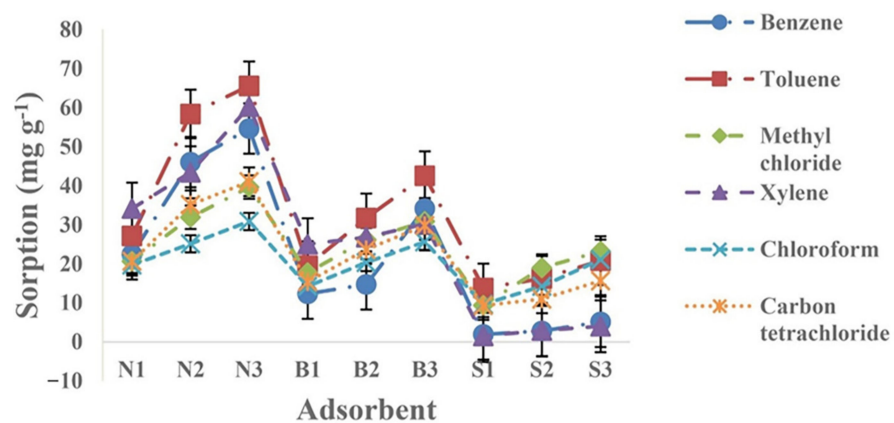**Figure 11.** Waste wood biochar, straw biochar, pig manure biochar [97].

Figure 12. Adsorption capacity of neem (Azadirachta indica) biochar (N1, N2, N3), bamboo (Bambusa pallida) biochar (B1, B2, B3), and sugarcane (Saccharum officinarum) biochar (S1, S2, S3) to VOCs [98] (1 for the pyrolyzing temperature of 350 °C), 2 for 450 °C and 3 for 550 °C).

To sum up, the biochar-modified capping layer efficiently removes organic pollutants from the soil, thereby reducing the degree of soil contamination. However, current research has focused on the adsorption of liquid-phase organic pollutants on biochar, and attention to the adsorption of gaseous organic pollutants (especially VOCs) on biochar is still limited. Nonetheless, the foremost problem in the containment and control of organic pollutants in the capping layer at organic-contaminated sites is gaseous VOCs. Furthermore, when biochar adsorbs liquid-phase VOCs, the biochar surface is covered by molecules of various components in the solution. In contrast, the adsorption of gaseous VOCs results in areas on the biochar surface that are devoid of adsorbed molecules, often referred to as "blank" areas. Molecules in the liquid phase are closer together, and the interaction forces between them are much stronger than the interaction forces between gas-phase molecules. Studies indicate that the adsorption capacity of the same biochar for xylene in water is more than ten-times that for xylene in the gas phase [100]. Therefore, the adsorption mechanisms of gaseous organic pollutants on biochar are significantly different from those in the liquid phase. Overall, to develop suitable biochar-modified capping layers for organic-contaminated sites, it is important to investigate the adsorption mechanisms of gaseous multicomponent VOCs on biochar.

6. Conclusions and Future Perspectives

This review offers a comprehensive examination of the VOCs within soil, their transport mechanisms, monitoring technology, and removal approach. Specifically, the theory of VOC transport in soil is systematically discussed first, focusing primarily on convective diffusion theory. Secondly, techniques for the in situ monitoring of VOCs are presented, mainly gas chromatography–mass spectrometry (GC-MS) and laser spectroscopy. Subsequently, the removal technologies for contaminated sites are summarized, namely, the capping layer. More importantly, the potential of a biochar-modified capping layer to remove VOCs is explored in depth. In conclusion, the transport of VOCs in soil primarily involves diffusion and convection processes. Employing suitable in situ monitoring techniques can effectively predict VOC concentrations in soil, and employing a biochar-modified capping layer can efficiently adsorb VOCs, reducing soil contamination. However, it is essential to recognize that current research in this field is not comprehensive enough, and several issues still require resolution, as outlined below:

(1) Predictions of gas fluxes using Fick's law are often inaccurate when volatile organic compounds have low permeability or are transported through the soil primarily by diffusion. In addition, existing unsaturated soil gas transport models do not consider the adsorption of gases by the soil or the effect of gas dissolution on their transportation. Therefore, it is imperative to consider the adsorption of multicomponent VOCs in the soil and the impact of gas dissolution in water on the transport and release behavior of gases within the capping layer.

(2) At present, research on reducing VOCs is quite limited, and the adsorption patterns and transport mechanisms of VOCs within the capping layer remain unclear. Furthermore, there is still a lack of in situ monitoring technologies for the real-time measurement of atmospheric VOC concentrations at contaminated sites. Meanwhile, field studies assessing the VOC reduction effectiveness of biochar-modified capping layers in organic pollutant sites are scarce.

(3) Capping layers effectively reduce VOCs, but the current designs, based on landfill closure standards, overlook VOC adsorption. Research is needed on barriers for specific VOCs, such as aromatic compounds and chlorinated hydrocarbons. Future studies should focus on improving capping layers to better reduce gaseous VOCs and evaluate their long-term effectiveness, leading to advanced risk control methods for soil contamination.

(4) Although biochar-modified capping layers have been studied, these studies often fail to consider the effectiveness of biochar-modified mulch in reducing VOC emissions. Furthermore, existing studies predominantly focus on the adsorption of liquid-phase organic pollutants on biochar, and studies on the adsorption of gaseous VOCs on biochar are still

insufficient. However, organic pollution control in capping layers for contaminated sites mainly involves VOCs. Furthermore, the adsorption mechanisms of gaseous organic pollutants on biochar are significantly different from those in the liquid phase. Hence, there is an urgent need to investigate the adsorption mechanisms of multicomponent gaseous VOCs on biochar to develop suitable capping layers for organic-contaminated sites. Meanwhile, future research should focus on investigating the performance of biochar-modified capping layers in reducing VOC emissions and assessing their long-term durability, ultimately developing comprehensive risk management techniques for soil-contaminated areas.

In summary, the modified capping layer technology has shown promise in the removal of VOCs from soil. However, the current state of research in this field is still incomplete, and many problems remain to be solved. This review aims to help researchers understand the VOCs within soil, their transportation mechanism, monitoring approach, and removal technologies, providing new insights for environmental protection and soil pollution management.

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