The Influence of Geotextile Type and Position in a Porous Asphalt Pavement System on Pb (II) Removal from Stormwater

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Abstract: Porous asphalt (PA) pavement systems with and without a geotextile layer were investigated in laboratory experiments to determine the impacts of the geotextile layer on the processes leading to lead ion (Pb^{2+}) removal from stormwater runoff. Two types of geotextile membranes that were placed separately at upper and lower levels within the PA systems were tested in an artificial rainfall experiment while using synthetic rainwater. The effect of storage capacity within the system on Pb^{2+} removal was also investigated. Results indicated that the use of a geotextile layer resulted in a longer delay to the onset of effluent. The non-woven geotextile membrane that was placed below the reservoir course improved the Pb^{2+} removal rate by 20% over the removal efficiency of the system while using a woven geotextile placed just below the surface but before the choker course. Pb^{2+} ions were reduced by over 98% in the effluent after being held for 24 h in reservoir storage. Results suggest that temporary storage of stormwater in the reservoir course of a PA system is essential to improving Pb^{2+} ion removal capability.

Keywords: porous asphalt pavement system; stormwater; stormwater runoff; heavy metals removal; geotextile membrane

1. Introduction

Impervious surfaces in urban areas can lead to stormwater related problems, including urban flood events, natural water quality degradation, groundwater level decline, etc. The impacts are becoming more and more severe due to the rapid urbanization that many regions are experiencing, which have led to large increases in impervious surface area [1,2]. In particular, stormwater runoff being generated by urban impervious surfaces has been regarded as an important contributor to the degradation of receiving waters, because it carries contaminants accumulated between storm events in the urban environment. These pollutants include suspended solids, organic matter, nutrients, heavy metals, oils, and even polycyclic aromatic hydrocarbons (PAHs) [3,4]. To mitigate these negative effects, and potentially start using stormwater as a resource instead of regarding it as a waste product, low impact development (LID) options, such as permeable pavement systems (PPS) are seeing an increase in implementation in low-traffic areas in place of impermeable surfaces [5–7].

PPS are comprised of various pavement layers of porous media resulting in a high infiltration capacity that allows for surface stormwater runoff to pass freely into a reservoir structure for temporary storage that may be harvested for later reuse or released slowly into the underlying soil, receiving water bodies, or drainage systems. Throughout this process, the stormwater is being treated through
mechanical filtration, physical sorption, chemical sorption, nutrient transformation, degradation, and chemical precipitation [8–10]. In this way, PPS not only significantly decreases the surface stormwater runoff volumes and peak flow rates, but effectively removes pollutants, such as total suspended solids (TSS), total nitrogen (TN), total phosphorus (TP), and heavy metals (such as Pb, Cu, Zn).

PPS commonly consists of a permeable surface (common examples are porous asphalt (PA), porous concrete (PC), permeable interlocking concrete pavers (PICPs), etc.) overlying a bedding course for PICPs and a choker course for PA and PC, above a reservoir structure for temporary stormwater storage (also referred to as the base course, which can involve an open graded aggregate bed with varying depths depending on water storage requirements and frost depth) [11,12]. Permeable geotextile membranes are traditionally used at one or two levels within the PPS to separate the layers and prevent the migration of stones and gravel, as well as for strengthening purposes [4,6,13,14].

Various studies have confirmed that a standard PPS incorporating a geotextile layer will improve stormwater quality. Dietz et al. [15], Legret et al. [16], Boving et al. [17], and Pagotto et al. [18] recognized that PA systems incorporating geotextile layers at the choker course or gravel reservoir were effective in helping to improve stormwater quality by retaining chloride, organics and selected heavy metals (Pb, Cu, Cd, and Zn) from stormwater runoff. Specifically, Legret et al. [16] found that a PA system, including a geotextile layer at the bottom of the gravel reservoir decreased Pb by 79%. Pagotto et al. [18] conducted research on the same site and observed that 74% of Pb was removed. Myers et al. [10] observed that a PICP system incorporated with a permeable geotextile under the bedding aggregate reduced Zn, Cu, and Pb by 94% to 99% in stormwater runoff after 144 h in storage in the reservoir. Pratt et al. [19] reported that a PICP system containing both upper and lower geotextile membranes was as an effective system for retaining and degrading oil. Tota-Maharaj and Scholz [20] performed laboratory-based experiments and found that PICPs incorporating a geotextile layer at the bedding course had maximum removal rates of 96% and 98% for ortho-phosphate-phosphors and ammonia-nitrogen, respectively. Nnadi et al. [6] used the water that was drained from a PICP system with a geotextile as irrigation water. Observations of selected heavy metals (Cd, Cu, Pb, Ni, Fe, and Zn) in the vegetation and soil irrigated with this water were under normal range and below toxicity levels. Huang et al. [12] examined the environmental performance of PA, PICPs, and PC systems containing a geotextile between the subbase and subgrade under cold climate conditions and observed that all three systems removed 76.3% to 86.1% of Pb. Brown et al. [21] proposed using a geotextile at the base course in both the PICP and PA systems and found that 90% to 96% of TSS was removed from the influent with the “sieving action” occurring primarily at the geotextile, and thus being important for TSS removal. Mullaney et al. [13,14] conducted a series of experiments in a field study of a PICPs system with and without a geotextile at the upper sub-base and concluded that having an upper geotextile had a better performance for removing Pb from stormwater over the long-term.

These studies indicate that commonly used PPS with an upper and/or lower geotextile may provide suitable conditions for trapping pollutants, such as heavy metals, oil, nutrients, TSS, and chloride, from stormwater runoff. However, very few research studies have been concerned with the direct impact that the geotextile itself has on stormwater runoff quality. Only one of the studies produced directly comparable observations of PPS with and without a geotextile layer. There are a plethora of geotextile materials available for pavement construction that vary in thickness and thread density. When a research study is conducted, the type of geotextile is given secondary consideration if at all. To the Authors’ knowledge, no study has considered the impact of different geotextile types on treatment levels. Greater evidence and data is needed to understand the role of geotextile membranes within PPS and to better recommend their usage in designs that lead to better stormwater quality performance.

In this study, the influence of the type and position of a geotextile layer on the removal of Pb ions is investigated in PA pavement systems. The objectives of this paper are to: (1) assess the role of geotextile layers within a PA system for removing dissolved lead from stormwater runoff;
(2) investigate the differences in the removal of Pb\(^{2+}\) ions in stormwater runoff by PA systems incorporating a non-woven or woven geotextile membrane place at the choker course or at the base of the reservoir structure; and, (3) examine the influence of a PA system working under different water detention capacities on the removal of Pb\(^{2+}\) ions in stormwater runoff. This study compares the system performances under artificial rainfall events of 120 min duration and monitors several water quality parameters over a period of 24 h.

2. Materials and Methods

The experiment was conducted in two stages: the first stage was to monitor the Pb\(^{2+}\) ion removal efficiency by PA systems during artificial rainfall event 1 (120 min); the second stage involved a temporary storage period (24 h) of the stormwater that was generated by artificial rainfall event 2 and stored within the reservoir course to analyze any changes in removal efficiency and estimate whether the stormwater discharged from the PA systems could be reused as irrigation water.

2.1. Materials

2.1.1. Models of Porous Asphalt Systems

Five model PA systems were constructed. Each contained three main courses (as shown in Table 1), including a 10 cm-thick surface of porous asphalt with a void ratio of 22%, a 10 cm-thick choker course of Large Stone Porous Asphalt Mixture (LSPM) that has a 23% void content, which sits above a 40 cm-thick base reservoir of 13.2 cm crushed limestone gravel with 35% void space. All of the system courses were designed in accordance with the Technical Specifications for Permeable Asphalt Pavement (CJJ/T 190-2012) [22] and other related standards in China. A non-woven or woven permeable geotextile membrane was placed either at an upper level, which separates the PA surface from the choker course, or a lower position at the reservoir base (see Figure 1).

Table 1. Details of the porous asphalt (PA) system models paved in test rigs.

| Test Rig | Mixtures or Materials for Model PA Pavement Layers |
|----------|---------------------------------------------------|
| A        | Surface Course | Choker Course | Upper Geotextile | Gravel Reservoir | Lower Geotextile |
| A        | PAC-16\(^1\)  | LSPM-25\(^1\) | -               | Limestone        | -               |
| B1       | PAC-16        | LSPM-25      | Non-woven       | Limestone        | -               |
| B2       | PAC-16        | LSPM-25      | Woven           | Limestone        | -               |
| B3       | PAC-16        | LSPM-25      | -               | Limestone        | Non-woven       |
| B4       | PAC-16        | LSPM-25      | -               | Limestone        | Woven           |

\(^1\) According to the Technical Specifications for Permeable Asphalt Pavement (CJJ/T 190-2012) [22] in China, PAC-16 and LSPM-25 are two common aggregate gradations for surface courses and choker courses that are designed with a maximum particle size of 16 mm and 26.5 mm crushed gravel, respectively.

Figure 1. (a) Test rig for paving PA system model; (b) Simplified schematic cross section of a PA system without a geotextile; (c) Simplified schematic cross section of a PA system with a geotextile layer at the upper level; and, (d) Simplified schematic cross section of a PA system with a geotextile layer at the lower level.
The physical characteristics of the materials for the three pavement layers and the hydraulic demands for providing a sufficient storage volume for infiltrated stormwater runoff during a rainfall event, were determined based on the average annual precipitation of 1259.5 mm in the 2011–2016 period in the City of Nanjing, China. PA mixtures were manufactured by using a rolling wheel compactor. Aggregate materials were thoroughly washed and dried prior to installation in the test rigs in order to minimize the occurrence of fine sediment in the experiment.

2.1.2. Test Rigs for Assembly of Pavement Models

Each test rig was made of acrylic with a 5 mm wall thickness and having a dimension of 30 cm (length) \( \times \) 30 cm (width) \( \times \) 65 cm (depth), as shown in Figure 1a. Acrylic is chosen because of its stable chemical properties and it provides a clear view of the system. A perforated PVC pipe (a diameter of 5 cm) with a tap was installed at the bottom of the test rig to convey the effluent drainage and facilitate sample collection. The sections of PA systems with and without a geotextile layer are shown in Figure 1b–d.

2.1.3. Preparation of Synthetic Rainwater

Heavy metal reduction provided by a PA system is based on multiple factors, including stormwater composition and pollutant loads, site-specific conditions, weather factors, design of PA system, maintenance service, etc. [23]. In particular, the specific ions existing in the stormwater is a major factor. To avoid the influence of other factors in this study, synthetic rainwater was used to supply a consistent water quality and only Pb (II) was used as the target pollutant in the synthetic rainwater. The selection of Pb (II) was also prompted by the fact that it is one of the highest heavy metal ions in both road-deposited sediment (RDS) and stormwater runoff posing an environmental risk in China [24,25]. RDS has been reported to be one of the greatest contributors to heavy metal pollution in urban stormwater runoff [25,26]. On this basis, a concentration of 10 mg/L of Pb\(^{2+}\) ions was used to create synthetic rainwater given the level of total Pb in RDS measured by the authors (results shown in Table 2) and local (Nanjing) historical rainfall event data from 2011 to 2016. Herein, a chemical reagent of Pb(NO\(_3\))\(_2\) (1000 mg/L) and deionized water (20 L) were used to create the synthetic water.

| Sampling Date in 2016 | Dry Period Prior to Sampling Date (h) | Mass of Collected Rds Per Unit Area (g/m\(^2\)) | Pb Concentration in Rds Sample (mg/g) |
|----------------------|--------------------------------------|-----------------------------------------------|--------------------------------------|
| 20 April             | 232                                  | 225                                           | 0.598                                |
| 23 July              | 96                                   | 225                                           | 0.384                                |
| 14 September         | 124                                  | 225                                           | 0.461                                |
| 8 December           | 210                                  | 225                                           | 0.648                                |

2.1.4. Rainfall Event Design

In this study, an artificial rainfall event with a total precipitation, average intensity, rainfall duration, and return period of 82.31 mm, 0.63 mm/min, 120 min, and five years, respectively, were determined while using the Rainstorm Intensity Formula of Nanjing. The well-known Chicago method [27] was used to design the temporal distribution of the simulated rainfall event. The rainfall event with a total duration of 120 min, time step of five min, return period of five years and \( \gamma = 0.40 \) is shown in Figure 2.
2.1.5. The Artificial Rainfall System

Synthetic rainwater was applied on each of the test rigs through an artificial rainfall system (as shown in Figure 3) that involved a tank, a pump, a dripper system, an electronic flow meter, and a flow controller. A primary pipe with a diameter of 2.5 cm was used to connect the pump in the tank to the dripper system. The dripper system consisted of 6 x 6 mini drippers that were connected by flexible tubing. The flow rate of simulated rainfall was measured and controlled by a flow meter and a flow controller, respectively, which were both installed on the primary pipe.

![Figure 3. The artificial rainfall system used in this study: (a) The artificial rainfall system with installed model PA pavements; and, (b) Model PA pavements installed in the test rigs.](image)

2.2. Methods

2.2.1. Experimental Procedure

Following the preparation of the pavement models and the synthetic rainwater, two separate rainfall events were simulated by the lab-made rainfall system. All five PA system models were tested during the first artificial rainfall event, but only the model that demonstrated the best performance in terms of Pb (II) removal was tested in the second rainfall event. The tap was open during the first rainfall test but kept closed for 24 h during the second rainfall test, except when sampling. A 7.41 L volume of synthetic rainwater was applied directly to the surface of each model to simulate the rainfall event. To maintain consistency in the comparison, the pavement model used in the second rainfall simulation, was washed with slow flowing deionized water for 2 h, followed by a drying period of five days.
Timing commenced immediately when the artificial rainfall began. The first stormwater sample was collected when the initial flush effluent occurred in order to assess the initial effects of the PA system on the \( \text{Pb}^{2+} \) removal. Subsequent samples were collected every five min until the end of the first rainfall test, and every hour for up to 24 h in the second rainfall test.

At each sampling event, effluent samples were acidized with nitric acid immediately, and then stored in a refrigerator at 4 °C. \( \text{Pb}^{2+} \) content in the synthetic rainwater and effluent samples were determined while using Microwave Digestion and the Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) method. Measurements of temperature, pH, and conductivity, followed Chinese standard methods.

2.2.2. Water Quality Data Analysis

Data obtained for the analysis were used to determine the efficiency ratio of \( \text{Pb}^{2+} \) removal from the PA systems with and without a geotextile layer, as follows:

\[
R_i = \left( \frac{C_0 - C_i}{C_0} \right) \times 100\%,
\]

where: \( R_i \) is the removal rate of \( \text{Pb}^{2+} \) at sampling time \( i \) (%); \( C_i \) is the concentration of \( \text{Pb}^{2+} \) in the effluent sample collected at time \( i \) (mg/L); and, \( C_0 \) is the concentration of \( \text{Pb}^{2+} \) in the synthetic rainwater (mg/L).

To evaluate the potential reuse of infiltrated stormwater as an irrigation water source in China, water quality parameters, including \( \text{Pb}^{2+} \) concentration, pH, conductivity, and the temperature of effluent from the PA system that provided a 24 h stormwater storage within its reservoir structure, were compared with standards for irrigation water quality (GB 5048-2005) [28] in China.

3. Results

3.1. Initial Effects

The measured and calculated results, sampling time, \( \text{Pb}^{2+} \) concentration and removal efficiency of \( \text{Pb}^{2+} \) of the stormwater runoff that infiltrated through the five test rigs during the first of the two artificial rainfall events are shown in Table 3. There was a five min delay in the timing of the onset of effluent between test rig A and group B (test rigs B1, B2, B3 and B4), with the latter producing a five min delay before the occurrence of outflow as compared with A, which did not have the geotextile layer.

| Test Rig | Design Parameters       | Sampling Time (min) | \( \text{Pb}^{2+} \) Concentration (mg/L) | Removal Rate (%) |
|----------|-------------------------|---------------------|------------------------------------------|------------------|
| A        | No geotextile           | 20                  | 7.38                                     | 26               |
| B1       | Non-woven, upper level  | 25                  | 7.04                                     | 30               |
| B2       | Woven, upper level      | 25                  | 7.42                                     | 26               |
| B3       | Non-woven, lower level  | 25                  | 6.88                                     | 31               |
| B4       | Woven, lower level      | 25                  | 7.27                                     | 27               |

The results also showed a reduction in \( \text{Pb}^{2+} \) level in the initial effluent. The mean concentration of \( \text{Pb}^{2+} \) in the initial infiltrated stormwater samples was 7.2 mg/L, which was 29% lower than the synthetic rainwater of 10 mg/L. This suggests that the PA system has the capability to remove \( \text{Pb}^{2+} \) from the first flush effluent, regardless of whether or not the system contains a geotextile layer.

Differences were also observed in the \( \text{Pb}^{2+} \) removal rate between B and A, ranging from −0.4% to 5.0%. B2 using a woven geotextile at the upper level resulted in a slightly lower removal rate than A with no geotextile; and, B3, which included a non-woven geotextile at the lower level, resulted in the best performance. The results suggest that a non-woven geotextile membrane used at the lower level.
within the PA system is likely to produce a higher removal rate of Pb^{2+} from the initial effluent stream draining from the system. But, the analysis of variance indicates that the presence of a geotextile layer in the PA system didn’t result in a statistically significant difference with respect to the removal of Pb^{2+} ions from the initial influent (p value equal to 0.15).

3.2. Removal Process of Pb(II) During a Rainfall Event

Stormwater infiltrating through the test rigs were collected every 5 min during the first rainfall event experiment and observed concentrations and removal rates of Pb^{2+} are shown in Figure 4. Figure 4a shows that the concentration of Pb^{2+} in the effluent samples that were collected from A and group B decreased gradually with sampling time. Moreover, changes in Pb^{2+} levels with sampling time had similar trends. The concentration of Pb^{2+} decreased slowly in the first 50–55 min, followed by a marked reduction, and then remained relatively stable in the last 30 min. In fact, Pb^{2+} concentration was quite a bit lower in group B than that observed in A. By contrast, there was a difference in the removal percentage of Pb^{2+} between rig A and group B, and this difference widened in the second half of the rainfall event as shown in Figure 4b. The average removal rate of Pb^{2+} in group B was 9% higher than A. At the end of the rainfall, B1, B2, B3, and B4 removed Pb^{2+} from the stormwater with an efficiency of 58%, 47%, 66%, and 54%, respectively—which were all greater than A. These results validate the ability of a PA system to effectively remove Pb^{2+} from stormwater during a rainfall event, with or without a geotextile layer. The tests did not seem to suggest that the presence of a geotextile membrane within a PA system is necessary for Pb^{2+} removal; however, the results do suggest that a geotextile layer in PA system can improve the removal efficiency of Pb^{2+} during the rainfall process.

A difference in removal rates between the test rigs with a geotextile layer positioned at different levels was observed. Overall, the concentrations of Pb^{2+} in the infiltrated stormwater samples collected from B3 and B4 were generally lower than that from B1 and B2, respectively. Moreover, the differences in the Pb^{2+} concentrations between B3 and B1 and between B4 and B2 increased over time. After 120 min of simulated rainfall, B3 and B2 had the best and worst performances for PA systems with a lower and upper geotextile layer, respectively. This result suggests that test rigs that include a lower geotextile layer are more efficient in removing Pb^{2+} from stormwater as compared with a geotextile layer that was positioned higher in the system. It also suggests that the use of a geotextile membrane at the lower level separating the reservoir structure from the sub-grade is advantageous for a PA system for Pb^{2+} removal from stormwater runoff.

For the test rigs with a geotextile layer placed at the same level but of different types, the data showed differences in performance between B1 and B2, and between B3 and B4, with the differences increasing over time. With the except of some individual sampling points, overall, the concentrations
of Pb$^{2+}$ in the water samples from B1 and B3 were found to be lower than those from B2 and B4, respectively. The average removal rate of Pb$^{2+}$ by B1 and B3 was about 12% higher than the average of B2 and B4 at the end of the rainfall event. The results suggest that rigs that include a non-woven geotextile layer can retain Pb$^{2+}$ from stormwater runoff better than those containing a woven geotextile layer. In addition, the retention increases with the time, regardless of its position.

3.3. Removal of Pb(II) with a Temporary Storage

The results in Figure 4 show that B3, which has a non-woven geotextile at the lower level with direct runoff drainage, had better Pb$^{2+}$ removal performance than the other rigs during the simulated rainfall. To understand fully the performance of this PA system that provides temporary storage for stormwater in the reservoir, parameters, including temperature, pH, conductivity, and Pb$^{2+}$ concentration of the stored stormwater, were monitored for 24 h during and after the second artificial rainfall. The results are shown in Figure 5. Throughout the 24 h of stormwater storage, the temperature of the effluent samples fluctuated from only 20.1 °C to 22.4 °C. Both the pH and conductivity levels increased with sampling time, but at different rates. The pH levels of effluent increased faster in the first 10 h and they remained relatively stable in the later stages, to 8.2, by the end of the experiment. By contrast, the conductivity levels increased significantly with sampling time and reached up to 111.5 µg/cm after 24 h, which was almost 3.5 times the value from the first water sample (Figure 5a).

![Figure 5](image1.png)

**Figure 5.** Results of the second artificial rainfall event on the PA system providing 24 h stormwater storage: (a) Conductivity and pH values of the stormwater samples; (b) Concentration and removal rate of Pb$^{2+}$.

Because the intensity, duration and pattern of the second artificial rainfall event was the same as the first event, the time of initial outflow occurrence and the concentration of Pb$^{2+}$ in the first flush effluent was roughly similar to that collected from the first artificial rainfall event. The concentration of Pb$^{2+}$ in the initial effluent was slightly higher than that measured in the first rainfall event, but nearly equal to the mean concentration of group B. However, there was a greater change in the Pb$^{2+}$ concentration throughout the 24 h of storage as compared with the 120 min of simulated rainfall (as shown in Figure 5b). Overall, the Pb$^{2+}$ concentration in stormwater decreased markedly in the initial 7 h, then continuously decreased with an increasing detention time, and finally remained relatively stable in the last 4 h. More than 98% of the Pb$^{2+}$ ions were removed from the stormwater runoff after 24 h of storage in the reservoir. The result indicates that Pb$^{2+}$ removal efficiency from the system providing a temporary storage of stormwater (B3) is much higher than the design that did not provide storage—by nearly 33%.

The regression between the removal rate and the sampling time were further analyzed and the results showed that there was a significant logarithmic correlation between them (as shown in Figure 5b). Equation (2) is the logarithmic formula.

$$R_{Pb} = 14.57 \ln(t) + 57.33 (R^2 = 0.90)$$

(2)
where \( R_{pb} \) is the removal rate of \( \text{Pb}^{2+} \) at sampling time \( t \) (%); and, \( t \) is the residence time of the stormwater runoff in the reservoir structure of the PA system (h).

This result indicates that the \( \text{Pb}^{2+} \) removal percentage is strongly dependent on the residence time—the longer the residence time, the more \( \text{Pb}^{2+} \) ions can be removed. But, Equation (2) cannot be directly used for predicting \( \text{Pb}^{2+} \) removal rate because the removal rate of a PA system is also influenced by other factors, such as weather/seasonal conditions and rainwater composition.

4. Discussion

4.1. Differences in Initial Effects between PA Systems with and without a Geotextile

The 5 min delay in the timing of initial effluent discharge between PA systems with and without a geotextile layer suggests that the presence of a geotextile membrane in the PA system has a direct effect on hydraulic performance because of the lower permeability of the geotextile layer as compared to other pavement layers. The difference in the \( \text{Pb}^{2+} \) removal efficiencies between PA systems with and without a geotextile is small, but B3 had the highest removal rate. This may be caused by the different geotextile types and by the different levels of placement of the geotextile, but is likely due, in larger part, to the relatively short period of residence time. Based on the results, it is recommended that to achieve greater efficiency in removal of \( \text{Pb}^{2+} \) from initial runoff, a PA system using a non-woven geotextile membrane at the lower level separating the reservoir from the sub-grade may be appropriate. But, it should be noted that the \( \text{Pb}^{2+} \) removal rate in this case is not as high as the result reported by Zhao et al. [8] (noting that they used synthetic stormwater that combined metals with organics).

4.2. PA Systems Offering Direct Drainage of Stormwater

4.2.1. Influence of a Geotextile Layer

A similar tendency in the \( \text{Pb}^{2+} \) concentration over time for both groups suggests that the use of a geotextile layer within PA systems does not necessarily affect the basic tendency to remove \( \text{Pb}^{2+} \) from stormwater runoff during rainfall. The only difference in the comparison for the PA systems is that the system with a geotextile layer is generally producing lower \( \text{Pb}^{2+} \) concentrations in the effluent at each sampling point. This implies that some water quality benefits are gained by a PA system incorporating a geotextile layer, which is consistent with Mullaney et al. [13], who applied a total of 10 years of metals to their system, although the mechanism for removal was not made obvious.

According to the previous studies that explored the use of natural limestone and porous asphalt surfaces for the removal of heavy metals from stormwater runoff or aqueous solutions [29–33] and the pavement models used herein, the reduction of \( \text{Pb}^{2+} \) concentration in the effluent samples observed in this study is possibly due to several processes occurring within PA system: (1) the adsorption onto materials at the air voids within pavement layers including the bitumen in the porous asphalt mixture and limestone gravel in the reservoir; (2) precipitation between the lead actions and the mineral in the limestone within the reservoir; and, (3) the retention of \( \text{Pb}^{2+} \) by the geotextile layer.

4.2.2. Influence of the Geotextile Position

During 120 min of artificial rainfall, the removal rates of \( \text{Pb}^{2+} \) by the test rigs containing a geotextile placed at the lower level are generally higher overall than those including a geotextile at the upper level. This result indicates that the position level of placement of the geotextile within the PA system will influence \( \text{Pb}^{2+} \) removal. The better removal performance of B3 and B4 may be attributed to buffering that is provided by the lower geotextile layer to the stormwater stored in the reservoir.

When the stormwater flows through the reservoir and then through the geotextile, a sharp reduction in the flow rate of stormwater occurs above the surface of the geotextile, which is a result of its much lower infiltration rate than the gravel reservoir that has a 35% void space. This extends the residence time between the stormwater and the limestone gravel in the reservoir before the
stormwater discharge. Because of the extension of residence time, the interactive reaction of Pb$^{2+}$ ions and limestone gravel in the reservoir is promoted. Based on the findings given by previous researchers [29–31,34], for the PA system containing a lower geotextile layer, the adsorption processes of Pb$^{2+}$ occur with the dissolution of limestone surfaces at the mineral-stormwater interface within the reservoir. This leads to the formation of lead-containing crystals growing on the surface of the calcite (the main component of limestone) and in the pores of the limestone gravel resulting in the decrease of Pb$^{2+}$ concentration in the outflow. By contrast, the upper geotextile layer in the PA system that is located between the base course and the reservoir do not result in improving the system removal capacity because the residence time for stormwater and limestone within the reservoir may not be affected—even through the upper geotextile can effectively slow the stormwater flow velocity in the base course as well.

4.2.3. Influence of the Geotextile Types

The difference in Pb$^{2+}$ removal efficiencies between the PA systems containing a non-woven geotextile and those of a woven geotextile is a reflection of the suggestion that various types of geotextile membranes used in PA systems can directly affect the system’s capacity to remove Pb$^{2+}$. Cook and Scholz noted in their studies [4,35] that non-woven geotextile is the preferred geotextile type for permeable paving applications because of its better filtration and separation properties than woven geotextile. But, no specific experimental data is presented for its removal capacity of heavy metals from stormwater or aqueous solutions. The results therefore, indicate that the use of a non-geotextile membrane within a PA system is more appropriate than a woven geotextile for both the hydraulic properties and pollutant removal performance.

On the basis of the above results, it can be suggested that the use of a non-woven geotextile membrane at the lower level separating the reservoir structure and the sub-soil is more appropriate for PA systems for improved performance in removing Pb$^{2+}$ from stormwater runoff during a rainfall event. Note that the concentration of Pb$^{2+}$ in the discharge from B3 (containing a non-woven geotextile at the lower level) resulted in the best Pb$^{2+}$ removal performance after 120 min of rainfall. However, this does not meet the Standard for Irrigation Water Quality (GB 5084–2005) [28] in China. This means that the stormwater runoff that was discharged from a PA system with a perfect geotextile layer is still too toxic for use as irrigation water after a rainfall event unless it is further treated by more advanced processes.

4.3. PA System Providing a Temporary Storage of Stormwater

4.3.1. Influence of Residence Time on the pH and Conductivity

When viewing the curves of pH and conductivity during the second artificial rainfall in Figure 5a, it can be clearly seen how the pH and conductivity increase with residence time (or sampling time). Because the stormwater penetrated into the PA system is stored in the reservoir, the increase in the pH and conductivity in the effluent samples is possibly attributed to the surface dissolution growth process of limestone gravel, as well as the formation of lead-containing precipitates. Under acidic conditions, the surface limestone dissolution in stored stormwater supplies a number of ions, such as Mg$^{2+}$, Ca$^{2+}$, OH$,^-$, and CO$_3^{2−}$, which increase the conductivity. Meanwhile, adsorption and precipitation processes between limestone and Pb$^{2+}$ ions form lead-containing products that therefore, increase both the conductivity and pH value of the stormwater. This has been investigated and described by previous works [29,31,36]. Moreover, Karageorgiou et al. [37] found that the dissolution of calcite is a fast process that initiates the reaction of metal cations and the limestone, so that both the conductivity and pH increase quickly in the early stages of the experiment.
4.3.2. Influence of Residence Time on the Pb(II) Removal

The removal performance of B3 when providing direct stormwater drainage was not as good as the performance of the same system that provided temporary storage of stormwater. In addition, a strong logarithmic correlation between the Pb\(^{2+}\) removal rate and the residence time was observed, indicating that the residence time directly influences the removal process of Pb\(^{2+}\) ions. These apparent changes are probably due to the sorption processes of Pb\(^{2+}\) ions occurring in the reservoir. Various researchers [29–31,36,38] have confirmed that the removal of Pb\(^{2+}\) ions from aqueous solutions by natural limestone is mainly due to both the adsorption and the chemical precipitation that is closely related to the dissolution of the solid surface.

This work suggests that the dissolution of surface limestone in stormwater under an acidic condition (initial pH = 4.2) constitutes the first step for Pb\(^{2+}\) removal and this leads to a rapid increase in pH and conductivity in stormwater. The removal of Pb\(^{2+}\) ions below pH 5.3 may be attributed to the possible ion-exchange reactions between the Pb\(^{2+}\) ions in the stormwater and Ca\(^{2+}\) ions of limestone, as well as through the formation of lead-containing precipitates (perhaps lead-hydroxide) [30]. Also, the removal rate increases with an increasing pH value. The enhanced removal of Pb\(^{2+}\) ions above pH 5.3 can be attributed to the precipitation of lead carbonate, which leads to a higher removal capacity of the system [36,39]. Thus, the removal process is predominantly governed by the precipitation of lead carbonate, since the stormwater pH remains above 5.3 for more than 20 h of the 24 h storage period.

Moreover, the findings by Németh et al. [30] verified that the precipitation forms both on the surface and in the pores of minerals. In addition, Sdiri et al. [40] pointed out that lead carbonate is more stable above pH 6.0. This perhaps is the reason why the removal amount of Pb\(^{2+}\) ions increases with longer residence time being created with storage, and why the removal rate increases more quickly in the initial stages but more slowly (eventually stabilizing) at a higher level in the later stages.

4.3.3. Evaluation of Stormwater Quality

With rapid urbanization in China, irrigation water quality has become a serious issue and heavy metal contamination in particular, presents a great risk for irrigation water because of the potential threat to living organisms and humans [10,31] if left untreated. In this study, the PA system containing a non-woven geotextile layer at the lower level and a temporary storage is suggested as an efficient technology for the treatment of dissolved lead in stormwater runoff. But, it is essential and important to determine an appropriate storage time for stormwater runoff when considering the possibility of reusing the discharge as irrigation water. The acceptable levels of temperature, pH and lead concentration for irrigation waters in China (GB 5084-2005) are 35 °C, 5.5–8.5, and ≤0.2 mg/L, respectively. It should be note that these standards refer to a total, or aggregate value for maximum levels of pollutants in irrigation waters.

Throughout the time in storage, the temperature of the effluent was between 20 °C and 23 °C, which is well below the limit indicated; the pH values did not exceed the limited range of 5.5–8.5 after 4 h of storage; and, the Pb\(^{2+}\) concentration did not exceed the limit of 0.2 mg/L after 20 h. These results recommend that the stormwater runoff drained from the tested PA system is appropriate for use as irrigation water after at least 20 h of storage in the reservoir.

5. Conclusions

Laboratory studies were designed to study the removal of Pb\(^{2+}\) ions in stormwater runoff from porous asphalt pavement systems with and without a geotextile layer, two different geotextile types, and two position levels within the pavement structure. In addition, the experiments included an additional design parameter dealing with stormwater detention in which observations were made when direct drainage of stormwater was allowed, and again when the system was constrained to provide temporary stormwater storage.
The decrease in concentration of Pb\(^{2+}\) ions in the initial effluent samples suggest that the use of a geotextile layer in PA systems has only a small effect on the removal efficiency of Pb\(^{2+}\) ions from initial stormwater runoff; but, it does provide a longer delay to the onset of discharge. Similar tendencies in Pb\(^{2+}\) ion removal rates over the sampling period were observed by the systems with or without a geotextile layer, and nearly 45% to 65% Pb\(^{2+}\) ions were successfully removed after 120 min of rainfall. It indicates that the presence of a geotextile layer within PA system does not necessarily change the basic tendency for Pb\(^{2+}\) removal over time, but it is able to improve the removal rate overall. Moreover, different geotextile types and their position in the PA system can directly affect the removal rate of Pb\(^{2+}\) ions. It is therefore recommended that for high Pb\(^{2+}\) removal rates, using a non-woven geotextile membrane at a lower level within the PA system is appropriate.

The higher removal capacity of Pb\(^{2+}\) ions by a PA system with a non-woven geotextile layer at the lower level and with 24 h of residence time in temporary storage, suggests that designing with a temporary storage for stormwater in a reservoir is important for the performance of a PA system as an effective LID technology for stormwater management. Stormwater quality analysis suggests that the stormwater runoff discharged from a PA system with a lower positioned non-woven geotextile layer that provides at least 20 h of storage in the reservoir course may be used as irrigation water.

The removal efficiency of Pb\(^{2+}\) ions in the present study was studied by the single factor experiment method. Generally, there are multiple factors simultaneously influencing the removal performance of PA system with an appropriate geotextile layer in practical conditions. For example, adsorption and removal efficiency are influenced by temperature, and the asphalt surfaces can reach very high temperatures on hot summer days. Therefore, for practical considerations, further research focusing on the influence of local weather conditions, stormwater composition, and load levels, on the removal of Pb(II) and other heavy metals from stormwater runoff are recommended.

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References
1. Kim, H.; Jeong, H.; Jeon, J.; Bae, S. The impact of impervious surface on water quality and its threshold in Korea. *Water* 2016, 8, 111. [CrossRef]
2. Xia, J.; Wang, H.P.; Stanford, R.L.; Pan, G.Y.; Yu, S.L. Hydrologic and water quality performance of a laboratory scale bioretention unit. *Front. Environ. Sci. Eng.* 2018, 12, 14. [CrossRef] [PubMed]
3. Hwang, H.M.; Foster, G.D. Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia River, Washington, DC, USA. *Environ. Pollut.* 2006, 140, 416–426. [CrossRef] [PubMed]
4. Scholz, M. Water quality improvement performance of geotextile within permeable pavement systems: A critical review. *Water* 2013, 5, 462–479. [CrossRef]
5. Valeo, C.; Gupta, R. Determining surface infiltration rate of permeable pavements with digital imaging. *Water* 2018, 10, 133. [CrossRef]
6. Nnadi, E.O.; Newman, A.P.; Coupe, S.J. Geotextile incorporated permeable pavement system as potential source of irrigation water: Effects of re-used water on the soil, plant growth and development. *Clean Soil Air Water* 2014, 42, 125–132. [CrossRef]
7. Charlesworth, S.M.; Beddow, J.; Nnadi, E.O. The fate of pollutants in porous asphalt pavements, laboratory experiments to investigate their potential to impact environmental health. *Int. J. Environ. Res. Publ. Health* 2017, 14, 666. [CrossRef] [PubMed]

8. Zhao, Y.; Zhao, C. Lead and zinc removal with storage period in porous asphalt pavement. *Water SA* 2014, 40, 65–72. [CrossRef]

9. Drake, J.A.P.; Marsalek, J. Review of environmental performance of permeable pavement systems: State of the knowledge. *Water Qual. Res. J. Can.* 2013, 55, 203–222. [CrossRef]

10. Myers, B.; Beecham, S.; van Leeuwen, J.A. Water quality with storage in permeable pavement basecourse. *Water Manag.* 2011, 164, 361–372. [CrossRef]

11. Ferguson, B.K. *Porous Pavements*; CRC Press: Boca Raton, FL, USA, 2005; pp. 457–512. ISBN 978-0-8493-2670-7.

12. Huang, J.; Valeo, C.; He, J.X.; Chu, A. Three types of permeable pavements in cold climates: Hydraulic and environmental performance. *J. Environ. Eng.* 2016, 142. [CrossRef]

13. Mullaney, J.; Jefferies, C.; Mackinnon, E. The performance of block paving with and without geotextile in the sub-base. In Proceedings of the 12nd International Conference Urban Drain, Porto Alegre, Brazil, 11–15 September 2011.

14. Mullaney, J.; Rikalainen, P.; Jefferies, C. Pollution profiling and particle size distribution within permeable paving system units-with and without a geotextile. *Manage. Environ. Qual. Int. J.* 2012, 23, 150–162. [CrossRef]

15. Dietz, M.E.; Angel, D.R.; Robbins, G.A.; McNaboe, L.A. Permeable asphalt: A new tool to reduce road salt contamination of groundwater in urban areas. *Groundwater* 2017, 55, 237–243. [CrossRef] [PubMed]

16. Legret, M.; Colandini, V.; Le Marc, C. Effects of a porous pavement with reservoir structure on the quality of runoff water and soil. *Sci. Total Environ.* 1996, 189–190, 335–340. [CrossRef]

17. Boving, T.B.; Stolt, M.H.; Augenstern, J.; Brosnan, B. Potential for localized groundwater contamination in a porous pavement parking lot setting in Rhode Island. *Environ. Geol.* 2008, 55, 571–582. [CrossRef]

18. Pagotto, C.; Legret, M.; Cloirec, L.P. Comparison of the hydraulic behaviour and the quality of highway runoff water according to the type of pavement. *Water Res.* 2000, 34, 4446–4454. [CrossRef]

19. Pratt, C.J.; Newman, A.P.; Bond, P.C. Mineral oil bio-degradation within a permeable pavement: Long term observations. *Water Sci. Technol.* 1999, 39, 103–109. [CrossRef]

20. Tota-Maharaj, K.; Scholz, M. Efficiency of permeable pavement systems for the removal of urban runoff pollutants under varying environmental conditions. *Environ. Prog. Sustain. Environ.* 2010, 29, 358–369. [CrossRef]

21. Brown, C.R.; Chu, A.; Duin, B.V.; Valeo, C. Characteristics of sediment removal in two types of permeable pavement. *Water Qual. Res. J. Can.* 2009, 44, 59–70. [CrossRef]

22. Ministry of Housing and Urban-Rural development of the People’s Republic of China. *Technical Specification for Permeable Asphalt Pavement*; China Building Industry Press: Beijing, China, 2012.

23. Maniquiz-Redills, M.C.; Kim, L.H. Understanding the factors influencing the removal of heavy metals in urban stormwater runoff. *Water Sci. Technol.* 2016, 73, 2921–2928. [CrossRef] [PubMed]

24. Jie, J.G.; Li, H.; Shi, J.Q. Partitioning of heavy metals in expressway stormwater runoff. *J. Southeast Univ. (Nat. Sci. Ed.)* 2010, 40, 1019–1024. [CrossRef]

25. Zhao, H.T.; Li, X.Y.; Wang, X.M.; Tian, D. Grain size distribution of road-deposited sediment and its contribution to heavy meta pollution in urban runoff in Beijing, China. *J. Hazard. Mater.* 2010, 183, 203–210. [CrossRef] [PubMed]

26. Zhao, H.T.; Li, X.Y.; Wang, X.M. Heavy metal contents of road-deposited sediment along the urban-rural gradient around Beijing and its potential contribution to runoff pollution. *Environ. Sci. Technol.* 2011, 45, 7120–7127. [CrossRef] [PubMed]

27. Silveira, A.L.L. Cumulative equations for continuous time Chicago hyetograph method. *Braz. J. Water Res.* 2016, 21, 646–651. [CrossRef]

28. General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China; Standardization Administration of the People’s Republic of China. *Standard for Irrigation Water Quality*; General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China and Standardization Administration of the People’s Republic of China: Beijing, China, 2005.

29. Farmaki, S.; Karakasi, O.; Moutsatsou, A. Pb and Ni adsorption on limestone and dolomite tailings. *J. Pol. Min. Eng. Soc.* 2014, 15, 199–204.
30. Németh, G.; Mlinářík, L.; Török, Á. Adsorption and chemical precipitation of lead and zinc from contaminated solutions in porous rocks: Possible application in environmental protection. *J. Afr. Earth Sci.* 2016, 122, 98–106. [CrossRef]

31. Sdiri, A.; Bouaziz, S. Re-evaluation of several heavy metals removal by natural limestone. *Front. Chem. Sci. Eng.* 2014, 8, 418–432. [CrossRef]

32. Barrett, M.E.; Kearfott, P.; Malina, J.F. Stormwater quality benefits of a porous friction course and its effect on pollutant removal by roadside shoulders. *Water Environ. Res.* 2006, 78, 2177–2185. [CrossRef] [PubMed]

33. Jiang, W.; Sha, A.; Xiao, J.; Huang, Y. Experimental study on filtration effect and mechanism of pavement runoff in permeable asphalt pavement. *Constr. Build. Mater.* 2015, 100. [CrossRef]

34. Godelitsas, A.; Kokkoris, M.; Misaelides, P. Investigation of the interaction of Greek dolomitic marble with metal aqueous solutions using Rutherford backscattering and X-ray photoelectron spectroscopy. *J. Radioanal. Nucl. Chem.* 2007, 272, 339–344. [CrossRef]

35. Cook, D.I. *Geosynthetics*; Rubber and Plastics Research Association Technology Limited: Shrewsbury, UK, 2003.

36. Sdiri, A.; Higashi, T. Simultaneous removal of heavy metals from aqueous solution by natural limestones. *Appl. Water Sci.* 2013, 3, 29–39. [CrossRef]

37. Karageorgiou, K.; Paschalis, M.; Anastassakis, G.N. Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent. *J. Hazard. Mater.* 2007, 139, 447–452. [CrossRef] [PubMed]

38. Ghazy, S.E.; Ragab, A.H. Removal of lead from water samples by sorption onto powered limestone. *Sep. Technol.* 2007, 42, 653–667. [CrossRef]

39. Sdiri, A.; Higashi, T.; Hatta, T.; Jamoussi, F.; Tase, N.; Bouaziz, S. Effects of impurities on the removal of heavy metals by natural limestones in aqueous systems. *J. Environ. Manag.* 2012, 93, 171–179. [CrossRef] [PubMed]

40. Sdiri, A.; Higashi, T.; Hatta, T.; Jamoussi, F.; Tase, N. Removal of heavy metals from aqueous solution by limestone. *Int. J. Glob. Environ. Issues* 2012, 12, 171–178. [CrossRef]

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