sustainability

MDPI

Article

Differences in Infiltration and Evaporation of Diesel and Gasoline Droplets Spilled onto Concrete Pavement

Bernat Adrià Mora * and **Markus Hilpert**

Department of Environmental Health Sciences, Columbia University School of Public Health, New York, NY 10032, USA; mh3632@cumc.columbia.edu
* Correspondence: bernat.adria.mora@gmail.com; Tel.: +1-667-231-9121

Received: 15 June 2017; Accepted: 13 July 2017; Published: 19 July 2017

Abstract: Pollution at gas stations due to small spills that occur during vehicle refueling have received little attention. We have performed laboratory experiments to assess evaporation and infiltration of fuel spilled onto concrete. Changes in the concrete mass after small amounts of diesel and gasoline were spilled have been analyzed. Variation in humidity, among other parameters, clearly affects the measured mass since condensed water is constantly added to or released from the concrete. This mass experiences an about exponential decay in time. The difference in behavior between both fuel types is important as the percentage of evaporated mass is much larger for gasoline, while infiltration is more significant for diesel. A statistical analysis suggests that the initial spill amount does not significantly affect the fraction of infiltrated fuel over time. This finding is in agreement with pore-scale simulations that we performed. A significant amount of fuel could be seeping into soil and groundwater underneath concrete pavement at gas stations or could be released to the atmosphere. Possible solutions for pavement and groundwater pollution are considered.

Keywords: fuel spills; concrete pavement; groundwater contamination; gas station; air pollution; evaporation; infiltration

---

1. Introduction

At gas stations, large amounts of unburned fuel are routinely released to the environment [1]. This is of concern because diesel and gasoline contain many chemicals that are harmful to environmental and human health. Among the volatile organic compounds (VOC), some of the most studied are the group known as BTEX (benzene, toluene, ethylbenzene, and xylene) due to its high toxicity. These pollutants can adversely affect public health and particularly populations, who spend significant amounts of time at or in the vicinity of gas stations, e.g., gas station attendants and workers [2]. Health effects associated with BTEX include central nervous system depression, eye, nose, skin, and throat irritation, chest constriction, kidney and liver impairment, and cancer [3]. Among the compounds listed above, benzene deserves special mention, because its relation with non-Hodgkin Lymphoma (NHL) and leukemia was proven [4].

Fuel is released to the environment in either liquid or vapor form, and can lead to environmental exposures [1]. Benzene and other toxic chemicals have been measured in air on [5,6] and in the vicinity [7,8] of gas stations. Releases to the atmospheric environment are usually related to vapor releases from tanks during refilling or during fuel storage due to over-pressurization of storage tanks [9]. Also groundwater has been frequently contaminated by gasoline and diesel fuel, where leaking underground storage tanks appear to be a primary contamination source [10]; furthermore, leaking product lines that deliver fuel from storage tanks to dispensing nozzles, leaky dispensing equipment, and spills during refueling of storage and vehicle tanks can cause subsurface contamination.

Dermal contact is another matter of concern when fuel spillage happens [11]. Spills during vehicle refueling have been quantified by the California Air Resources Board (CARB) [12]. Approximately 0.01% of dispensed fuel is spilled due to these small spills [1]. Even though this percentage is small, the total amount of fuel spilled at a gas station is significant because of the large volume of fuel sold [13]. For instance, at a small gas station selling 100,000 gallons of gasoline, 120 gallons of fuel are spilled, on average per year. For a mega-gas station that sells 1,000,000 gallons of fuel per month, 1200 gallons of fuel are spilled, on average per year. The New Hampshire Department of the Environment recommends that stormwater should not be permitted to flow over the gas station refueling zones [14], presumably because the stormwater can pick up spilled fuel and then contaminate downstream water bodies. Indeed surface runoff from gas stations has been found to be contaminated by fuel constituents [15,16].

It is important to understand how much of spilled fuel infiltrates into the underlying subsurface or is released in vapor form to the atmosphere, because both processes can result in environmental exposures. Infiltrated fuel may contribute to groundwater contamination, while vapors can be inhaled. Only very few studies have attempted to quantify the fate of fuel spilled onto surfaces such as pavement. Stocking et al. [17] performed a theoretical study, which estimated the risk of groundwater contamination due to spillage of a “small” volume of gasoline; however, their small volume was about 0.5 L, much larger than was observed in the CARB study [12], in the order of 0.01 L. Hilpert and Breysee [13] performed the first study in which the fate of spilled droplets of gasoline was truly investigated. They developed a theoretical pore-scale model for fuel droplet infiltration and evaporation, and also performed spill experiments with gasoline droplets with an about 1-g mass. They concluded that the amount of fuel, which is able to infiltrate into the concrete typically present underneath gasoline dispensing stations, poses a threat to underlying soil and groundwater. The objectives of this study are: (1) to examine the effects of droplet size on infiltration and evaporation of spilled fuel droplets and (2) to examine the effects of fuel type (diesel versus gasoline).

2. Experimental Methods

Overview: In order to understand the processes of evaporation and infiltration of fuel spilled onto concrete pavement at gas stations, we performed experiments in the laboratory. In the experiments, we placed a concrete sample onto an electronic balance and spilled a small amount of fuel over the sample. The added mass due to the deposition of the fuel droplet, m_{fuel}, was measured as a function of time. This mass gives an indication for the sum of liquid fuel present as a sessile droplet on the top surface of the concrete sample, $m_{droplet,}$ and of the infiltrated fuel present within the concrete, m_{infil}:

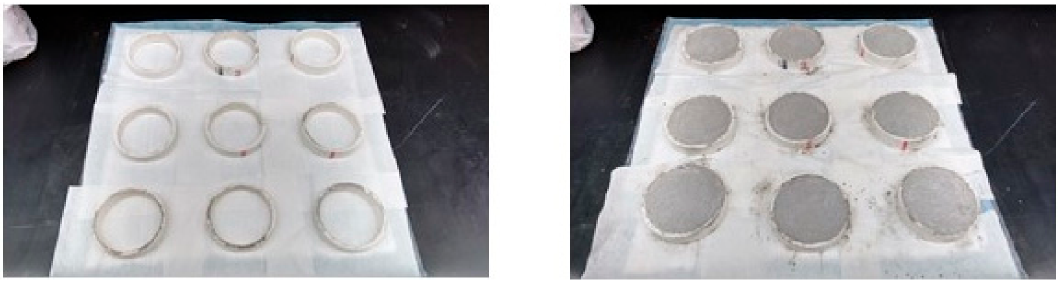
$$m_{fuel}(t) = m_{droplet}(t) + m_{infil}(t). \tag{1}$$

The difference between the initial droplet mass, $m_{fuel}(0)$, and the mass remaining at any given time, $m_{fuel}(t)$, gives an indication for how much fuel has evaporated.

Droplet size: In the experiments, the mass of the spilled fuel droplets was varied, because the volume of gasoline droplets spilled during vehicle refueling is non-uniformly distributed [12]. The mass of diesel droplets was increased in 0.2-g increments and varied between 0.2 and 1.6 g. The mass of gasoline droplets (87 octane rating, winter-grade) was also increased in 0.2-g increments and varied between 0.6 and 2.0 g. The minimum mass in these experiments was chosen such that no mass decayed to 0 too quickly, within less than an hour. The maximum mass was limited by the areal extent of the concrete sample. A Pasteur pipette and a syringe were used to release known fuel amounts to the concrete samples.

Balances: We used two electronic balances, an OHaus SP602 and an OHaus SP402. The main difference between the two balances is that the first one has a capacity of 600 g while the second one has a capacity of 400 g. Both have an accuracy of 0.01 g, and their sample holding plates have a diameter of 12 cm. These features imposed limitations with regard to the maximum weight of the concrete samples and the minimum spill size. Balances were calibrated regularly. Measured mass data were read out to a computer via a USB port. The mass data were collected and processed with the LoggerPro^{TM} software, which allowed us to control the frequency of the readings and the length of the experiment. After each experiment, data were stored in electronic spreadsheets.

Concrete samples: It is difficult to achieve concrete samples with the right size and shape from actual gas station pavement. Therefore, we made our own concrete samples in the laboratory considering the technical specifications of the balances. By estimating the density of concrete and bearing in mind the surface and the maximum capacity of the balance, we decided to make circular molds of 2.5 cm height and an inner diameter of 10 cm. Proper amounts of concrete powder (Quikrete) and water were mixed in a bucket, and then concrete was poured into the molds (see Figure 1). Thus, concrete samples of less than 400 g were obtained with very similar characteristics.



(**a**) (**b**)

Figure 1. (**a**) Plastic molds of proper size. (**b**) Concrete mix was poured into molds to create the concrete samples.

Fume hood: All experiments were performed in a fume hood to avoid human exposure to hazardous fuel vapors. We noticed small variations in the mass readings of the balances in the fume hood due to air currents therein. We reduced these currents by placing a cardboard shield around the balances (see Figure 2).

Figure 2. Components of the experiment.

Atmospheric conditions: Humidity affects the amount of water sorbed onto and into the concrete. Therefore, variations in the collected mass data occurred that cannot be solely attributed to fuel evaporation. In order to assess the influence of the changes in humidity over the readings, we measured relative humidity (RH) and temperature using a USB humidity logger (Lascar EL USB 2 LCD+). The sensor was placed between the two balances. This device has an accuracy of ±2% for RH and ±0.3 °C for temperature under the conditions in which we were working. At the end of each experiment, we exported the data to the electronic spreadsheet, in which the mass data were stored.

The temperature in the fume hood was quite stable, about 19–20 °C during the diesel experiments, and about 24–25 °C during the gasoline experiments. However, relative humidity could vary within a wide range, between 35% and 70%. The variations occurred during the course of a day and were likely affected by air-conditioning and changing weather.

Experimental Protocol

1. Concrete samples were placed into the fume hood several hours before the start of the actual spillage experiments, so that they could pre-equilibrate with the atmospheric water vapor present in the fume hood.
2. We placed two concrete pieces onto the two balances. A bubble level was used to level the surface of the concrete piece such that it mimicked the usually level pavement at gasoline dispensing facilities. If needed, we put coins below the concrete pieces to achieve an upper surface that was completely horizontal.
3. The balances were zeroed.
4. Mass data collection was started at a frequency of 30 per minute during the first ten minutes, and 1 per minute thereafter. Also, humidity and temperature data were collected during the whole experiment at a frequency of one reading per minute.
5. A small amount of fuel was then spilled over the surface of each concrete sample.
6. Data were recorded for 24 h, and the experiment was terminated.

For each type of fuel, gasoline and diesel, eight 24-h experiments with different initial masses were carried out.

3. Data Analysis

Humidity is a significant parameter when it comes to assessing the long-term behavior of the liquid fuel that is present in and on a concrete sample. This is because the mass of the concrete sample does not only change due to fuel evaporation but also due to absorption and desorption of water that occur because of a changing RH. We observed a clear relationship between RH(t) and the measured mass $m(t)$ after a certain period of time (usually after the fuel mass levels off). The measured mass $m(t)$ is the sum of the mass of the fuel, which is present either as a sessile droplet on the surface or infiltrated into the concrete according to Equation (1), and the mass of absorbed water:

$$m(t) = m_{fuel}(t) + m_{water}(t). \tag{2}$$

In the following, we present an approach that allows us to separate the effects of fuel evaporation and water absorption and that therefore allows us to estimate the actual fuel mass m_{fuel} on and in the concrete. Figure 3 illustrates our approach. For each experiment, we created plots showing the evolution of mass and humidity for a 24-h period. Pearson correlations were obtained to evaluate a linear relationship between each pair of variables [18,19]. In our statistical analysis, the exponential of negative time, together with humidity, were used as they provided a good description of reality. However, we also examined regression models working with other functions of time. Trend lines obtained as a result of linear regressions using the square root of time can also give quite good approximations for subsets of data (e.g., during the first hours), but do not offer accurate descriptions of the entire data sets. Therefore, the evolution of measured liquid mass is modeled as follows:

$$m(t) = \alpha_0 + \alpha_1 \cdot \mathrm{RH}(t) + \alpha_2 \cdot e^{-t} \tag{3}$$

where the coefficients α_0, α_1, and α_2 were calculated using regression models. The regressions permitted the creation of trend lines, which describe the behavior of fuel mass in the hypothetical event that the atmospheric moisture is constant (and equal to the initial RH_0 value).

Figure 4 illustrates how fuel mass would monotonically decrease if RH changes did not occur, behavior expected due to the continuously ongoing fuel evaporation. In order to evaluate the model fit and accuracy of the trend lines, we calculated the coefficient of determination, R^2.

It is difficult to independently validate our method for separating the measured mass changes due to fuel evaporation from those due to RH variations. Ideally, one would measure the actual water and fuel contents in a concrete sample, a difficult task because concrete is a consolidated porous medium with a very fine pore size, which makes it difficult to separate the liquids from the porous medium.

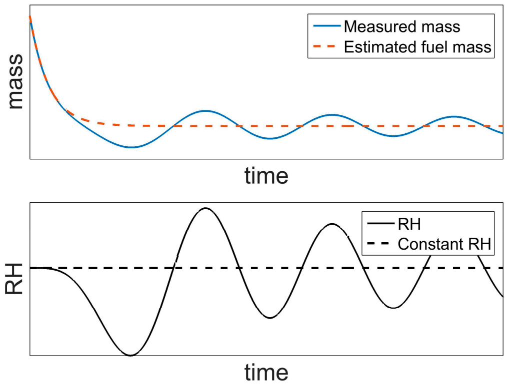


Figure 3. Illustration of how a fluctuating relative humidty RH(*t*) affects the measured mass of the concrete sample. For a temporally variable RH (solid black line in lower plot), one observes a non-monotonic relationship between the measured mass and time *t* (blue line in upper plot). If RH was constant (dashed solid line in lower plot), one would measure a monotonically decreasing mass (red dashed line in upper plot).

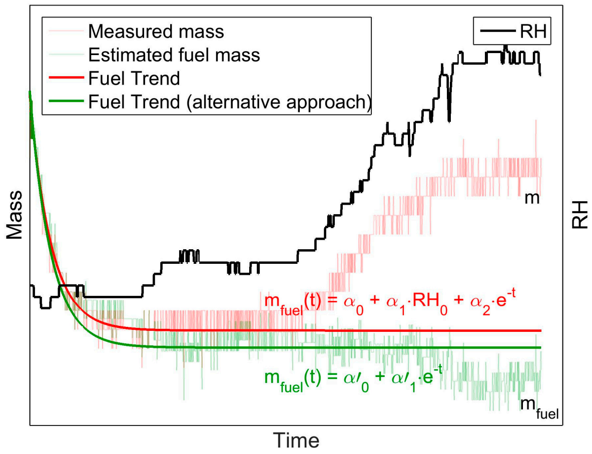
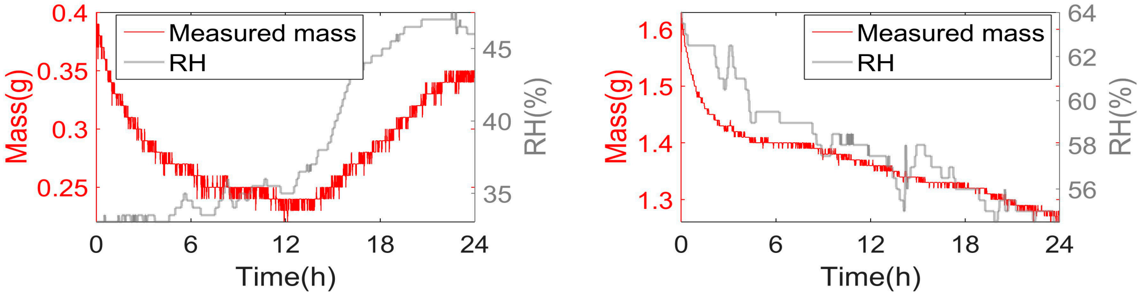


Figure 4. Two trend lines showing the estimated fuel mass in and on the concrete as a function of time. Both approaches produce similar results. In red, measured data and trend line of estimated fuel mass obtained directly from linear regressions. An alternative approach, explained in Appendix A, leads to the trend line shown in green. Measured data is clearly related to relative humidity.

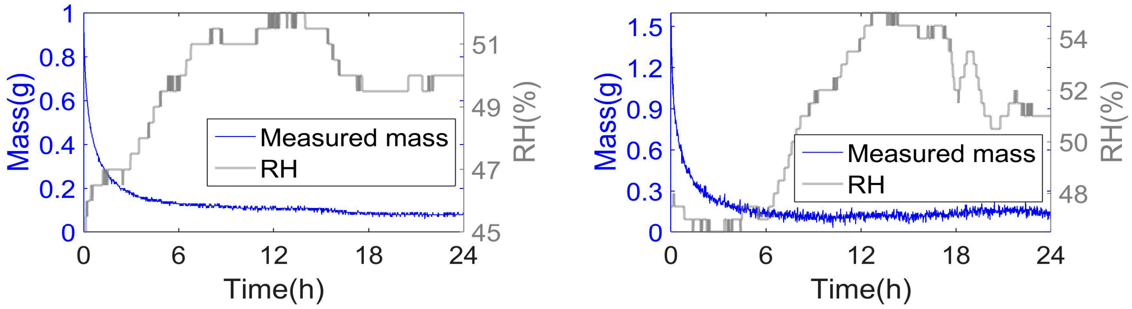
However, we came up with an alternative, sensible approach for estimating the fuel mass in and on the concrete that agreed well with our regression analysis. In this alternative approach, we inferred the fuel mass from the measured mass change of the concrete sample by assuming a linear relationship between the relative humidity variation and the water absorbed by the concrete (please see Appendix A). This assumption is analogous to the widely used approach for modeling sorption of a contaminant dissolved in groundwater to sediment particles, where one routinely assumes chemical equilibrium based on a linear sorption isotherm [20]. To confirm that both estimations are similar, the average R^2 for diesel and gasoline experiments were compared with the same R^2 obtained by the alternative approach, and no significant differences were found (p-value = 0.2093). Our method for inferring the fuel mass from the measured mass data according to Equation (3) has therefore passed another plausibility check, in addition to good model fit.

4. Results

In the scatter plots shown in Figure 5, significant differences of behavior between some diesel and gasoline experiments are revealed. In the plots, both axes are delimited by the maximum and minimum values of mass (red/blue) and relative humidity (grey). The evolution of gasoline mass appears to be barely affected by the humidity. In the diesel experiments, however, RH plays a major role and masks the about exponential decay of the fuel mass.



DIESEL



GASOLINE

Figure 5. Mass and humidity data (grey) of selected experiments. The diesel mass (red) is strongly affected by humidity changes. The gasoline mass (blue) shows an about exponential decay, which is apparently not affected by the humidity variation. Note the different ranges of the ordinate between diesel and gasoline experiments.

Linear regressions considering RH were performed to obtain trend lines, which represent an accurate description of the fuel evolution. For gasoline experiments, the regression models always give a very good description (R^2 ~0.98). In the case of diesel, some regressions are better than others (average R^2 about 0.90), but in general, estimations are quite good. In Figure 6, two trend lines are shown that predict the evolution of fuel mass if relative humidity had been held constant during the spillage experiments.

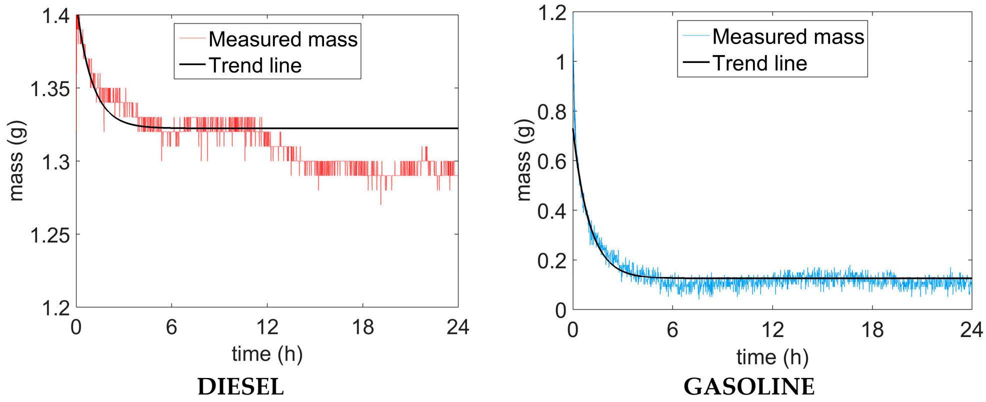


Figure 6. Examples of trend lines calculated from diesel (red) and gasoline (blue) data. The trend lines are based on regression models that take into account relative humidity (RH) changes. The trend lines show the expected behavior of fuel under conditions of constant RH. Descriptions are usually better for gasoline experiments.

Figure 7 shows 3D plots of the fraction f [−] of the estimated remaining fuel mass for selected times during the first 4 h of each experiment. We chose this range, because the mass levels off within a few hours; therefore not much additional information would be gained by displaying results for later times. The left plot shows that the fraction of diesel remaining in and on the concrete is variable, but there is not a clear trend. On average, about 80% to 90% of the initial mass remains in concrete after 4 h. For the gasoline experiments, different initial droplet sizes lead to similar final fractions of mass, and only about 10% to 15% remains in the concrete. Note also that, for gasoline, about half of the mass had evaporated during the first 15 min.

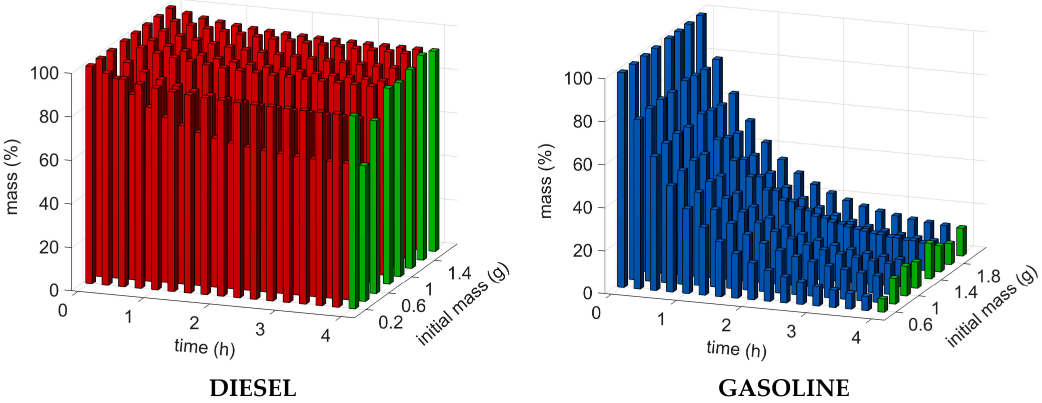


Figure 7. Percentage of fuel mass remaining in or on concrete during the first 4 h of every experiment. Initial fuel masses are shown on the backward pointing horizontal axis to prove how these are related to the remaining mass at the end of the experiments. The plots illustrate the different behavior between both fuel types.

We used linear regression modeling in order to predict the fraction of fuel remaining in the concrete, f, as a function of the initial spill mass m_0:

$$f(t) = \frac{m_{fuel}(t)}{m_0} = f_0 + \alpha(t)\, m_0 \tag{4}$$

where f_0 [−] is the fraction that is approached in the limit where the initial droplet mass approaches zero, and α [M^{-1}] is a slope factor which quantifies by how much f changes due to a change of m_0. For the diesel experiments, the 95% confidence intervals (CI) for α were (8.21 ± 8.57) g^{-1} at t = 1 h and

(13.00 ± 13.56) g^{-1} at t = 24 h, while for gasoline they were (1.35 ± 3.04) g^{-1} at t = 1 h and (2.13 ± 4.81) g^{-1} at t = 24 h. As zero is within the CI, no significant changes were found in f with regard to the initial droplet mass. Regressions can be determined for any time and plotted including the CI (see Figure A2 in Appendix B).

We performed supporting pore-scale modeling based on previously developed models [13,21] in order to explore why the initial droplet mass does not significantly affect the fraction of infiltrated and evaporated fuel. This mathematical model describes the dynamics of a spilled fuel droplet, which infiltrates into porous medium and evaporates into a turbulent atmosphere. The porous medium is described as a bundle of vertical capillary tubes, and the model assumes a sharp wetting front during infiltration. Hilpert and Breysse [13] have already used this model to show that the initial droplet mass does not affect these fractions very much for gasoline. They attributed this to the fact that the thickness of a sessile gasoline droplet does not change much when the droplet mass is changed from 0.9 to 4.5 g. We now performed similar simulations for diesel. For the diesel fuel, we assumed a density $\rho = 0.83$ g/cm^3 [22,23], a dynamic viscosity $\eta = 3 \times 10^{-3}$ kg m^{-1} s^{-1} [22,24], an interfacial tension $\sigma = 28$ mN/m [23,25], and a vapor pressure $e = 0.5$ mmHg [26,27]. We also assumed an evaporation rate $E_{po} = 1$ mm/day. The contact angle was $\theta = 20°$, and the permeability $\kappa = 1.4 \times 10^{-2}$ m^2, and porosity $\varepsilon = 0.15$ of concrete were the same as used in Hilpert and Breysse [13]. Figure 8a,b shows the initial shapes of two modeled sessile diesel droplets with quite distinct masses of 0.5 and 4.0 g. Due to gravitational forces, the air-liquid interface does not have the shape of a spherical cap but looks rather like a pancake. The two sessile droplets have quite similar thicknesses. As a result, the modeled fractions of infiltrated and evaporated diesel (see Figure 8c,d) do also not differ very much. This is entirely consistent with the diesel experiments of this paper.

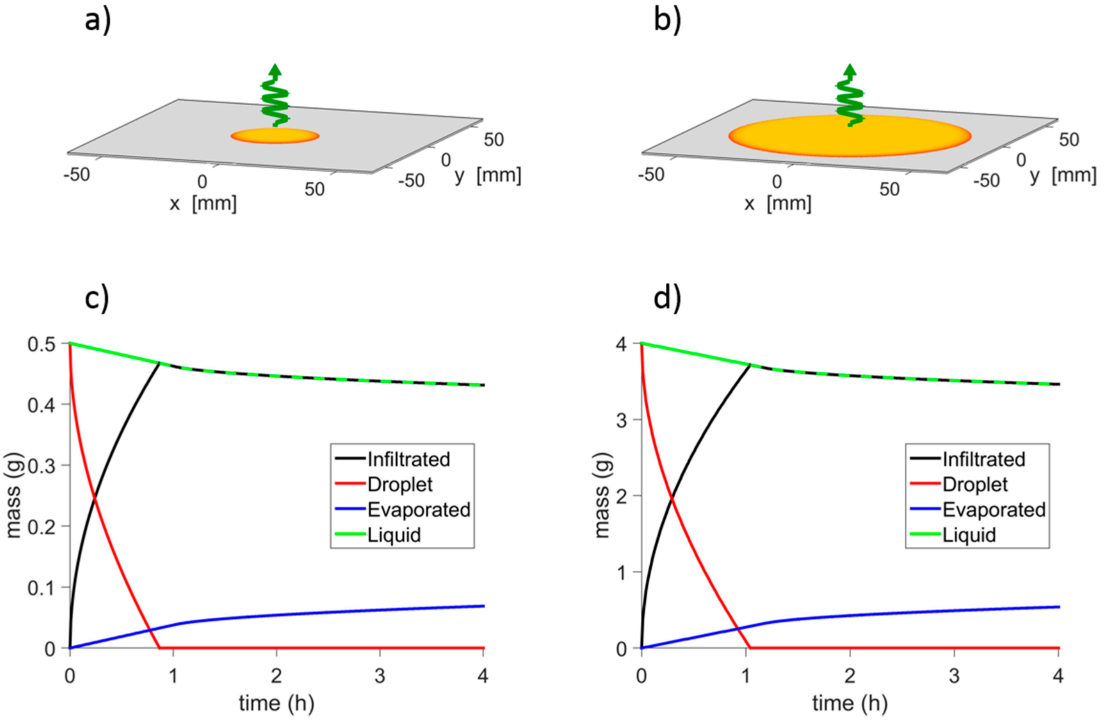


Figure 8. Upper plots show the theoretical shapes of the diesel droplets for the masses 0.5 g (**a**) and 4.0 g (**b**). The plots at the bottom show the evolution of the masses of the fuel that is present in the concrete as an infiltrated liquid, is present as a sessile droplet on top of the concrete, or evaporated. Droplets vanish in about an hour independently of the initial mass spilled. Most of the fuel infiltrates, and the evaporation rate is small.

5. Discussion

Accidental fuel spillage, which chronically occurs during the refueling of automobiles, are of concern because fuel contains toxic chemicals such as BTEX. Not many studies have been conducted with regard to these spills, while more research has been devoted to other pollutant releases at petrol stations, including fuel release related to Stage I/II vapor recovery [5], leaking underground storage tanks (LUST) [10,28], and Onboard Refueling Vapor Recovery (ORVR) in vehicles [29,30]. CARB staff has reported accidental spillages of gasoline as one of the sources of vapor emissions in gas stations [8]. Our study suggests that pollution due to small spills should also be considered in studies since fuel could infiltrate towards ground water, in addition to being released into the atmosphere.

Initially, it was difficult to understand the mass changes of the concrete samples that occurred after fuel droplets were deposited. Instead of the expected stabilization of this mass, we observed, particularly for the diesel spills, oscillations for a few hours after droplet deposition. Many different experiments were performed prior to the ones shown in this study in order to understand the source of the oscillations and to improve the accuracy of our results. We considered many different factors that could have caused these unexpected observations, such as changes in atmospheric pressure, malfunction of the initially solely available electronic balance (OHaus SP402), and variations in air currents within the fume hood. We therefore performed multiple experiments (that also involved purchasing a second balance, OHaus SP602) to reject these hypotheses. Eventually, we hypothesized that mass oscillations are related to humidity changes and acquired a humidity meter. Indeed, mass changes correlated well with RH changes in the diesel experiments (see Figure 5). These effects are less obvious for gasoline, but occur as well. Apparently, water vapor mostly condenses onto (or is released from) concrete independently of the fuel type spilled. By measuring humidity during the experiments, we were able to develop models that account for the changes in mass of the concrete sample due to humidity variations. These models allowed us to separate water and fuel masses. They correct for humidity effects, and model predictions resulted in a good description of fuel behavior.

The temporal behavior of the liquid fuel mass in and on the concrete can approximately be described by an exponential decay. However, the difference in behavior between both fuel types is significant. The percentage of evaporated mass is much larger for gasoline (~85% to 90%) than for diesel (~10% to 20%). This is because gasoline is more volatile than diesel, not only because of its base constituents but also due to the fuel additives [31]. The composition of gasoline and its Reid vapor pressure, and hence its volatility, are seasonally dependent so that evaporation rates could be slightly different. Although the percentage of infiltrated mass varies in some experiments, the initial amount of fuel spilled does not significantly affect the fraction of remaining liquid at the end of an experiment, as supported by the pore-scale model developed by Hilpert and Breysse [13]. Using that model, we examined the effects of different initial fuel mass. We found that the wetted surface increases with the initial mass, but the heights of the sessile fuel droplets are not affected much (as gravity affects the droplet shapes). Therefore, infiltrated and evaporated fractions remain almost constant.

Thus, evaporation is more important initially for spilled gasoline, while the infiltrated fuel mass is greater for spilled diesel, meaning that an important quantity of fuel could be seeping into the soil and groundwater or could be released to the atmosphere. These differences in behavior between diesel and gasoline also apply to accidental spillages in other circumstances (e.g., leaking tanks in old vehicles or spills due to road accidents). More research is needed to estimate the losses of fuel into soil underneath concrete pavement [13] and to predict the human exposure at gas stations and surrounding neighborhoods.

Additional studies could be conducted to measure directly the evolution of the amounts of liquid in concrete by using accurate 3D imaging techniques and in this way support our results. X-ray computed microtomography (micro-CT), performed using a synchrotron beamline, is a powerful method to examine fluid flow in porous media [32] and is, together with other experimental techniques, also useful to estimate porosity [33], permeability [34], and diffusivities [35,36]. Micro-CT is a non-invasive tool which permits analysis of the moisture content [37] of a concrete sample, also prior to the spillage of fuel. Recent developments in neutron radiography and synchrotron-based micro-imaging technologies not only are a useful tool to visualize and quantify the penetration of liquid into concrete [38] but also permit high contrast imaging so that it is possible to study a two-liquid system [39,40], and hence measure mass of water and fuel separately. We also considered analytical extraction techniques [41] to assess the fate of fuel spilled onto concrete, however, the small pore size of consolidated concrete makes it difficult to quantify the remaining amounts of liquid [42].

Given that part of spilled fuel, diesel more so than gasoline, infiltrates into concrete, from which it can reach soil and groundwater, and part can be carried away by stormwater runoff, regular removal of these pollutants should be considered by policies. Frequent, appropriate cleaning of pavement at gas stations could be implemented, taking into account that not only accidental fuel spills occur, but also that engine oil from vehicles and refrigerants from air conditioning units (containing CFCs) are routinely spilled [43]. Major spills should be immediately addressed with dry cleanup methods using, for example, rags and absorbents [44], amongst other best management practices (BMPs) [45]. Canopies above fuel dispensing areas are nowadays widespread but not installed at all gas stations. This is key to preventing pollutants from being washed away by stormwater runoff. Bioretention systems have been used in urban areas to control stormwater flows and to attenuate pollution [46–48], although more research is needed to ascertain their efficiency in gas station settings [49].

Acknowledgments: This study was funded by a seed grant from the Environment, Energy, Sustainability and Health Institute at Johns Hopkins University and by NIH grant P30 ES009089.

Author Contributions: Markus Hilpert designed the study. Bernat Adria Mora performed the experimental work and developed the statistical methods used to interpret the experiments. All authors participated in the interpretation of the results and contributed to the writing of the article.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Alternative Approach for Estimating Fuel Mass

We developed an alternative method for estimating the fuel mass in and on a concrete sample from the measured mass of a concrete sample, onto which a fuel droplet was spilled. This method consisted of adding mass to (or removing from) the mass readings, depending on the changes in humidity. We know with certainty the amount of fuel at time $t = 0$, when no humidity changes could possibly have affected the mass reading, because the balance had recently been zeroed. Considering that the initial relative humidity RH_0 was known and that the initial mass m_0 represented 100% fuel, we estimated the actual fuel mass m_{fuel} at any point in time by the following formula:

$$m_{fuel}(t) = m(t) + \beta \cdot [\mathrm{RH}_0 - \mathrm{RH}(t)] \tag{A1}$$

where $m(t)$ is the measured liquid mass. The measured initial relative humidity is represented by RH_0 and $\mathrm{RH}(t)$ is the measured relative humidity. The coefficient β depends on parameters such as concrete sample size and the initial fuel mass as explained in Section 2. This coefficient is different for each experiment and was estimated by the following finite-difference expression:

$$\beta = \frac{m(\mathrm{RH}_{\max}) - m(\mathrm{RH}_{\min})}{\mathrm{RH}_{\max} - \mathrm{RH}_{\min}} \tag{A2}$$

where $m(\mathrm{RH}_{\max})$ is the liquid mass measured when the humidity is maximum, and $m(\mathrm{RH}_{\min})$ is the liquid mass measured when the humidity is minimum. Our range of interest excludes the first hours of the experiment, when the change in liquid mass was dominated by evaporation, thereby masking mass changes due to humidity variations. In Figure A1, the prediction of fuel mass behavior for a hypothetical constant humidity is shown by the thin red line.

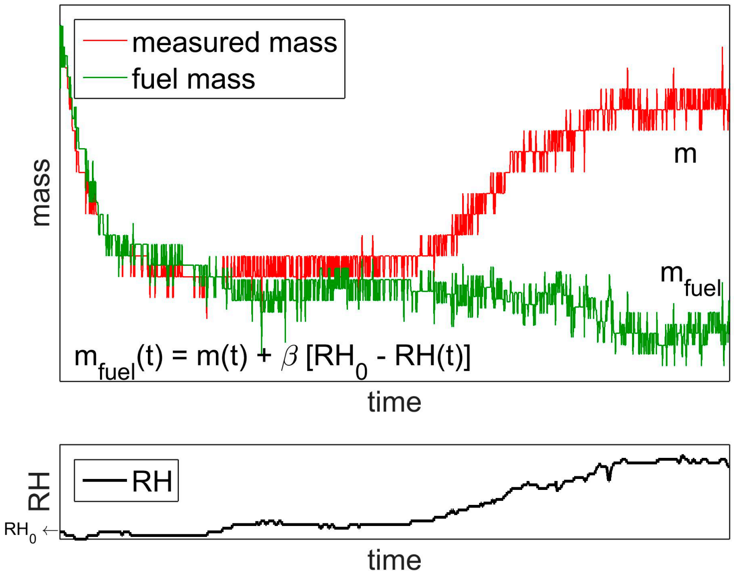


Figure A1. The upper plot shows the measured and estimated fuel mass. The equation shown is used to estimate the actual fuel mass from the measured mass. Relative humidity changes are shown in the lower plot. Note the relationship between RH and measured mass.

Our model does not provide a perfect representation of the actual water vapor exchange between the concrete and the atmosphere. However, as shown in the Figure A1, the predicted fuel mass is maintained almost constant, as expected after the initial fast evaporation. We then performed another regression to obtain trend lines from this corrected data, using the equation

$$m_{fuel}(t) = \alpha'_0 + \alpha'_1 \cdot e^{-t}. \tag{A3}$$

Trend lines of the alternative method and the one based on Equation (3) are shown in Figure 4 and agree well with one another.

Appendix B. Linear Regression Modeling to Assess Infiltrated Fractions as a Function of the Spill Mass

We performed regressions to analyze the fraction of fuel in the concrete $f(t)$ as a function of initial spill mass as a function of time. As explained in *Results*, the experimental data were described by the following formula:

$$f(t) = \frac{m_{fuel}(t)}{m_0} = f_0 + \alpha(t)\, m_0. \tag{A4}$$

Figure A2 illustrates results for both fuel types for t = 1 h and t = 24 h, and compares the corresponding $\alpha(t)$. Values of α and f_0 displayed in the plots were obtained together with their standard errors. These errors permitted calculating the 95% confidence intervals. We cannot conclude that the remaining mass increases or decreases when initial mass spilled changes since the slopes of trend lines are not statistically different from 0.

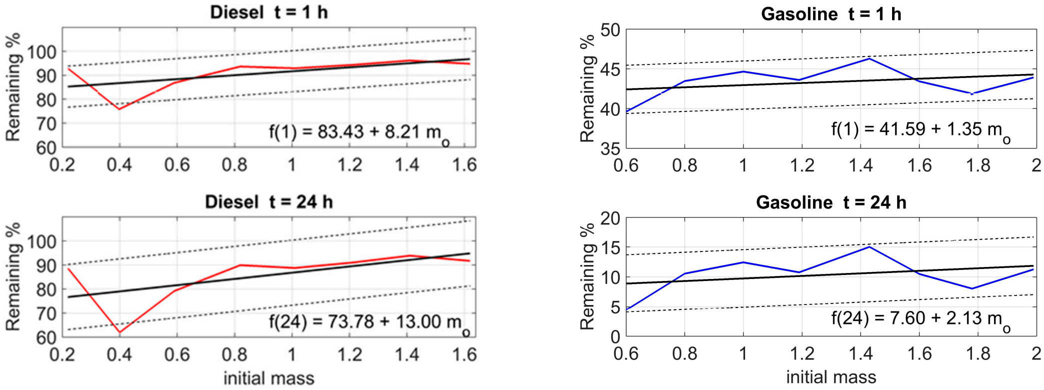


Figure A2. Trend lines (solid black) based on regression models for selected times t = 1 h and t = 24 h of both fuel types. Color lines represent the fraction of fuel mass in concrete as a function of the initial amount spilled in each experiment. Dotted lines represent 95% confidence interval of each trend line.

References

1. Hilpert, M.; Adria-Mora, B.; Ni, J.; Rule, A.; Nachman, K. Hydrocarbon release during fuel storage and transfer at gas stations: Environmental and health effects. *Curr. Environ. Health Rep.* **2015**, *2*, 412–422. [CrossRef] [PubMed]
2. Moolla, R.; Curtis, C.J.; Knight, J. Occupational exposure of diesel station workers to BTEX compounds at a bus depot. *Int. J. Environ. Res. Public Health* **2015**, *12*, 4101–4115. [CrossRef] [PubMed]
3. Moolla, R.; Curtis, C.J.; Knight, J. Assessment of occupational exposure to BTEX compounds at a bus diesel-refueling bay: A case study in Johannesburg, South Africa. *Sci. Total Environ.* **2015**, *537*, 51–57. [CrossRef] [PubMed]
4. Chaiklieng, S.; Pimpasaeng, C.; Thapphasaraphong, S. Benzene exposure at gasoline stations: Health risk assessment. *Hum. Ecol. Risk Assess. Int. J.* **2015**, *21*, 2213–2222. [CrossRef]
5. Hakkola, M.A.; Saarinen, L.H. Customer exposure to gasoline vapors during refueling at service stations. *Appl. Occup. Environ. Hyg.* **2000**, *15*, 677–680. [PubMed]
6. Lagorio, S.; Fuselli, S.; Iavarone, I.; Vanacore, N.; Carere, A. Exposure to benzene of service station employees and composition of benzene. *La Medicina del Lavoro* **1994**, *85*, 412–421. [PubMed]
7. Bravo, H.; Sosa, R.; Sanchez, P.; Bueno, E.; Gonzalez, L. Concentrations of benzene and toluene in the atmosphere of the southwestern area at the Mexico City metropolitan zone. *Atmos. Environ.* **2002**, *36*, 3843–3849. [CrossRef]
8. Craft, D.; Demyanovich, S.; Giraudo, M.; Johnston, J. *Gasoline Service Station Industrywide Risk Assessment Guidelines*; Toxics Committee of the California Air Pollution Control Officers Association (CAPCOA), Ed.; California Air Resources Board (CARB): Sacramento, CA, USA, 1997.
9. Statistics Canada. Gasoline evaporative losses from retail gasoline outlets across Canada 2009. In *Environment Accounts and Statistics Analytical and Technical Paper Series*; Statistics Canada: Ottawa, ON, Canada, 2012.
10. Levy, B.S.; Riordan, P.J.; Schreiber, R.P. Estimation of leak rates from underground storage tanks. *Ground Water* **1990**, *28*, 378–384. [CrossRef]
11. Ahmed, F.E. Toxicology and human health effects following exposure to oxygenated or reformulated gasoline. *Toxicol. Lett.* **2001**, *123*, 89–113. [CrossRef]
12. Morgester, J.J.; Fricker, R.L.; Jordan, G.H. Comparison of spill frequencies and amounts at vapor recovery and conventional service stations in California. *J. Air Waste Manag. Assoc.* **1992**, *42*, 284–289. [CrossRef]
13. Hilpert, M.; Breysse, P.N. Infiltration and evaporation of small hydrocarbon spills at gas stations. *J. Contam. Hydrol.* **2014**, *170*, 39–52. [CrossRef] [PubMed]
14. New Hampshire Department of Environmental Services. *Preventing Groundwater Contamination at Gas Stations—What Municipalities and Water Suppliers Can Do*; New Hampshire Department of Environmental Services: Concord, NH, USA, 2012.
15. Borden, R.C.; Black, D.C.; McBlief, K.V. MTBE and aromatic hydrocarbons in North Carolina stormwater runoff. *Environ. Pollut.* **2002**, *118*, 141–152. [CrossRef]

16. Drapper, D.; Hornbuckle, A. Case studies of a hydrocarbon capture technology for stormwater quality class 1 compliance against en bs858.1–2002 and subsequent field evaluation. *Water* **2016**, *8*, 48. [CrossRef]
17. Stocking, A.; McDonald, S.; Woll, B.; Kavanaugh, M. *Evaluation of Fate and Transport of Methyl Tertiary Butyl Ether (MTBE) in Gasoline Following a Small Spill*; National Ground Water Association and American Petroleum Institute: Westerville, OH, USA; Washington, DC, USA, 1999; pp. 229–246.
18. Sharma, A. *Text Book of Correlations and Regression*; Discovery Publishing House: New Delhi, India, 2005.
19. Zou, K.H.; Tuncali, K.; Silverman, S.G. Correlation and simple linear regression. *Radiology* **2003**, *227*, 617–628. [CrossRef] [PubMed]
20. Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13*, 241–248. [CrossRef]
21. Hilpert, M.; Ben-David, A. Infiltration of liquid droplets into porous media: Effects of dynamic contact angle and contact angle hysteresis. *Int. J. Multiph. Flow* **2009**, *35*, 205–218. [CrossRef]
22. Aworanti, O.A.; Agarry, S.E.; Ajani, A.O. A laboratory study of the effect of temperature on densities and viscosities of binary and ternary blends of soybean oil, soy biodiesel and petroleum diesel oil. *Adv. Chem. Eng. Sci.* **2012**, *2*, 9. [CrossRef]
23. Esteban, B.; Riba, J.R.; Baquero, G.; Puig, R.; Rius, A. Characterization of the surface tension of vegetable oils to be used as fuel in diesel engines. *Fuel* **2012**, *102*, 231–238. [CrossRef]
24. Methanol Institute. *Methanol Safe Handling Technical Bulletin*; Methanol Institute: Alexandria, VA, USA, 2011.
25. Wang, F.; Wu, J.; Liu, Z. Surface tensions of mixtures of diesel oil or gasoline and dimethoxymethane, dimethyl carbonate, or ethanol. *Energy Fuels* **2006**, *20*, 2471–2474. [CrossRef]
26. North Central Missouri College. *Material Data Safety Sheet for #2 Diesel*; North Central Missouri College: Trenton, MO, USA, 1999.
27. Hess Corporation. *Safety Data Sheet. Material Name: Diesel Fuel, All Types*; Hess Corporation: New York, NY, USA, 2012.
28. Sacile, R. Remote real-time monitoring and control of contamination in underground storage tank systems of petrol products. *J. Clean. Prod.* **2007**, *15*, 1295–1301. [CrossRef]
29. The International Council On Clean Transportation (ICCT). *Onboard Refueling Vapor Recovery: Evaluation of the Orvr Program in the United States*; The International Council On Clean Transportation (ICCT): San Francisco, CA, USA, 2011.
30. Yang, X.; Liu, H.; Cui, H.; Man, H.; Fu, M.; Hao, J.; He, K. Vehicular volatile organic compounds losses due to refueling and diurnal process in China: 2010–2050. *J. Environ. Sci.* **2015**, *33*, 88–96. [CrossRef] [PubMed]
31. Speight, J.G. *The Biofuels Handbook*; Royal Society of Chemistry: London, UK, 2011.
32. Wildenschild, D.; Culligan, K.A.; Christensen, B.S.B. *Application of X-ray Microtomography to Environmental Fluid Flow Problems*; SPIE: Bellingham, WA, USA, 2004; pp. 432–441.
33. Cnudde, V.; Cwirzen, A.; Masschaele, B.; Jacobs, P.J.S. Porosity and microstructure characterization of building stones and concretes. *Eng. Geol.* **2009**, *103*, 76–83. [CrossRef]
34. Okabe, H.; Blunt, M.J. Prediction of permeability for porous media reconstructed using multiple-point statistics. *Phys. Rev. E* **2004**, *70*, 066135. [CrossRef] [PubMed]
35. Berson, A.; Choi, H.-W.; Pharoah, J.G. Determination of the effective gas diffusivity of a porous composite medium from the three-dimensional reconstruction of its microstructure. *Phys. Rev. E* **2011**, *83*, 026310. [CrossRef] [PubMed]
36. Zhang, M.; He, Y.; Ye, G.; Lange, D.A.; van Breugel, K. Computational investigation on mass diffusivity in portland cement paste based on x-ray computed microtomography (µct) image. *Constr. Build. Mater.* **2012**, *27*, 472–481. [CrossRef]
37. Zhang, M.; Xu, K.; He, Y.; Jivkov, A.P. Pore-scale modelling of 3d moisture distribution and critical saturation in cementitious materials. *Constr. Build. Mater.* **2014**, *64*, 222–230. [CrossRef]
38. Zhang, P.; Wittmann, F.H.; Zhao, T.J.; Lehmann, E.H.; Tian, L.; Vontobel, P. Observation and quantification of water penetration into strain hardening cement-based composites (SHCC) with multiple cracks by means of neutron radiography. *Nucl. Instrum. Methods Phys. Res. Sec. A Accel. Spectrom. Detect. Assoc. Equip.* **2010**, *620*, 414–420. [CrossRef]
39. Murison, J.; Moosavi, R.; Schulz, M.; Schillinger, B.; Schröter, M. Neutron tomography as a tool to study immiscible fluids in porous media without chemical dopants. *Energy Fuels* **2015**, *29*, 6271–6276. [CrossRef]

40. Wildenschild, D.; Sheppard, A.P. X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Adv. Water Resour.* **2013**, *51*, 217–246. [CrossRef]
41. Lau, E.V.; Gan, S.; Ng, H.K. Extraction techniques for polycyclic aromatic hydrocarbons in soils. *Int. J. Anal. Chem.* **2010**, *2010*, 9. [CrossRef] [PubMed]
42. Zimmerman, A.J.; Weindorf, D.C. Heavy metal and trace metal analysis in soil by sequential extraction: A review of procedures. *Int. J. Anal. Chem.* **2010**, *2010*. [CrossRef] [PubMed]
43. United States Environmental Protection Agency (EPA). *Preventing Leaks and Spills at Service Stations. A Guide for Facilities*; United States Environmental Protection Agency (EPA): Washington, DC, USA, 2003.
44. Alachua County Environmental Protection Dep artment. *Pollution Prevention. Best Management Practices for Controlling Runoff from Gas Stations*; Alachua County Environmental Protection Department: Gainesville, FL, USA, 2003.
45. Connecticut Department of Energy and Environmental Protection. *Best Management Practices for Fueling Stations*; Connecticut Department of Energy and Environmental Protection: Hartford, CT, USA, 2015.
46. Lucke, T.; Nichols, P.W.B. The pollution removal and stormwater reduction performance of street-side bioretention basins after ten years in operation. *Sci. Total Environ.* **2015**, *536*, 784–792. [CrossRef] [PubMed]
47. Nichols, P.; Lucke, T. Evaluation of the long-term pollution removal performance of established bioretention cells. *Int. J. GEOMATE* **2016**, *11*, 2363–2369. [CrossRef]
48. Hong, E.; Seagren, E.A.; Davis, A.P. Sustainable oil and grease removal from synthetic stormwater runoff using bench-scale bioretention studies. *Water Environ. Res.* **2006**, *78*, 141–155. [CrossRef] [PubMed]
49. Dietz, M.E. Low impact development practices: A review of current research and recommendations for future directions. *Water Air Soil Pollut.* **2007**, *186*, 351–363. [CrossRef]