

**A Rapid Field Method to Estimate the Concentration of  
Sorbing Particulate Amendments in Soil Samples**

by  
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## **Author's Declaration**

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I understand that my thesis may be made electronically available to the public.

## **Abstract**

The immobilization of plumes of contaminants in groundwater via in-situ adsorption is an emerging remediation technology. This technology involves injecting adsorbent particles into the subsurface to form a stationary barrier that intercepts a contaminant plume. As the plume travels through the barrier, the target contaminants can adsorb onto the injected particles and become immobilized. In-situ immobilization has been utilized for the treatment of groundwater contaminated with petroleum hydrocarbons and chlorinated solvents. It has also been applied or proposed for the treatment of a variety of other compounds, including per- and polyfluoroalkyl substances (PFAS), which are emerging groundwater contaminants that have garnered worldwide attention.

There are a wide variety of adsorbents that could be used to form an in-situ barrier, including activated carbon (AC). The ability of an AC barrier to immobilize contaminants partially depends on the concentration and distribution of AC particles. Ideally, the concentration of AC in a barrier would be sufficient to adsorb all target compounds entering the barrier. Additionally, AC particles should be uniformly distributed so that the plume is fully intercepted. A common method used in the field to determine if these two criteria have been met is to visually inspect soil cores taken shortly after an injection event. Although visual inspection can indicate if the distribution of AC particles in the barrier is uniform, this approach is prone to human bias. Moreover, this method cannot quantitatively assess if the AC concentration is sufficient (i.e., falls within the range specified for the barrier design) or if additional injections are required. Alternatively, the concentration of AC in a soil core could be quantitatively determined via total organic carbon (TOC) analysis. However, TOC analysis is time-consuming and generally cannot be performed in the field. Therefore, there is a need for a rapid and simple method to quantify AC in soil samples to provide real-time or near-real-time feedback to the injection team. The objective of this research was to develop such a method. The method was

designed to be rapid (less than 30 min), simple, easily performed in the field, and was envisioned to rely upon a tracer that adsorbs to AC particles. By quantifying the percent of the tracer adsorbed, the concentration of AC in the soil sample could be determined.

The development of the tracer method commenced with screening for a tracer that adsorbs preferentially to AC than to soil (Phase 1). Of the tracers tested, Orange G, which is a hydrophilic dye that can be readily measured using a portable spectrophotometer, did not appreciably adsorb (<10 %) to nine types of sandy soils. To further assess if Orange G could be employed as a tracer, the relationship between the concentration of AC in artificial samples (i.e., soils spiked with known amounts of AC) and the amount of Orange G adsorbed was investigated (Phase 2). Reproducible, linear adsorption trends between these variables were observed for PlumeStop<sup>®</sup> colloidal activated carbon and Calgon WPC powdered activated carbon, which are two AC materials that are widely used in in-situ applications. Finally, the method was validated using samples collected from two AC-soil column studies and soil cores collected from two field sites where AC was injected (Phase 3). The AC concentration in these soil samples was measured based on Orange G adsorption as well as by TOC analysis. For eight of the nine tested samples in which the AC concentrations derived via Orange G adsorption fell within the tracer method limits (i.e., between 0.065 – 0.75 wt. % for PlumeStop<sup>®</sup> or between 0.2 – 1 wt. % for Calgon WPC), the percent difference between the AC concentrations derived via the two methods was below 35 %. This confirms that the tracer analysis has the potential to be a quick and robust method for the quantification of AC in soil samples. While this research focused specifically on AC, the developed approach (i.e., tracer adsorption) and methodologies could potentially be used to quantify other types of adsorbents utilized in in-situ immobilization.

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## List of Abbreviations

Activated Carbon	AC
Cation Exchange Capacity	CEC
Chromophoric Dissolved Organic Matter	CDOM
Colloidal Activated Carbon	CAC
Environmental Isotope Laboratory	EIL
Granular Activated Carbon	GAC
Per- and Polyfluoroalkyl Substances	PFAS
Petroleum Hydrocarbons	PHCs
Point of Zero Charge	pzc
Polyethersulfone	PES
Powdered Activated Carbon	PAC
Soil Organic Matter	SOM
Total Organic Carbon	TOC

# Chapter 1 - Research Motivation

The immobilization of plumes of contaminants in groundwater by in-situ adsorption is an emerging remediation technology [1] [2]. This technology involves injecting adsorbents into the subsurface to form a stationary barrier that intercepts contaminant plumes. As shown in Figure 1.1, as a plume of contaminants in groundwater travels through the barrier, target contaminants adsorb onto the injected particles and become immobilized, while the groundwater passes through the barrier and continues to flow downgradient.

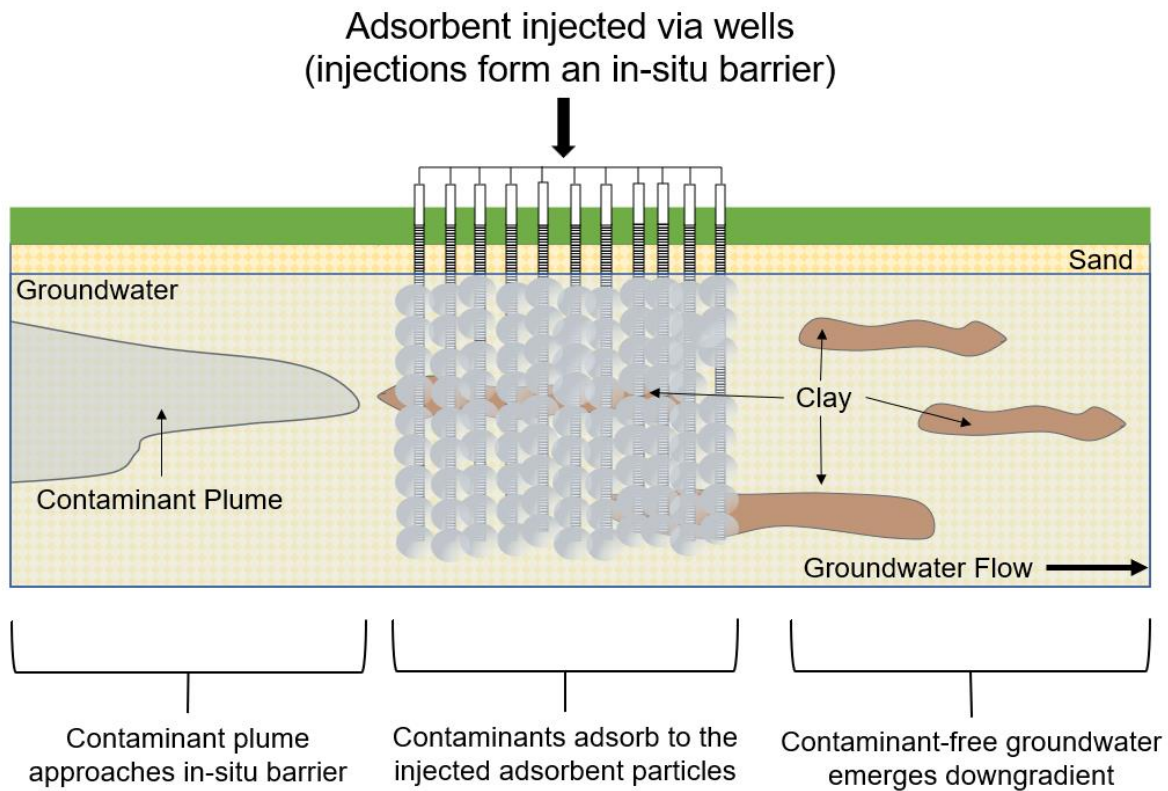


Figure 1.1- An illustration of an in-situ adsorbent barrier, for the immobilization of a plume of contaminants in groundwater

There are many different adsorbents that can be used to form an in-situ barrier, including activated carbon (AC) [2] [3]. In-situ AC barriers have been used for the treatment of petroleum

hydrocarbons and chlorinated solvents, as well as other contaminants, including per- and polyfluoroalkyl substances (PFAS), which are emerging groundwater contaminants that have garnered worldwide attention [2] [4]. Moreover, several commercial products have also been developed that pair AC immobilization with degradation, such as biodegradation or chemical oxidation [5]. As a result, in-situ adsorption by AC may be useful at a wide variety of field sites where a range of remediation strategies, from immobilization to degradation, may be applied.

Commercial AC products used for in-situ barriers are composed of three different particle sizes: granular (GAC), powdered (PAC), or colloidal (CAC) activated carbon. For example, PlumeStop<sup>®</sup> is a commercial product which contains CAC, while BOS-100 and BOS-200 are commercial products which contain GAC and PAC, respectively [5]. Commercial AC products can also contain additional additives, such as zerovalent iron particles (e.g., BOS-100) or nutrients, facultative bacteria, and electron acceptors (e.g., BOS-200) [5]. The size differences between AC types are relatively large: GAC particles have diameters ranging between 500 – 1000  $\mu\text{m}$  [6], while PAC and CAC particles are much smaller, with nominal diameters ranging between 10 – 100  $\mu\text{m}$  and 1 – 2  $\mu\text{m}$ , respectively [2] [6]. The sizes of AC particles impact the injection pressure as well as the type of subsurface where AC barriers can be installed. For example, since CAC particles are very small, they can be injected into the subsurface under low pressures. Generally, CAC particles are injected into high-permeability areas in the subsurface, such as sand layers. This is because CAC particles are normally smaller than the pore spaces between sand grains, and thus, they can travel away from the injection point without the need for fracturing the subsurface via high-pressure injection [2]. Additionally, CAC particles can be mixed with stabilizing polymers, which increase the mobility of CAC particles and allow them to spread across the subsurface, resulting in a more

uniform/homogeneous dispersion of particles (compared to larger particles, such as PAC) across the injection zone [2] [7].

Contrary to CAC, PAC particles will require higher injection pressures. In low-permeability areas (e.g., clay layers), the high injection pressure creates fractures, which are then filled with PAC grains [2]. The fractures also create preferential flow paths through the soil, directing groundwater flow to the PAC grains. In higher-permeability areas (e.g., sand layers), PAC particles have been observed to distribute heterogeneously and concentrate in larger pore spaces [8] [9]. This could be because sand layers can be difficult to fracture compared to areas of lower permeability [5] [10]. Thus, the transport of PAC particles from an injection point depends upon the pore size distribution of the sand layer, and whether there are pore spaces large enough for the PAC grains to enter. For example, one study reported that the pore throat spaces between sand grains can be as low as 10  $\mu\text{m}$ , which could prevent larger PAC particles from entering the pore [2]. It should be noted that while possible, the injection of larger GAC particles can be difficult even at high pressures, due to their larger size [2, 5, 8]. The application of in-situ GAC barriers is more commonly achieved via the formation of an AC-filled trench in the subsurface [8].

The ability of an AC barrier to immobilize target compounds in groundwater partially depends on the concentration and distribution of the AC particles. Ideally, the AC concentration in a barrier should be sufficient for the adsorption of all target compounds entering the barrier. A typical design concentration of CAC particles in-situ could range from 0.1 to 0.5 wt. % (units assumed to be the mass of AC per mass of dry soil) [11]. Note that in the absence of additional information and for the purposes of the development of the tracer method, this range was also assumed to represent a typical design concentration for in-situ barriers containing PAC. Additionally, AC particles should be uniformly distributed so that the plume is fully intercepted. A common method used in the field

to determine if these two criteria have been met is to visually inspect the soil cores taken shortly after an injection event. By examining the cores for the dark colour of carbon against lighter-coloured soil grains, practitioners in the field can estimate whether the distribution of AC could be considered to be uniform. However, this is a qualitative analysis that is prone to human bias. Visual inspection could be especially unreliable if the colour of the soil is also dark [12]. Additionally, visual inspection of soil cores cannot be used to determine if the AC concentration is sufficient (i.e., falls within the range specified by the remediation design) or if additional injections are required. Although the concentration of AC in a soil sample can be quantitatively assessed via total organic carbon (TOC) analysis, this analysis is time-consuming and generally cannot be performed in the field. Therefore, there is a need for a same-day field method to quantify the concentration of AC in soil samples for sites employing the remediation of contaminated groundwater via in-situ AC barriers. Such a method would assist practitioners in determining whether the concentration of AC within a barrier is sufficient or if additional AC injections are required.

The research presented in this thesis describes the development of such a method. The method was envisioned to rely upon a tracer that adsorbs to AC particles. It was hypothesized that by quantifying the percent of the tracer adsorbed, the concentration of AC in the soil sample could be determined. The sequence of steps for the proposed method is presented in Figure 1.2.

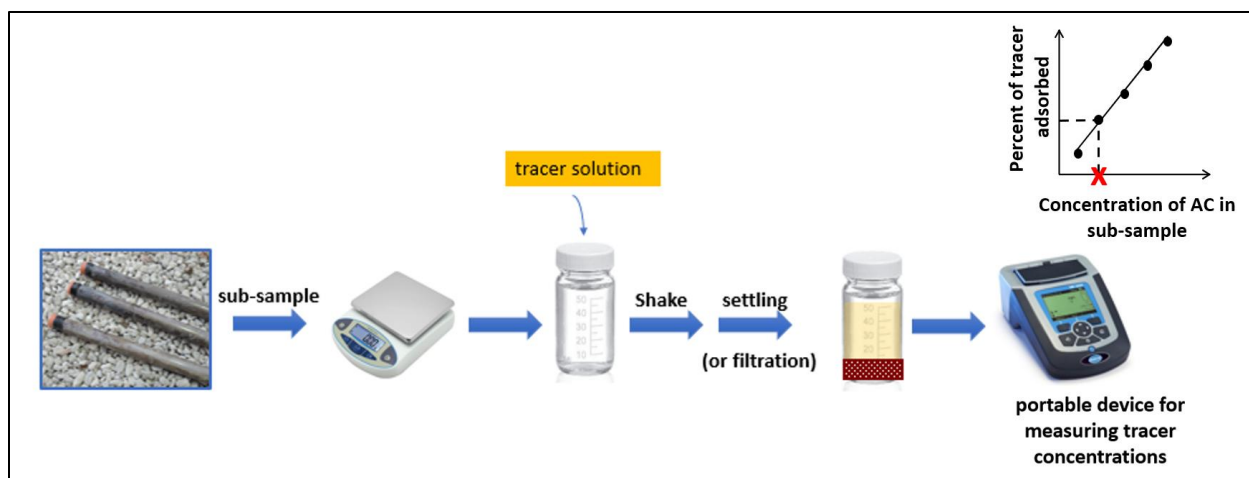


Figure 1.2- Schematic of the proposed method

In the proposed method, soil cores would be taken shortly after AC injection and could be visually inspected. A soil sample would then be taken from a core, weighed, and added to a vial containing a known concentration of a tracer. The vial would be shaken by hand for a short time (e.g., less than 30 min), allowing the tracer in the suspension to adsorb to AC particles. The soil and AC particles would then be separated by filtration, and the amount of tracer remaining in the solution would be quantified using a portable device. The AC concentration in the soil would then be determined using a pre-established relationship between the amount of tracer adsorbed and the concentration of AC in a soil sample.

The following Chapters detail the development and validation of the proposed method. Specifically, Chapter 2 presents the rationale for selecting tracer candidates, the experimental approach and techniques used to test these tracers, and the development and validation of the tracer method using artificial and real soil samples loaded with AC. In Chapter 3, experimental results are presented and discussed. The final chapter, Chapter 4, summarizes key findings and conclusions.

## Chapter 2 - Materials and Methods

The development of the proposed tracer method was divided into three phases, starting with selecting a tracer (Phase 1), followed by developing a relationship between the percent of the tracer adsorbed to AC and the concentration of a varying amount of AC in spiked soil samples (Phase 2), and finally validating the developed tracer method using 1) soil samples from two AC-soil column studies, and 2) soil samples collected from two field sites where AC was injected (Phase 3). The experimental approach and the methods and materials used in each phase are described in the following sections.

### 2.1 Phase 1 - Tracer selection

#### 2.1.1 Selection criteria and tracer candidates

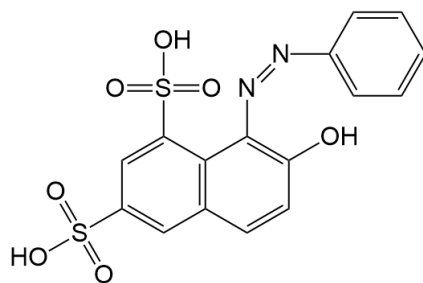
As the proposed method would rely on the adsorption of a tracer to AC, several criteria were considered when selecting tracer candidates. *Firstly*, the tracer must adsorb to AC, and the adsorbed fraction must be easily quantified. Because of this criterion, it was hypothesized that organic dyes could potentially be utilized as tracers, as organic dyes are known to have a strong affinity to AC surfaces [13 – 15]. Additionally, dyes absorb light over the visible spectrum and, thus, can be easily measured by a portable spectrophotometer. *Secondly*, the tracer should adsorb predominately to AC over soil, even when the AC concentration in soil is low (i.e., 0.1 – 0.5 wt. %, as discussed in Chapter 1). This is because the adsorption of the tracer to materials other than AC can lead to an overestimation of the concentration of AC in a soil sample. Because the adsorption of dyes onto surfaces can be strongly influenced by hydrophobic interactions [16], it was hypothesized that hydrophilic or semi-hydrophobic (i.e.,  $\log K_{ow} < 4$ ) organic dyes would

preferentially adsorb to AC over soils. *Finally*, because electrostatic attraction could also be an important mechanism of dye adsorption to soil [16], the dye candidate should have a constant charge across environmentally relevant pH values (i.e., pH = 5 – 9) so that the electrostatic affinity of the tracer to AC and soil does not vary with pH.

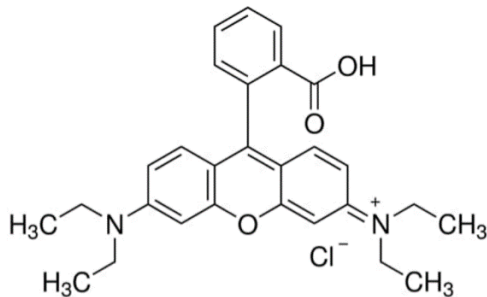
Based on these criteria, three dyes were selected as tracer candidates, namely Orange G, Rhodamine B, and Congo Red. These three selected candidates are hydrophilic or semi-hydrophobic, have a wavelength at which the maximum light absorption occurs ( $\lambda_{max}$ ) in the visible spectrum, and have  $pK_a$  values outside the pH 5 – 9 range. The properties of Orange G, Rhodamine B, and Congo Red are presented in Table 2.1, and their chemical structures are presented in Figure 2.1.

*Table 2.1- The properties of the tracer candidates [14, 17 – 23]*

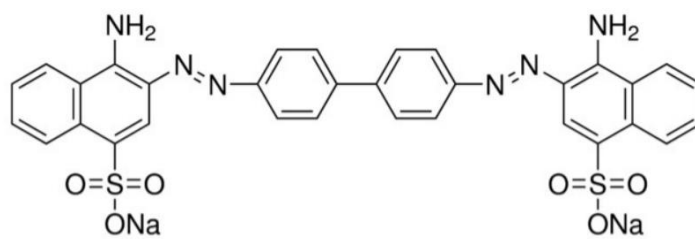
Parameter (unit)	Orange G	Rhodamine B	Congo Red
Log $K_{ow}$ (-)	-4.56	2.28	2.63 – 3.57
$pK_a$ (-)	11.5	3.1 – 3.22	4.1
$\lambda_{max}$ (nm)	480	550	497



Orange G



Rhodamine B



Congo Red

Figure 2.1- The chemical structures of the tracer candidates

### **2.1.2 Adsorption of tracer candidates to soils**

As mentioned above, the tracer utilized in the method should adsorb predominantly to AC over soil. Therefore, a series of experiments were conducted to assess the adsorption of Orange G, Rhodamine B, and Congo Red to a range of soils. The overall objective of this assessment was to determine which dye would adsorb the least to the tested soils. The soils utilized in this work included a commercially available Ottawa sand (denoted herein as Ottawa) and eight aquifer soils. The Ottawa sample consisted of particles with grain sizes ranging between approximately 0.2 and 0.8 mm. The eight aquifer soils were collected from various locations across Canada and the United States and are denoted herein as NFF, USU, LSU, Borden, MAAP, Dover, NIROP, and NCS. Based on the information presented in Xu and Thomson (2008), Jaber et al. (2022), and the additional data provided by Dr. Neil Thomson, the aquifer soils were composed primarily of sandy and silty fractions [24 – 26]. As AC barriers can be installed in aquifers containing both sand and clay media, testing a wider range of soil types would have been beneficial. However, materials other than sandy and silty soils were not available for this study.

All aquifer soils except for NCS were dried at 80 °C and sieved to less than 2 mm [24]. The physical and chemical properties of the sieved fractions were reported in Xu and Thomson [24], and select properties are reproduced in Table 2.2. The NCS soil was air dried before being gently mixed, crushed, and sieved to less than 0.5 mm to remove large particles and aggregates. This smaller diameter was selected following discussions with Dr. Najmeh Jaber, who had previously conducted experiments with NCS. The properties of this soil were characterized by Jaber et al. [25], and select properties are also presented in Table 2.2. Additional information with regard to the physical and chemical properties of NFF were provided by Dr. Neil Thomson [26]. Additional information with regard to the physical and chemical properties of NCS was provided by Dr.

Najmeh Jaber and Maxxam Analytics [27]. Select properties of Ottawa sand were obtained from Sigma Aldrich in 2022 [28].

Table 2.2- Selected physical and chemical properties of soil as presented in Xu and Thomson, 2008 [24] and Jaber et al., 2022 [25], with additional data provided by Thomson, 2021 [26], Maxxam, 2017 [27], and Sigma Aldrich, 2022 [28]

Soil ID	Description	Effective Grain Size ( $d_{10}$ ) (mm)	Soil pH (–)	Cation Exchange Capacity (CEC) (cmol +ve/Kg)	Total Organic Carbon (TOC) <sup>1</sup> (mg/g)
Borden	Fine/medium sand	0.075	8.4	3.5	0.24
Dover <sup>2</sup>	Fine to medium silty sand	0.003	6.1	2.6	0.28
LSU	Sand and silty sand	0.065	8.6	12.8	1.84
USU	Sand and silty sand	0.085	8.8	8.3	0.878
MAAP	Sand	0.15	7.0	0.9	0.77
NIROP	Sand/silty gravels, sand layers	0.040	8.9	17.6	0.315
NFF	Loamy fine sand	0.075	3.7	5.7	3.93
NCS	Silty sand	0.0009	unknown	unknown	8.8 ± 0.8
Ottawa	Silica	unknown	5 – 8	unknown	unknown

<sup>1</sup> For all soils (excluding Ottawa and NCS), TOC values were measured using the sieved soil fraction (<2 mm) where possible. Where not available (i.e., for Borden, Dover, and MAAP), TOC values were obtained from samples taken from the bulk soil. In terms of the NCS data, it is unknown whether the TOC analysis was performed on the sieved (< 1mm) or bulk fraction of the soil utilized in Jaber et al.'s work.

<sup>2</sup> In Xu and Thomson, Dover was denoted as DNTS [24]

The procedures employed to evaluate the adsorption of the tracer candidates to the soil samples were as follows. Two grams of dry soil were placed into a 20 mL glass vial. Subsequently, 20 mL of a tracer solution consisting of 1 mM sodium bicarbonate ( $\text{NaHCO}_3$ , which served as the background electrolyte and a pH buffer) and 25 mg/L of either Orange G, Congo Red, or Rhodamine B was added to the vial. The tracer solutions were prepared using 18.2 M $\Omega$ ·cm MilliQ water (Millipore System). To ensure that the soil mixed well with the tracer solution, the volume of the soil was set to less than 10 % of the volume of the liquid within an experimental vial. As a result, the soil concentration in all vials was 100 g/L (i.e., 2 g of soil in a 20 mL solution). The vial was capped with a phenolic screw-top closure lined with a polyvinyl-faced pulp liner, and then shaken by hand for 20 minutes. The shaking duration was chosen such that this activity would not be considered too extensive to be inconvenient or undesirable for field practitioners. At the same time, the shaking duration should be long enough to allow the tracer to adsorb onto the AC. While 20 minutes was the only shaking duration tested in this work, the shaking duration could be altered as needed.

Following shaking, an aliquot of the suspension was filtered through a 0.2  $\mu\text{m}$  polypropylene or 0.2 – 0.22  $\mu\text{m}$  polyethersulfone (PES) syringe filter. Two types of filters were used because the polypropylene product was discontinued during this work, and an acceptable polypropylene replacement was difficult to obtain. This challenge was compounded by supply chain issues during the COVID-19 pandemic, which made it difficult to obtain supplies in a timely manner. The tracer remaining in the filtrates was measured on a portable DR 1900 HACH spectrophotometer, using a wavelength of 480 nm for Orange G, 550 nm for Rhodamine B, and 497 nm for Congo Red. The filtrates were analyzed directly or after dilution with MilliQ water. The spectrophotometer was calibrated using a series of standard solutions containing 0 – 15 mg/L Orange G, 0 – 12 mg/L

Congo Red, or 0 – 5 mg/L Rhodamine B. Instrument calibration was performed daily, using freshly prepared standard solutions.

In parallel to experimental vials, control vials (i.e., those that contained only the tracer solution but did not contain any soil) were utilized to account for any adsorption of tracers to the vial caps and vial walls. The percent of the tracer removed due to adsorption was calculated as shown below.

$$\% \text{ tracer removed} = 100\% \times \frac{([\text{tracer}]_{\text{control}} - [\text{tracer}]_{\text{experimental}})}{[\text{tracer}]_{\text{control}}} \quad (1)$$

where % *tracer removed* represents the percent of the tracer removed in an experiment vial (%),  $[\text{tracer}]_{\text{control}}$  is the tracer concentration in the control vial (mg/L), and  $[\text{tracer}]_{\text{experimental}}$  is the tracer concentration in the experimental vial (mg/L).

### **2.1.3 Adsorption of Orange G to polymer-free CAC and PAC in soil-free systems**

As will be discussed in Chapter 3, the results of the experiments described in the above section suggested that Orange G would be the most promising tracer candidate, as the adsorption of this dye to the tested soils was less than 10 %. As such, the next step in the development of the tracer method involved examining the adsorption of Orange G to AC. Two CAC materials and one PAC material were utilized in this work. The CAC materials were provided by Regensis, a company specializing in the development and application of remediation technologies for contaminated sites. Regensis offers a product known as PlumeStop<sup>®</sup>, which is a coconut-based CAC material used for in-situ applications [29]. PlumeStop<sup>®</sup> consists of CAC particles (approximately 1 – 2 μm in diameter) suspended in water [6] [7]. The particles are formed via mechanical milling of larger PAC (10 – 100 μm in diameter) or GAC (500 – 1000 μm in diameter) particles in the presence of

water and additional milling additives. Following milling, a polymer is added to prevent CAC particles from aggregating and settling. The polymer increases the mobility of the CAC, allowing the particles to spread further away from the injection point [7]. As the polymer is proprietary, it is unclear how it affects the adsorption capacity of CAC. However, according to Regensis, once CAC is injected into the subsurface, the polymer will eventually be biodegraded and/or washed away, although the expected timeline for this to occur is unknown.

To examine how the presence of the stabilizing polymer in PlumeStop<sup>®</sup> CAC affects the adsorption of Orange G to CAC (and, therefore, affects the tracer method), two materials were obtained from Regensis, namely a polymer-free CAC material and the conventional PlumeStop<sup>®</sup> material. According to Regensis, the PlumeStop<sup>®</sup> material was expected to contain approximately 20 wt. % of CAC (in this instance, wt. % units represent the mass of AC per mass of suspension), but it was noted that the exact concentration of AC could vary slightly between batches. Additionally, the density of the suspension can vary between 1 and 1.2 g/mL [30] [31]. This means that the concentration of CAC in the suspension could range from approximately 200 – 240 g/L.

Due to the potential variations in AC content and suspension density between CAC batches, the carbon contents and densities of both CAC materials were estimated. To this end, approximately 10 mL of each CAC suspension was added to a pre-weighed glass vial. The vial was then weighed before and after drying at 104 °C, and any mass remaining after water evaporation was assumed to be CAC. There could be some error associated with the CAC concentrations derived from this assumption, as additional non-volatile solids or milling/polymer additives could have been present within the stock suspensions. However, this analysis (which was conducted in triplicate) indicated that the CAC concentrations in the utilized materials were consistent with the solid concentration indicated by Regensis.

The density of the CAC suspensions was estimated by measuring the mass of a given volume (0.02 – 1 mL) of each material in triplicate. These analyses indicated that the densities of the polymer-free CAC and the PlumeStop<sup>®</sup> suspensions were  $1.11 \pm 0.03$  g/mL and  $0.92 \pm 0.03$  g/mL, respectively. Note that the latter value is below the expected density range of 1 – 1.2 g/mL. This could be because some CAC in the PlumeStop<sup>®</sup> suspension stuck to pipet tips during the experiment resulting in a possible underestimation of the suspension density. The CAC content and density values were then used to calculate the volume of CAC suspension that should be spiked into an experimental vial to obtain the pre-determined AC concentration, as shown below.

$$V_{CAC\ suspension} = [CAC]_{target} \times V_{vial} \times \left( \frac{1}{(\% \text{ wt AC}/100)} \right) \times \left( \frac{1}{\rho_{CAC\ suspension}} \right) \times 1000 \quad (2)$$

where  $V_{CAC\ suspension}$  is the volume of CAC suspension to be added to a vial to achieve the desired CAC concentration ( $\mu\text{L}$ ),  $[CAC]_{target}$  is the target CAC concentration in an experiment vial (g/L),  $V_{vial}$  is the volume of the liquid within a vial (L), % wt AC is the percent of CAC within the suspensions, on a per weight basis (wt. %),  $\rho_{CAC\ suspension}$  is the density of the CAC suspensions (g/mL), and a factor of 1000 is used to convert volumes from mL to  $\mu\text{L}$ .

The PAC material used in this work was WPC PAC procured from Calgon. Similar to the CAC materials utilized in this work, the WPC PAC was also a coconut-based material [32]. However, unlike PlumeStop<sup>®</sup> or the polymer-free CAC, WPC PAC was a solid powder rather than a liquid suspension. In terms of particle distribution, Calgon estimates that over 99 wt. % of particles will have diameters less than 150  $\mu\text{m}$  and 90 wt. % of particles will have a diameter of less than 45  $\mu\text{m}$  [32]. To spike the solution with PAC, a known mass of powder was weighed out and placed into vials. The exact masses and volumes utilized in experiments are detailed in the following paragraph.

An experimental procedure similar to the one described in Section 2.1.2 was employed to investigate the adsorption of Orange G to AC. Briefly, 20 to 60 mL of a solution containing 25 mg/L of Orange G and a pH buffer of 1 mM NaHCO<sub>3</sub> was also added to a 20, 40, or 70 mL glass vials. The lids of the 20 and 40 mL vials contained a polyvinyl-faced pulp liner, while the lids of the 70 mL glass vials were lined with aluminum foil. Between 10 – 20 mg of PAC or 31 – 52 µL of the polymer-free CAC suspension were added to the vials, such that the concentration of AC was less than 1 g/L (a rationale for this concentration range is provided in the following section).

It should be noted that the PlumeStop<sup>®</sup> CAC was not utilized in this preliminary investigation to avoid potential complications by the polymer to result interpretations. This was because the polymer could compete with Orange G for adsorptive sites on AC and/or affect the analysis of Orange G by spectrophotometry. Additionally, the polymer may absorb light, thereby contributing to the light absorption by a filtrate.

Following the addition of AC to the experiment vials, the vials were then capped and shaken for 20 minutes. Subsequently, an aliquot of the suspension was taken from each vial and filtered. The concentration of Orange G in the filtrate was measured on a DR 1900 HACH spectrophotometer, and the percent of Orange G adsorbed was then calculated based on Equation 1 presented above.

## **2.2 Phase 2 - Development of the relationship between Orange G adsorption and the AC concentration in AC-spiked soils**

As will be discussed in Chapter 3, based on the results of the Phase 1 experiments, Orange G was selected as an acceptable tracer for use in the tracer method. The next step was to examine the adsorption of Orange G in samples containing both AC and soil and determine whether a

relationship could be established between the amount of tracer adsorbed and the concentration of AC in the sample.

As stated in Chapter 1, the design concentration of AC in a barrier may be between 0.1 and 0.5 wt. % [11]. However, the distribution of AC particles may not be uniform across the barrier. Specifically, due to the dispersion of particles upon injection, the AC concentration could be higher near injection points and lower towards the edge of the barrier. As such, AC concentrations above 0.5 wt. % could be present, particularly near injection points. A larger quantity of AC than theoretically required could also be injected in order to provide a factor of safety within the remediation design. Therefore, the tracer method was designed such that it could measure an AC concentration as high as 1 wt. %. Additionally, once the AC suspension is injected into the subsurface, it will spread across the injection zone, and can be diluted with groundwater. As such, it is also possible that AC concentrations below 0.1 wt. % could be found at an injection site. Therefore, the method was developed to measure concentrations below this value. In this study, the lowest CAC concentration that the tracer method could measure was 0.065 wt. %. This lower concentration limit was constrained by the smallest volume (i.e., 20  $\mu$ L) of CAC slurry that could be reproducibly subsampled from the polymer-free CAC and PlumeStop<sup>®</sup> stock suspensions when spiking CAC into the solution or to soil sample. The lowest PAC concentration utilized in experiments was 0.2 wt. %. This value is slightly higher than the target concentration of 0.1 wt. % because PAC concentrations were constrained by the minimum mass (10 mg) of PAC that could be measured on the analytical balance used in this study. Lower CAC and PAC concentrations were also constrained by the largest size of glass vials available for use in this study (i.e., 70 mL).

The above rationale explains why an AC concentration range of up to 1 wt. % was utilized in method development. It also explains why the experiments detailed in the previous section utilized

an AC concentration range of 0 – 1 g/L. As the concentration of soil in subsequent experiments was set as 100 g/L, an AC concentration range of 0 – 1 g/L was required for the mass of AC per mass of soil in experiments to range between 0 – 1 wt. %.

An experimental procedure similar to the one described in Section 2.1.2 was employed to investigate the adsorption of Orange G to AC-spiked soil samples. Briefly, between 2 – 6.7 g of one of the dry soil materials (i.e., NFF, MAAP, Dover, Ottawa, LSU, USU, NCS, or Borden) was added to a 20, 40, or 70 mL glass vial. The vial lids were made of phenolic screw-top closures. The 20 and 40 mL vial lids were lined with a polyvinyl-faced pulp liner, while the 70 mL vial lids were lined with aluminum foil. The soils were spiked with 20 – 92  $\mu$ L of the polymer-free CAC or the PlumeStop<sup>®</sup> suspension, or 10 – 20 mg of PAC, such that the concentration of the AC in the spiked soils was between 0.065 and 1 wt. %. Between 20 and 67 mL of a solution containing 25 – 150 mg/L of Orange G and a pH buffer of 1 mM NaHCO<sub>3</sub> was then added to the vials. In several experiments, the pH buffer utilized was 100 mM formic acid (HCOOH) and 100 mM sodium formate (HCOONa). This pH buffer was chosen to maintain the pH of the solution in a vial in the acidic range, in order to investigate how the solution pH affects Orange G adsorption. Following the addition of a given pH buffer and the Orange G solution, the vials were then capped and shaken for 20 minutes. The pH of the solution was measured using a Fisher Science Education pH meter at 0, 5, and/or 20 minutes. After 20 minutes, an aliquot of the suspension was taken from each vial and filtered. The concentration of Orange G in the filtrate was measured on a DR 1900 HACH spectrophotometer. The percent of Orange G adsorbed, calculated based on Equation 1 presented above, was then used to establish a relationship between the percent of tracer adsorbed and the concentration of AC in a soil sample.

## 2.3 Phase 3 - Method validation

The relationship between the percent of Orange G adsorbed and the concentration of AC in a soil sample developed in Phase 2 was used to calculate the concentration of AC in four validation sample sets. These samples were collected from two soil columns loaded with PlumeStop<sup>®</sup>, as well as from soil cores taken from two field sites. PlumeStop<sup>®</sup> was injected at one of the field sites, while Calgon WPC PAC was injected at the other field site. The AC concentration in these samples was determined using the developed tracer method, and the results were compared with those obtained by a total organic carbon (TOC) analysis. The validation process is illustrated in Figure 2.2, and details regarding validation samples are presented in Table 2.3. As blind samples were employed in the validation study, limited information or context regarding the column experiments or site conditions was made available by the sample providers.

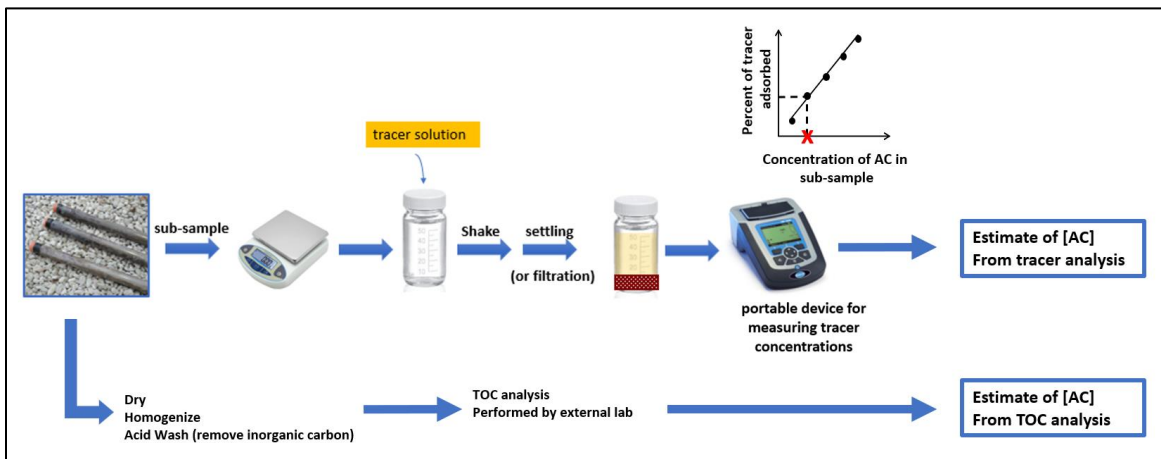


Figure 2.2- An illustration of the procedures utilized in the validation experiments

Table 2.3- An overview of the validation sample sets

Validation Sample Set	Sample Description	Number of samples	Sample Provider	Time between AC injection and sampling	AC Type	Known Contaminants
1	Samples from two column experiments Column 1: contains CAC Column 2: control, no CAC	12 (6 from each column)	APTIM Government Solutions, LLC	3 months	PlumeStop®	PFAS
2	Samples from a column experiment	5	Regenesis	Approximately 3 years	PlumeStop®	PFAS
3	Samples from a field site with PlumeStop® injection	8	Regenesis	Within approximately 1 month	PlumeStop®	Unknown
4	Samples from a field site with PAC injection	11	Dr. Neil Thomson's Research Group, University of Waterloo	Within 48 hours <sup>1</sup>	Calgon WPC PAC	Possible PHCs

<sup>1</sup>Following the collection of the validation sample set 4 cores in May of 2019, the cores were transported to the University of Waterloo, where they were stored at approximately 4 °C for approximately 3 years until they were opened in February of 2022.

### **2.3.1 Validation sample sets 1 and 2**

Validation sample set 1 was provided by APTIM Government Solutions, LLC (subsequently referred to herein as APTIM). The samples were collected from two column experiments conducted by APTIM, which aimed to investigate the transport of various PFAS through a column loaded with PlumeStop<sup>®</sup>. APTIM used two vertical columns (Column 1 and Column 2) in the study. Both columns were packed with sandy soil collected from the aquifer at a PFAS-impacted field site. PlumeStop<sup>®</sup> was injected into Column 1 to simulate an in-situ AC barrier, while Column 2 contained no CAC and served as a control. The PFAS-impacted groundwater collected from the site was passed through both columns over a period of approximately three months. Following the completion of the experiment, APTIM drained and opened the columns, and collected six soil samples from both Column 1 and Column 2. APTIM identified the samples by column name followed by a numerical number from 1 to 6 (e.g., the sample ID Col-2-4 represents sample number 4 from Column 2) and labelled the samples based on the flow direction in the column; sample 1 was collected from the column base (i.e., the inlet), and sample 6 was collected from the column top (i.e., the outlet). The samples were placed on ice and shipped to the University of Waterloo, where they were stored at 4 °C until use.

Validation sample set 2 was provided by Regensis. According to Regensis, the samples were collected from a soil column that had been used in a study investigating the transport of various PFAS through a column loaded with PlumeStop<sup>®</sup>. The column was composed of packed soil and was injected with PlumeStop<sup>®</sup> to simulate an in-situ AC barrier, and water containing PFAS was passed through the column. Following the completion of the study, Regensis drained and opened the column, and collected five soil samples, which were labelled from PS-1 to PS-5. The samples

were placed on ice and shipped to the University of Waterloo, where they were stored at 4 °C until use.

### **2.3.2 Validation sample sets 3 and 4**

Validation sample set 3 was also provided by Regenesis. This sample set contained soil cores taken from a field site after an injection of PlumeStop<sup>®</sup>. Five cores were collected from the site and were identified by a 2-letter code (i.e., SC or CC), a location number (i.e., 3, 3B, 3C, 4, or 5), and a depth in feet below ground surface (e.g., 12 – 13'). The letters SC represent a soil core taken before PlumeStop<sup>®</sup> injection, while CC represents a confirmation core, taken after PlumeStop<sup>®</sup> injection. The cores were provided in foot-long intervals, from 12 – 14', 18 – 20', and 26 – 28'. It was noted by Regenesis that locations 3, 3B, and 3C were close to each other. The presence or concentration of contaminants found within the cores is unknown, as are any additional details regarding the injection process. The SC core was collected on August 9<sup>th</sup>, 2022, and the CC cores were collected on September 12<sup>th</sup>, 2022. Therefore, while the exact date of the PlumeStop<sup>®</sup> injection is unknown, it can be said that the CC cores were taken up to approximately one month after the PlumeStop<sup>®</sup> injection. After collection, the cores were capped, placed on ice, and shipped to the University of Waterloo, where they were stored at 4 °C until use.

Validation sample set 4 was provided by Dr. Neil Thomson's research group at the University of Waterloo. This sample set contained soil cores taken from the University of Waterloo Groundwater Research Facility at Canadian Forces Base Borden, up to 48 hours after an injection of Calgon WPC PAC. As the area has been utilized for previous studies, the soil cores could contain contaminants, such as petroleum hydrocarbons (PHCs), in addition to PAC, although this possibility was noted by Dr. Neil Thomson as being unlikely. Four soil cores were taken from

depths of 1.5' to 15' and were labelled as PAC 1 to PAC 4. The cores were composed of three segments (1.5 – 5', 5 – 10', and 10 – 15'), and all depths were measured in terms of feet below ground surface. The cores were capped and transported to the University of Waterloo, where they were stored at 4 °C for approximately 3 years until use. Additionally, the Borden site is also where the Borden sand used in the previous experiments, as described in Section 2.1.2 and Section 2.2, was collected.

The soil cores from validation sample sets 3 and 4 were stored in acetate core sleeves and sealed with tape and/or plastic caps on each end. The depth below ground surface was marked on each end of the plastic tube. For example, for a core segment between 1.5 – 5', one end of the core would be marked with a T, for top, and 1.5', and the other end marked with B, or bottom, and 5'. To subsample the cores, the tape and caps were removed, and the plastic tubing was split lengthwise. The soil was removed as needed to expose the undisturbed center of the core. A measuring tape was placed alongside the core segment to measure the location of the subsamples from the top of the segment.

The core segments were then visually inspected to identify the presence of PAC (via dark lines of marks within the soil) or CAC (areas of solid black soil). Photos of the segments were also taken. Because the concentration of AC in cores was unknown, a visual inspection was used to qualitatively estimate which core sections may have had relatively high and low AC concentrations, and these qualitative observations were then utilized to collect subsamples across what were indicated to be a range of AC concentrations. Subsamples were taken from the cores with a metal spoon, and placed into 50 mL polypropylene vials which were then stored at 4 °C. The subsamples were composed of soil taken from the center of the core, rather than the edges. This is because the soil at the edge of the core was in contact with the acetate core sleeve, which

was pushed through the subsurface and could collect soil on the inside of the tube across the core depth.

Due to time constraints, it was not possible to analyze all subsamples collected from soil cores. Therefore, the photos of cores taken prior to subsampling were inspected, and several subsamples were selected for the tracer and the TOC analyses. These included subsamples containing small amounts of black colour to completely black soil, thus theoretically covering a wide range of AC concentrations.

### **2.3.3 Quantification of AC in validation samples using the tracer method**

The adsorption of Orange G by validation samples was investigated using a procedure similar to that described in Section 2.2. That is, approximately 2 – 3 g of soil from a validation sample was placed in a vial. Since the validation samples were wet, the moisture content of a validation sample was determined to ensure that the solids concentration in a vial was similar to the concentration used in the Phase 2 experiments (i.e., 100 g/L, or 2 g of dry soil in a 20 mL glass vial). This was performed by placing approximately 4 to 15 g of soil in a pre-weighed aluminum dish, drying it at 104 °C in an oven, and measuring the sample mass before and after drying. The moisture content was then used to calculate the mass of the wet soil that needed to be added to experiment vials to achieve a solids concentration of approximately 100 g/L.

Upon placing the required mass of wet soil into a vial, 20 mL of a solution containing 100 – 150 mg/L of Orange G and 100 mM HCOOH/100 mM HCOONa was added, and the vial was then capped and shaken for 20 minutes. Subsequently, the suspension in the vial was filtered, and the light absorption by the filtrate was measured using a HACH spectrophotometer. The concentration of AC present in each sample was then determined from the percentage of Orange G adsorbed,

using the relationships between Orange G adsorption and the concentration of AC in spiked samples that were developed in Phase 2.

#### **2.3.4 Quantification of AC in validation samples by TOC analysis**

TOC analysis was performed by the Environmental Isotope Laboratory (EIL) at the University of Waterloo. Quantitative TOC analyses on solid samples can be conducted using a variety of methods, including the combustion of a sample at high temperatures to convert the carbon within the sample to CO<sub>2</sub> [33]. The carbon content of a sample can then be quantified using the resulting CO<sub>2</sub> gas and a variety of procedures and equipment, including infrared, flame ionization, or thermal conductivity detectors [33]. The method used by EIL involved converting carbon in a sample into CO<sub>2</sub> by combustion and determining the  $\delta^{13}\text{C}$  in the gas phase via an elemental analyzer and continuous flow isotope ratio mass spectrometer. The uncertainty associated with the analysis was estimated to be  $\pm 2\%$  of the reported carbon content.

Since a sample can contain both organic and inorganic carbon, the inorganic carbon fraction was removed prior to TOC analysis. To this end, a portion of each validation sample was dried at 104 °C, following which approximately 1 to 5 g of the dried soil material was then ground by hand with a pestle and mortar to a fine powder and placed into pre-weighed 40 mL glass vials. The soil samples were washed three times with a solution of 5 – 6 % hydrochloric acid (HCl) over a period of 72 hours. For each wash, the glass vials were placed on a hot plate, which was set to between 30 – 50 °C. The vials were filled to approximately the 2/3 mark with the HCl solution (i.e., approximately 25 mL of solution per 40 mL vial), and the suspension was then stirred with a glass rod. Following stirring, the vials were left on the hot plate for a period of 4 – 6 hours, after which the vials were removed from heat and left overnight to allow the soil particles to settle. After a

settling time of approximately 24 hours, the supernatant liquid was removed from vials, and the process was repeated for the next two washes. The samples were then washed four times with MilliQ water over a period of 96 hours to remove any remaining HCl from the samples. The process for the MilliQ water washes was similar to that utilized for the HCl washes, except that the vials were not heated during washing. Following the seven washes with HCl and MilliQ water, the soils were dried at approximately 45 °C, for a period of approximately 3 – 12 days until no water or moisture was observed within the vial, and the surface of the soil within vials consisted of a cracked and flaked material. Following drying, the weights of the soil samples were again recorded, and the lost mass was calculated. The dried samples were ground by hand with a pestle and mortar to re-homogenize the samples and were then refrigerated at approximately 4 °C until submission to EIL for TOC analysis.

The carbon content obtained from the TOC analyses represents the mass of carbon in a sample per mass of acid-washed soil. As some mass (attributed to inorganic carbon, in addition to potentially other compounds, such as metal oxides) was removed during sample preparation, the AC concentrations were adjusted to represent the mass of carbon in a sample per mass of pre-acid washed soil. Using the recorded masses of soil samples before and after acid washing, the sample masses lost during the acid wash process were calculated. The mass loss of the validation samples from sets 1 and 2 (i.e., the column experiments) ranged from approximately 1 – 3 wt. % (units represent the mass lost during acid wash per mass of original dry soil). The mass loss of the validation set 3 and 4 samples (i.e., the field samples) ranged from 9 – 15 wt. %, with one sample (sample C of validation set 4) having a higher mass loss of approximately 25 wt. %. Using the mass of acid-washed soil utilized in the TOC analyses, the mass of soil prior to the acid wash was

then calculated. This mass was used to adjust the reported TOC values and represent the carbon contents and AC concentrations of the original validation samples.

## Chapter 3 - Results and Discussion

### 3.1 Phase 1 - Tracer selection

#### 3.1.1 Adsorption of tracer candidates to soils

The percent of Orange G, Rhodamine B, and Congo Red removed by adsorption onto Ottawa, NCS, and Borden is presented in Figure 3.1. Under the experimental conditions employed in this study, Orange G did not adsorb appreciably to the tested soils, with the average removal being less than 2 %. In contrast, Congo Red and Rhodamine B had higher adsorption affinity to the tested soils, particularly to NCS. The average removal by NCS was approximately 79 % and 100 % for Rhodamine B and Congo Red, respectively.

The fraction of dye adsorbed to the tested soils appeared to increase with the dye's hydrophobicity. The semi-hydrophobic Congo Red ( $\log K_{ow} = 2.63$  to  $3.57$ ) was adsorbed the most to the tested soils, followed by Rhodamine B ( $\log K_{ow} = 2.28$ ), and then followed by the most hydrophilic compound, Orange G ( $\log K_{ow} = -4.56$ ). This trend is consistent with the hypothesis mentioned in Section 2.1.1, that hydrophilic compounds such as Orange G could potentially be used as a tracer.

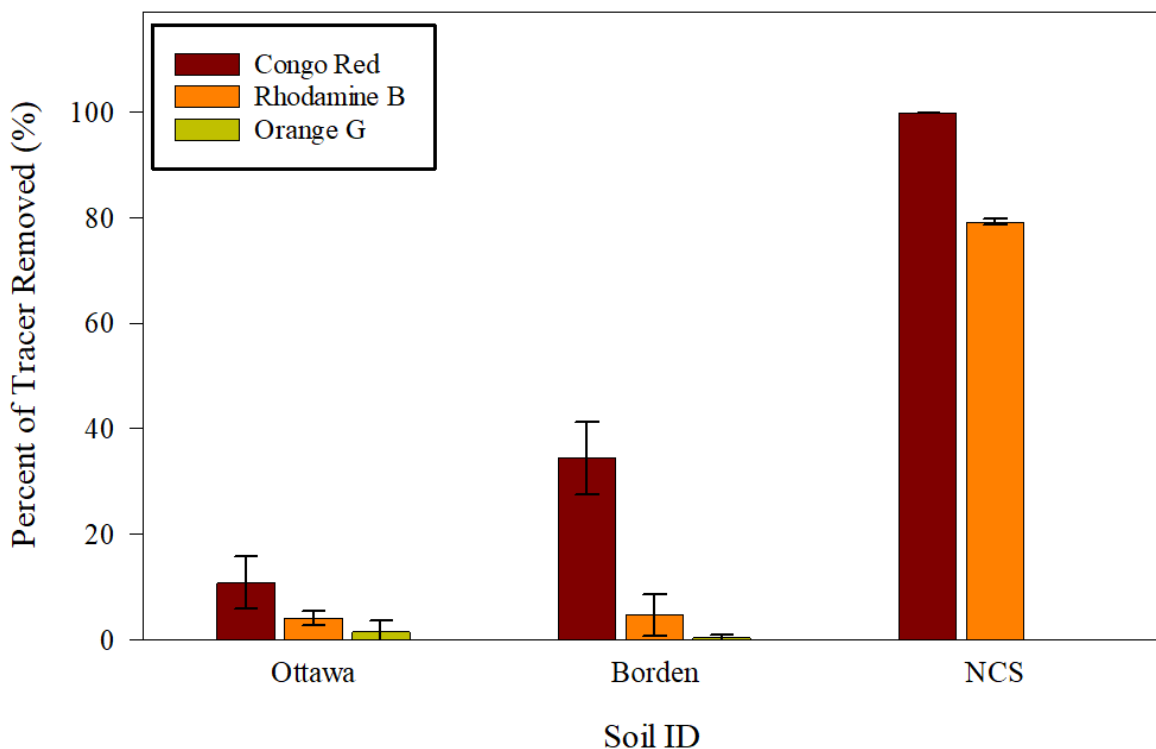


Figure 3.1- The adsorption of the three tracer candidates to Ottawa, Borden, and NCS after 20 minutes. All solutions contained 25 mg/L of a given tracer and 1 mM NaHCO<sub>3</sub>. The concentration of the soil was 100 g/L. Experiments were conducted in triplicate, and the average percent of tracer removed along with one standard deviation (i.e., error bar) are presented.

To further assess the utility of Orange G as a tracer, the adsorption of Orange G to the other six soil samples was investigated. As in the experiments with Ottawa, Borden, and NCS, the average fraction of Orange G removed in the experiments with LSU, USU, MAAP, and NIROP was also less than 2 % (Figure 3.2). Note that due to limited availability, NIROP was utilized in the experiments presented in Figure 3.2, but not in the subsequent experiments.

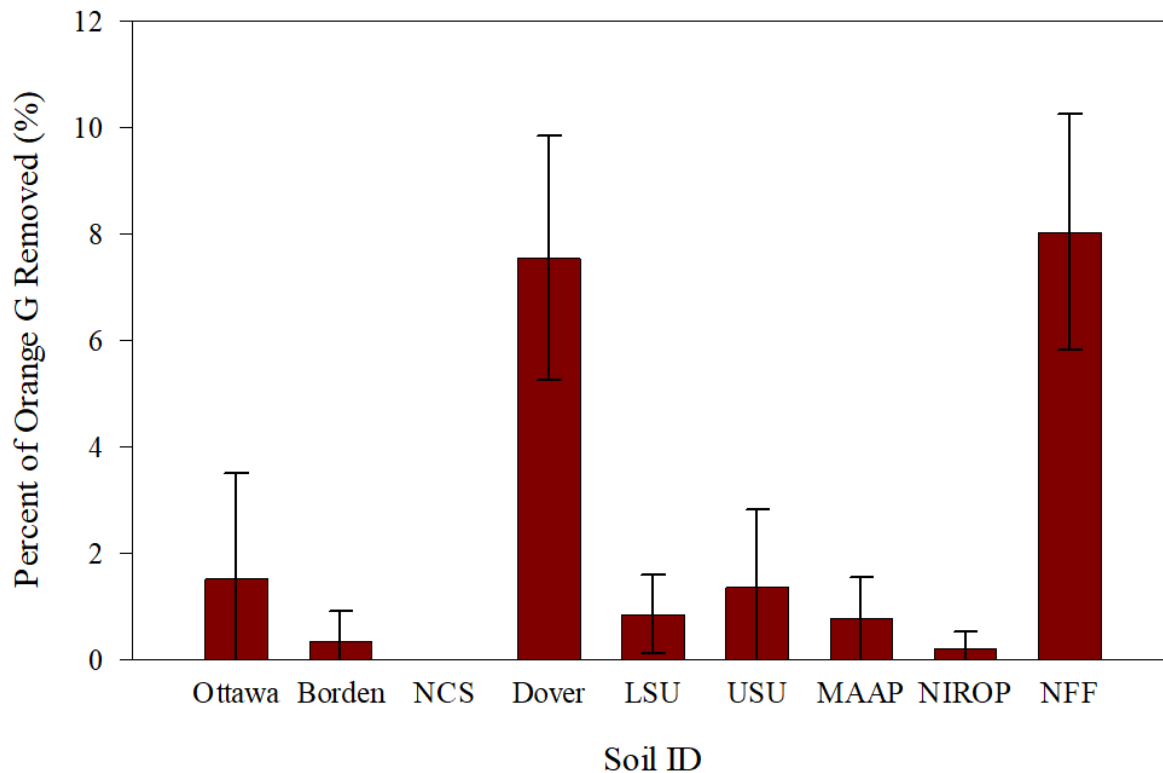


Figure 3.2- The adsorption of Orange G onto nine soils after 20 minutes

All solutions contained 25 mg/L Orange G and 1 mM NaHCO<sub>3</sub>. The concentration of the soil was 100 g/L. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

Of the studied soils, NFF and Dover adsorbed Orange G to the greatest extent (7.5 – 8 %, Figure 3.2). The higher adsorption to NFF compared to other soil types could be due to stronger hydrophobic interactions between the Orange G molecules and soil organic matter (SOM). Compounds can adsorb to both the inorganic and organic components of soil, but the adsorption to organic components is dominant when there is a sufficient level of SOM, i.e., when the fraction of organic carbon ( $f_{oc}$ ) in the soil is > 0.01 to 0.1 wt. % [34]. As seen in Table 2.2, NFF has a comparatively higher total organic carbon (TOC) content of 3.93 mg/g, while the TOC values of the other soils range from 0.24 – 1.84 mg/g (which are equivalent to  $f_{oc}$  values of 0.393 wt. % and 0.024 – 0.184 wt. %, respectively). This means that the higher organic carbon content of NFF

compared to the other soils could have resulted in a higher Orange G adsorption. However, this hypothesis cannot be used to explain the comparatively higher Orange G adsorption to Dover, as the  $f_{oc}$  value of Dover is lower than that of NFF, and similar to that of the other tested soils. For example, the  $f_{oc}$  values of Dover and Borden are 0.028 and 0.024 wt. %, respectively. However, the average adsorption of Orange G to Dover ( $7.5 \pm 2.3$  %) was higher than that of Borden ( $0.33 \pm 0.57$  %). This indicates that there might be additional mechanisms that control the adsorption of Orange G to Dover, although investigating these mechanisms is outside the scope of this research.

For the experiments shown in Figure 3.2, the light absorption by several of the filtrates was larger than the absorption by the initial Orange G solution. For example, the absorption value of one filtrate taken from a vial in the experiment with NCS was 0.527, while the absorption value of the control vial (i.e., the vial that only contained the Orange G solution) was 0.507. These absorption values resulted in a negative dye removal value when Equation 1 was used. An increase in the light absorption by the filtrate could be due to the presence of light-absorbing species leached out from the soil into the experimental solution. Some examples of these species could include chromophoric dissolved organic matter (CDOM) or dissolved iron, both of which can absorb light in the visible spectrum [35], including the wavelength utilized in this work (480 nm). An increase in the light absorption could also be due to light scattering and/or absorption by particles that are smaller than the nominal cut-off size (i.e., 0.2  $\mu\text{m}$ ) of the filter used to separate the soil from the experimental solution [36].

Since the percent of dye removed from a solution cannot be negative, all negative values were set as zero. When applying the tracer method in the field, the potential impact of soil on the light absorption of a solution could be accounted for by using a blank. In this scenario, a soil sample from a core would be split into two fractions. The first fraction would be added to a vial containing

a pH buffer and a dye (vial 1), while the other fraction would be added to a blank vial containing only the pH buffer (vial 2). Both vials would be shaken, and the light absorption by the filtrates would be measured. Light absorption by the filtrate from vial 1 would be attributed to the absorption by the dye and the solutes contributed by soil. For vial 2, light absorption would only be due to the background solutes contributed by soil. Thus, the difference in the absorption values between the two vials could then be attributed to the light absorption by the dye. However, due to the heterogeneous nature of aquifer soils, the composition of two given soil samples (and the resulting compounds and particles that could appear in the filtrate) could differ. As such, absorption correction using a blank could be uncertain and, thus, further investigations into the utility of this approach are warranted.

Overall, given that Orange G did not adsorb appreciably (i.e., < 10 %) to the nine tested soils that have a wide range of physical-chemical properties, this dye was deemed as a promising candidate for the tracer method.

### **3.1.2 Adsorption of Orange G to polymer-free CAC and PAC in soil-free systems**

The results of the experiments conducted with Orange G, PAC, and polymer-free CAC are presented in Figure 3.3. As the concentration of PAC in the suspension increased, as did the percent of Orange G removed. For example, at a PAC concentration of 0.25 g/L, approximately  $57 \pm 4$  % of Orange G was removed from experimental vials. Meanwhile,  $99 \pm 0.2$  % of Orange G was removed from the solution when the PAC concentration was 1 g/L. As discussed in the previous section, the adsorption of Orange G to 100 g/L of tested soils under a similar condition was less than 10 % (Figure 3.2). The removal of Orange G in the solution containing PAC was over 6 – 10 times higher, even when the concentration of PAC was 100 – 400 times lower than the soil

concentration. This indicates that Orange G would preferentially adsorb onto PAC over soil even if the AC concentration is low (i.e., < 1 wt. %).

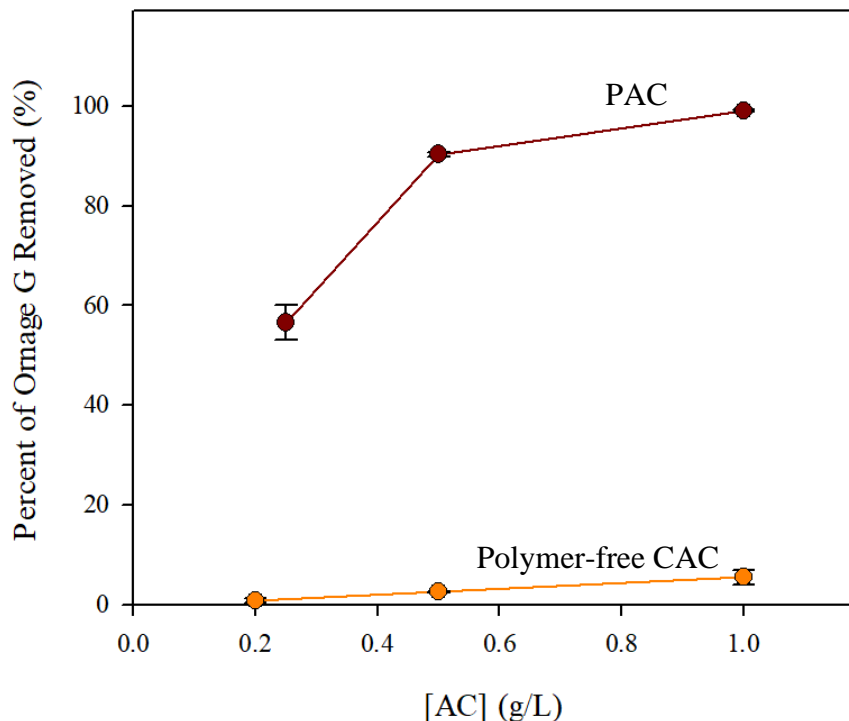


Figure 3.3- The adsorption of Orange G to PAC or polymer-free CAC

All solutions contained 25 mg/L Orange G and 1 mM NaHCO<sub>3</sub>. The concentration of the PAC ranged from 0.25 – 1 g/L, and the polymer-free CAC ranged between 0.2 – 1 g/L. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

Contrary to the results of the PAC experiments, very little adsorption of Orange G was observed to polymer-free CAC. At the highest tested CAC concentration of 1 g/L, only 5.5 ± 1.5 % of Orange G was removed from the experimental solutions. Despite these results, based upon the limited adsorption of Orange G to tested soils (i.e., < 10 %), and the preferential adsorption of the tracer to PAC, Orange G was selected for use as a potential tracer candidate. However, this decision was made pending additional investigation into the adsorption of Orange G to polymer-free CAC-spiked soils. This investigation was completed during Phase 2 of this work (results and discussions are detailed in the following section). As will be discussed in Section 3.2.1, the

adsorption of Orange G to polymer-free CAC over soil was observed to be predominant when the pH of the experimental solution was acidic, confirming that Orange G could be used as a suitable tracer candidate for method development for both the polymer-free CAC and PAC materials.

## **3.2 Phase 2 - Development of the relationship between Orange G adsorption and the AC concentration in AC-spiked soils**

### **3.2.1 Adsorption of Orange G to NFF and Dover spiked with polymer-free CAC**

One of the criteria for the selection of a dye candidate was that the dye should preferentially adsorb to AC over soil. To further examine whether Orange G is able to meet this criterion for polymer-free CAC, the adsorption of this tracer to AC-spiked soil samples was assessed. Initially, Dover and NFF were used for this investigation, since they were the soils that adsorbed Orange G to the greatest extent (Figure 3.2) and, thus, the competition between the soil grains and the AC particles for Orange G is likely the highest. The results of experiments with AC-spiked Dover and NFF were also compared to the results of experiments conducted in the presence of no soil, to investigate the potential cause of the negligible Orange G adsorption observed in Figure 3.3.

As mentioned earlier, between 7.5 % and 8 % of Orange G was removed from the solution by NFF and Dover (i.e., when the concentration of polymer-free CAC was 0 g/L) (Figure 3.2). The Orange G loss fraction increased as the amount of polymer-free CAC added to the soil increased (Figure 3.4). For example, when the concentration of polymer-free CAC was 0.5 g/L (i.e., 0.5 wt. % AC/soil), the loss fractions were 24 % and 94 % in the experiments with Dover and NFF, respectively. Given that the mass of the polymer-free CAC was 200 times smaller than that of the soil, these results indicate that Orange G was preferentially adsorbed by CAC than by NFF or Dover.

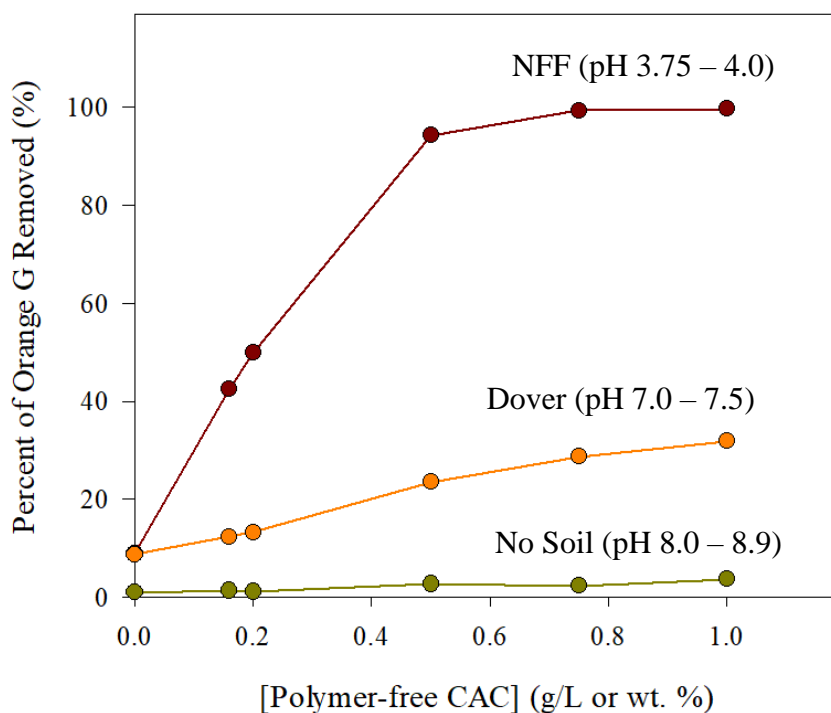


Figure 3.4- The relationship between the percent of Orange G removed and the concentration of the polymer-free CAC in spiked NFF and Dover samples, and in the absence of soil

The final pH was 3.75 – 4.0 in the experiment with NFF, 7.0 – 7.5 in the experiment with Dover, and 8.0 – 8.9 in the experiment with no soil. All solutions contained 25 mg/L Orange G and 1 mM NaHCO<sub>3</sub>. The concentration of the polymer-free CAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of the polymer-free CAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Due to the limited amount of soil available, only one experiment was performed with each soil type.

Overall, as the concentration of polymer-free CAC in a sample increased, so did the amount of Orange G removed from the experimental solution. There also appeared to be a linear relationship between these two variables. This relationship extended up to a polymer-free CAC concentration of 1 g/L in the Dover and soil-free systems, but only up to 0.5 g/L in the NFF system, as above this CAC concentration, more than 99 % of Orange G was removed. Additionally, more Orange G was removed in the NFF system compared to the removal in the Dover system, resulting in the slope of the linear line representing the NFF system being steeper than that of the line representing

the Dover system. Similarly, the removal of Orange G in the spiked soil systems was higher than the removal in the soil-free system, resulting in the slope of the linear line representing the soil-free system being lower than the NFF or Dover systems. Increasing the slope of the line that represents the relationship between the amount of Orange G adsorbed and the concentration of AC in a sample would increase the sensitivity of the tracer method, thereby making it easier to determine AC concentrations. For example, in the Dover system, the adsorption of Orange G when the concentration of polymer-free CAC was 0.16 g/L and 0.2 g/L was 12 and 13 %, respectively (i.e., differed only by 1 %). This means that even small errors in the measurement of Orange G could impact the derived concentration of CAC. By increasing the difference in Orange G adsorption between two AC concentrations, measurement errors would have less of an impact on CAC concentrations. For example, in the NFF system, the adsorption of Orange G when the concentration of polymer-free CAC was 0.16 g/L and 0.2 g/L was 43 and 50 %, respectively (i.e., differed by 7 %, which is larger than the difference seen in the Dover system). Therefore, in general, the steeper the slope of the linear relationship between Orange G adsorption and the concentration of AC in a sample, the more sensitive the method would be.

In addition to differences in the amount of Orange G removed, a major observed difference between the NFF, Dover, and soil-free systems was the final solution pH. Although the experiments were conducted under similar initial conditions, in the vials containing NFF, the final pH of the solution was acidic (pH of 3.75 – 4.0), while the final solution pH of the vials containing Dover were neutral (pH of 7.0 – 7.5), and the final solution pH of the vials containing no soil were basic (8.0 – 8.9). Based on these results, it was hypothesized that the adsorption of Orange G to polymer-free CAC increases as the pH of a solution decreases. This hypothesis is consistent with the findings of a study conducted by Hu et al. [16], in which the authors noted that the pH of a

solution can influence the adsorption of dyes to a surface by impacting the electrostatic interactions between a dye molecule and an adsorbent surface. Generally, electrostatic attraction is expected to exist between oppositely charged molecules and adsorbent surfaces, which could increase adsorption. Conversely, electrostatic repulsion is expected to exist between surfaces and molecules with similar charges, which could decrease adsorption [16]. The higher adsorption of Orange G to CAC at acidic pH was therefore hypothesized to be due to the Orange G molecules and the CAC surface being oppositely charged. Specifically, Orange G should be negatively charged under the experimental condition of this study. As seen in Figure 2.1, Orange G consists of three functional groups that control its charge: two sulfonic acid groups ( $-\text{SO}_3\text{H}$ ) and a phenolic ( $-\text{OH}$ ) group. The  $\text{p}K_a$  of sulfonic acids is less than 1 [37], meaning that  $-\text{SO}_3\text{H}$  will dissociate into  $\text{SO}_3^-$  at  $\text{pH} > 1$ . As such, an Orange G molecule will carry a negative charge of -2 under environmentally relevant pH conditions. The charge of the molecule will become -3 when the solution pH rises above 11.5 (i.e., when  $\text{pH} > \text{p}K_a$  of the phenolic group). Therefore, Orange G will be anionic under both acidic and basic conditions.

The surface charge of CAC in a suspension can also vary significantly with pH. Generally, a surface will be negatively charged above a pH known as a “point of zero charge” (pzc). When the pH of a solution is equal to the pzc, the surface is neutrally charged. Below this value, the surface tends to become positive, as excess hydrogen ions in the solution attach to the surface. Overall, the charge of a surface becomes more positive as pH decreases, meaning that the surface of the polymer-free CAC could have been more positively charged at  $\text{pH} = 3.75 - 4.0$  than at  $\text{pH} = 7.0 - 7.5$ , or  $\text{pH} = 8.0 - 8.9$ . As Orange G is an anionic molecule, this could increase electrostatic attraction between the tracer and the AC, causing Orange G molecules to have a higher affinity for

more positively charged surfaces as pH decreases, resulting in more Orange G adsorption in the NFF system compared to that in the Dover or soil-free systems.

The pzc of the polymer-free CAC used in this work was not measured. It is difficult to make an assumption regarding the pzc of an AC material based on values found in literature, as pzc values have been shown to depend on a variety of factors, including the raw material used to produce AC, the activation and treatment processes, and whether the material is milled to smaller diameters [38] [39]. For example, one study exposed a coconut-based GAC to acid oxidation or a range of high temperatures and examined the impact of each treatment on the material properties. The pzc of the original GAC was found to be 5.4, but under different treatments, it ranged from 3.4 to 11.1 [38]. Another study examined the effect of milling PAC to CAC and found that the pzc of the tested PAC materials, which were created from coal, wood, or coconut, ranged from 5.39 to 11.4 [39]. Following milling to CAC, pzc values tended to decrease and ranged from 4.85 to 10.73 [39]. Based on the pzc range reported in the previous studies, the pzc of the polymer-free CAC might have been between 3.4 – 11.4. However, as stated above, regardless of the pzc value of the polymer-free CAC, the surface of this material will be more positively charged at an acidic pH than at a neutral pH.

Despite the limited adsorption of Orange G to soils (< 10 % at a soils concentration of 100 g/L), and the strong adsorption of Orange G to PAC (> 90 % at a PAC concentration of 0.5 g/L or above), the limited adsorption of Orange G to polymer-free CAC observed in Figure 3.3 had caused concern regarding the suitability of Orange G as a tracer. However, this limited adsorption was attributed to the impact of pH on the system, as the adsorption of Orange G increased as the pH of the system decreased. At an acidic or neutral pH, (i.e., 3.75 – 4 or 7.0 – 7.5), the adsorption of Orange G to polymer-free CAC was observed to be predominant over the adsorption of Orange

G to NFF or Dover. Based on these findings, the limited adsorption of Orange G to polymer-free CAC observed in Figure 3.3 was no longer considered a cause for concern. Therefore, Orange G was confirmed as an acceptable tracer for method development. Additionally, because more Orange G was removed at an acidic pH (i.e., as in the NFF system), it is hypothesized that acidifying the tracer solution could enhance the sensitivity of the tracer method. Therefore, the next step in the method development was to investigate how the system pH can be acidified.

### **3.2.2 Determination of a buffer capable of controlling the solution pH in the acidic regime**

As discussed in the previous section, the pH of the system containing NFF was more acidic than that of the Dover system. Because the tracer solution initially contained 1 mM  $\text{NaHCO}_3$  (pH = 7.5), this result indicates that this pH buffer was not able to resist the pH change caused by NFF. Generally, the pH of the solution is expected to be impacted by the soil type present. Given that the objective of this research is to develop a tracer method that could be used at a range of field sites, and that the adsorption of Orange G by AC is hypothesized to be dependent upon the solution pH, understanding how soils affect the solution pH will help develop a strategy to control the solution pH in the tracer method. The change in the solution pH following the addition of a soil is dependent upon the pH of the soil. As shown in Table 2.2, the pH of NFF (3.7) is lower than that of Dover (6.1). Thus, it is not surprising that the solution containing NFF was more acidic (pH = 3.75 – 4.0) than the solution containing Dover (pH = 7.0 – 7.5). However, the ability of a soil to affect the solution pH is also dependent upon the soil's buffering capacity (i.e., the ability of a soil to resist changes in pH). The buffering capacity of a soil is controlled by a variety of factors,

including the soil composition (e.g., the content of carbonate-, aluminum-, iron-, and silicon-containing minerals) and cation exchange capacity (CEC) [40 – 42].

As noted in Figure 3.4, the final pH of the NFF system (3.75 – 4.0) was similar to the NFF's pH value (3.7). Meanwhile, the solution pH of the Dover system ranged from 7.0 – 7.5, compared to the soil pH of Dover (6.1). This indicates that the buffering capacity of NFF is stronger than that of Dover, and that the NFF system was able to resist changes in pH due to the presence of other solutes in the solution, such as the NaHCO<sub>3</sub> buffer (pH 7.5) or the polymer-free CAC (pH 8 – 10 [30]).

The pH values of the soils utilized in this work ranged from 3.7 to 8.9 (Table 2.2). As discussed in the previous section, it is hypothesized that changes in solution pH can impact the adsorption of Orange G to AC, and therefore to maintain a consistent Orange G adsorption trend the pH of the solution should be kept constant regardless of the soil type present. One method to control the pH of the solution is to increase the concentration of the pH buffer. As noted above, 1 mM NaHCO<sub>3</sub> was insufficient to resist pH change when NFF was present. This result indicates that the concentration of the buffer should be increased. Additionally, the selected pH buffer should maintain the pH of the experimental solution at an acidic value, given that a lower pH could enhance the sensitivity of the method. This means that a compound that could buffer the solution pH in the acidic regime should be selected.

As an alternative to the use of a buffer, the solution could be acidified by the addition of a strong acid, such as hydrochloric acid (HCl) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). However, due to the various buffering capacities of soils, it is likely that varying amounts of a strong acid would be required. Moreover, soils with a high buffering capacity will require high amounts of acid, which is not ideal for safe use in the field. Additionally, it would be more difficult to control the pH of a solution

through acid addition, compared to using a pH buffer. For example, overestimating the amount of strong acid required could result in a very acidic pH solution, thereby dissolving soil components (e.g., carbonate, iron (hydr)oxide, aluminum (hydr)oxide). As previously discussed in Section 3.1.1, species that leach out of soils could absorb light, and impact the light absorption by a filtrate.

Based on the rationales discussed above, a mixture of formic acid (HCOOH) and sodium formate (HCOONa) was selected as a pH buffer, as this mixture could potentially maintain the pH of the experimental solution at 3.75, i.e., the  $pK_a$  value of HCOOH [43]. Additionally, HCOOH does not absorb visible light to an appreciable extent, and thus, will not affect the analysis of Orange G via spectrophotometry [43]. Finally, the concentration of the pH buffer was raised (compared to the 1 mM NaHCO<sub>3</sub> buffer), and a concentration of 100 mM of HCOOH and 100 mM of HCOONa was utilized in this work.

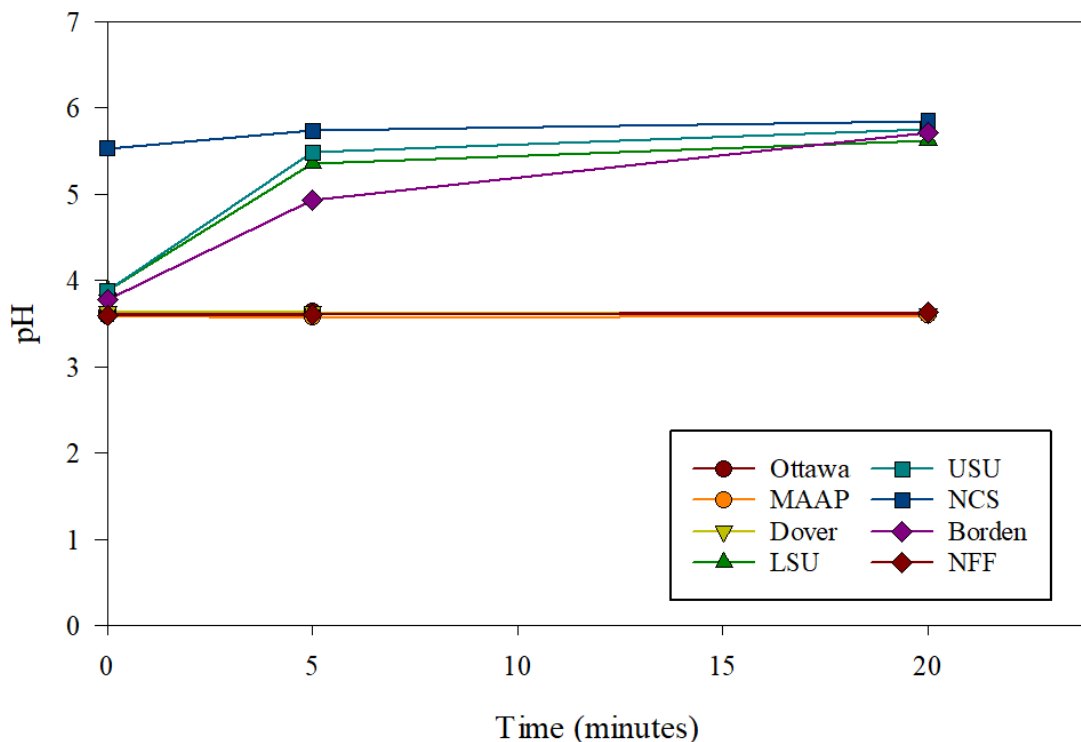


Figure 3.5- The pH-time profile of vials containing eight soils after twenty minutes

All solutions contained 25 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of the soil was 100 g/L. Due to the limited amount of soil available, only one experiment was performed.

The pH-time profiles of the vials containing Orange G, 100 mM HCOOH, 100 mM HCOONa, and eight different soils are presented in Figure 3.5.

In the experiments with NFF, MAAP, Ottawa, and Dover, the solution pH varied between 3.6 and 3.7, i.e., close to the  $pK_a$  value of HCOOH (3.75). As the reported soil pH values of Ottawa, Dover, and MAAP range from 5 – 8, these results indicate that the 100 mM HCOOH/100 mM HCOONa buffer was able to resist the impacts of soil on the solution pH. The soil pH of NFF is 3.7 and is similar to the  $pK_a$  value of HCOOH. Therefore, it is not surprising that the pH of the NFF system remained between 3.6 and 3.7 throughout the experiment.

For the vials containing LSU, USU, or Borden, the pH of the solution at the beginning of the experiment ranged from 3.8 to 3.9. However, the solution pH rose to between 4.9 and 5.8 by the

end of the experiment. As the soil pH values of LSU, USU, and Borden range from 8.4 to 8.8, this indicates that the 100 mM HCOOH/100 mM HCOONa buffer was only able to partially resist the impacts of these soils on the solution pH. In the case of NCS, the solution pH was 5.5 at the onset of the experiment, suggesting that the soil buffering capacity of NCS is high, and this soil was able to strongly counteract the pH buffering effect of the 100 mM HCOOH/100 mM HCOONa buffer.

While further increasing the concentration of HCOOH and HCOONa could help maintain the solution pH of the LSU, USU, Borden, and NCS experiments in the 3.6 – 3.7 range, the high concentrations of these compounds could result in the dissolution of metal species in soil, due to the complexation between metals and the carboxylic acid group (i.e., -COOH), [44] [45]. As previously discussed in Section 3.1.1, dissolved species could affect the analysis of Orange G. Thus, considering the trade-off between maintaining the solution pH in a narrow range and the potential dissolution of soil, it was deemed appropriate to keep the concentrations of HCOOH and HCOONa at 100 mM each. As a result, the pH of the solution containing one of the eight tested soils would fall either in the range of approximately 3.6 – 3.7 or 5 – 6. If the adsorption of Orange G on AC is dependent on pH, as previously hypothesized in Section 3.2.1, then the relationship between the percent of Orange G adsorbed and the concentration of AC in the soil sample would need to be developed for each pH range. As will be discussed in the following section, this turned out to be not the case.

### **3.2.3 Relationship between the percent of Orange G removed and the concentration of polymer-free CAC in spiked soils**

The adsorption of Orange G by eight soil samples spiked with varying quantities of polymer-free CAC is presented in Figure 3.6. For these experiments, the initial concentration of Orange G

was raised from 25 mg/L to 100 mg/L. This is because in the previous experiments wherein the concentration of Orange G was 25 mg/L, almost all Orange G was removed in the systems containing NFF and > 0.5 g/L polymer-free CAC (Figure 3.4). Thus, increasing the initial concentration of Orange G was deemed necessary, as this would enable the quantification of CAC concentrations greater than 0.5 g/L (i.e., 0.5 wt. %).

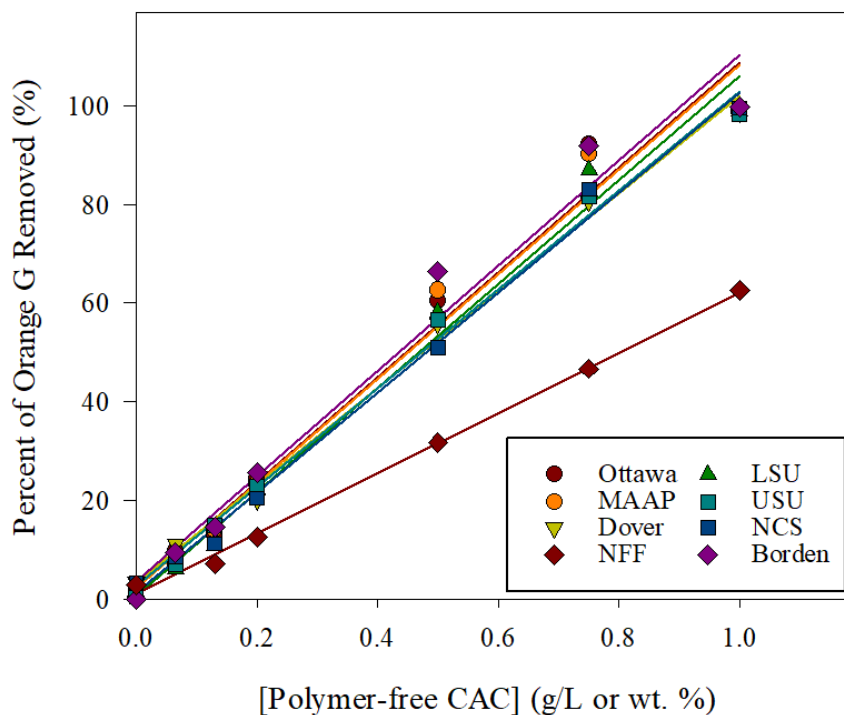


Figure 3.6- The relationship between the percent of Orange G removed and the concentration of the polymer-free CAC in eight spiked soil samples

Linear regressions of the experimental results are shown in the figure. The parameters of these linear regressions are provided in Table 3.1. The pH range of experiments was 3.6 – 6.1. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of the polymer-free CAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of the polymer-free CAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Due to the limited amount of soil available, only one experiment was performed with each soil type.

The adsorption of Orange G to the samples that were not spiked with polymer-free CAC (i.e., samples with a polymer-free CAC concentration of 0 g/L) was less than 4 %, indicating that the

adsorption of Orange G to the eight tested soils was not appreciable. These results are similar to those observed in the previous experiments, in which the adsorption of Orange G to nine tested soils was less than 10 % (Figure 3.2). The previous experiments were conducted in the presence of a solution of 25 mg/L of Orange G and 1 mM of NaHCO<sub>3</sub>, and as such it appears as though the change in the type and concentration of the pH buffer did not impact the adsorption of Orange G to the tested soils.

In the samples spiked with the polymer-free CAC, as the concentration of CAC in a sample increased, as did the percent of Orange G removed from the experimental solution. Due to the apparent relationship between these two variables, a linear regression was fit to the adsorption data obtained from each experiment. The coefficients of each regression equation (i.e., the slope and y-intercept) as well as the coefficient of determination ( $R^2$ ) are presented in Table 3.1 below.

*Table 3.1- The regression parameters and the coefficients of determination for the linear regressions of the results of experiments conducted with polymer-free CAC-spiked soils*

Soil ID	Regression Parameters		
	$y = a*x + b$		
	a	b	$R^2$
Ottawa	106	3	0.977
MAAP	106	2	0.977
Dover	99	3	0.994
LSU	106	1	0.986
USU	100	3	0.994
NCS	102	1	0.993
Borden	107	4	0.972
NFF	61	1	0.997

The coefficients of determination ( $R^2$ ) for these regressions were between 0.972 and 0.997, indicating a strong linear relationship between the removal of Orange G and the concentration of polymer-free CAC in a sample. Additionally, the slopes of all regression lines (with the exception of the NFF system) were similar, and ranged from 99 – 107 (i.e., differed by less than 8 %). The slope of the NFF system was much lower, at a value of 61.

The difference in the regression slopes between the NFF and other soil systems was unexpected. It had been hypothesized in Section 3.2.1 that more Orange G would be adsorbed at lower pH. However, significantly less Orange G was removed in the NFF system (Figure 3.6), even though the pH of this system (3.6 – 3.7) was similar to those of Dover, Ottawa, and MAAP (3.6 – 3.8). Upon discussing these results with the researchers who had previously employed NFF in various experiments, it was learnt that the results obtained with NFF were often inconsistent with the results of the experiments with other soils. However, even if the results of the NFF system were omitted, the similarity in the regression slopes of the other seven soil systems was also unexpected. Overall, the Orange G adsorption was similar across a pH range of 3.6 – 6.1, and therefore appeared to not be in agreement with the stated hypothesis. In order to examine whether the differences in the adsorption of Orange G across the two pH regimes were statistically significant, two-tailed t-tests were conducted on the results of the experiments with MAAP, Dover, Ottawa, LSU, USU, NCS, and Borden. The data collected from these seven soil experiments was combined to generate an average value and standard deviation of the percent of Orange G removed at each tested polymer-free CAC concentration (i.e., from 0.065 to 1 wt. %). The MAAP, Dover, and Ottawa systems were utilized for the low pH range (i.e., 3.6 – 3.8), and the LSU, USU, NCS, and Borden systems were utilized for the high pH range (i.e., 4.8 – 6.1). The results are shown in Figure 3.7.

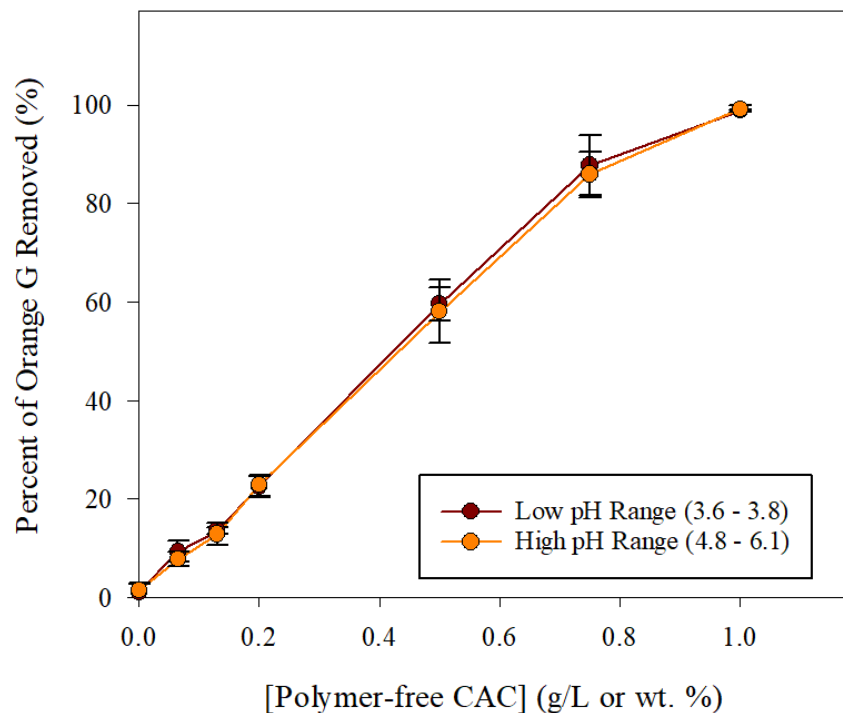


Figure 3.7- The relationship between the percent of Orange G removed and the concentration of the polymer-free CAC in spiked soils, at a low pH range (3.6 – 3.8), and a high pH range (4.8 – 6.1)

All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of the polymer-free CAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of the polymer-free CAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Due to the limited amount of soil available, only one experiment was performed with each soil type. The average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

The t-tests utilized an alpha value (or significance level) of 0.05, or 5 %, which is a commonly used significance level in statistical testing [46]. The results of the analysis showed that the differences between the adsorption of Orange G to polymer-free CAC at each concentration were not statistically significant. This means that the adsorption of Orange G to polymer-free CAC did not increase as pH decreased, which is contrary to the hypothesis that was developed from the preliminary experiments with Dover, NFF, or no soil (Figure 3.4). The results of the experiments conducted with NFF have previously been noted as often being inconsistent with the results of the

experiments conducted with other soils, meaning that the adsorption of Orange G to AC-spiked NFF could have been an anomaly. However, in this case, the results of the Dover and no soil systems would still support the established hypothesis, with regard to the role of pH on Orange G adsorption to polymer-free CAC.

An alternate explanation could be that the experiments presented in Figure 3.4 were conducted under a low ionic strength (1 mM NaHCO<sub>3</sub>), while the experiments presented in Figure 3.6 were conducted in the presence of a 100 mM HCOOH and 100 mM HCOONa buffer, meaning that the ionic strength in these systems was, depending on the solution pH, approximately 100 – 200 times higher than those presented in Figure 3.4. This is an important distinction as, in addition to the solution pH, ionic strength can also impact the adsorption of dyes to a surface [16]. Although a full investigation into the role of ionic strength on Orange G adsorption to AC was considered to be outside the scope of this work, it is understood that the impact of ionic strength on adsorption can vary. Specifically, an increase in ionic strength can increase or decrease the adsorption of a compound, depending on the surface charge of a given adsorbent and the charge of the adsorbate in a system [16]. Therefore, while it is still expected that the surface charge of the polymer-free CAC was more positive at the low pH range of 3.6 – 3.8, it is possible that the effect of this drop in pH was counteracted by the impact of ionic strength on adsorption. This could explain why the differences in the adsorption of Orange G to polymer-free CAC at a pH of 3.6 – 3.8 and a pH of approximately 5 – 6 were not statistically significant.

As stated in Section 2.1.3, the experiments presented thus far were performed with polymer-free CAC, to avoid potential complications by the polymer to result interpretations. However, the commercial product PlumeStop<sup>®</sup> is utilized at field sites, rather than polymer-free CAC. Therefore, the next step was to develop a relationship between Orange G adsorption and the concentration of

PlumeStop<sup>®</sup> in a sample. By comparing the results of the experiments performed with polymer-free CAC and PlumeStop<sup>®</sup>, insight can be gained into the effect of the polymer on Orange G adsorption to CAC.

### 3.2.4 Relationship between the percent of Orange G removed and the concentration of PlumeStop<sup>®</sup> in AC-spiked soils

The adsorption of Orange G to PlumeStop<sup>®</sup> in the presence of seven different soils is presented in Figure 3.8.

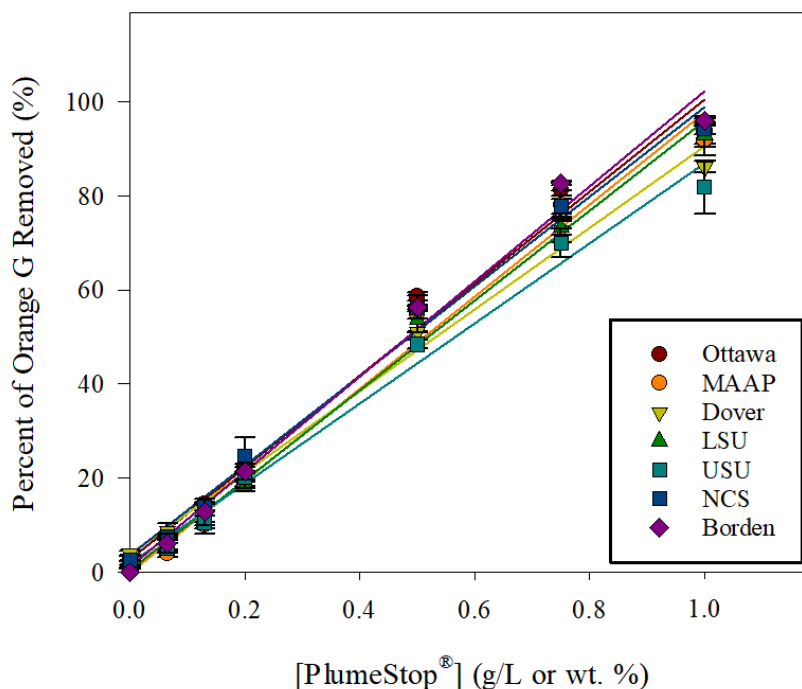


Figure 3.8- The relationship between the percent of Orange G removed and the concentration of the PlumeStop<sup>®</sup> in seven spiked soil samples

Linear regressions of the experimental results are shown in the figure. The parameters of these linear regressions are provided in Table 3.2. The pH range of experiments was 3.6 – 6.0. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of PlumeStop<sup>®</sup> ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of PlumeStop<sup>®</sup> per mass of soil ranged between 0 – 1 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

The results of the experiments conducted with PlumeStop<sup>®</sup> were similar to those previously conducted with polymer-free CAC, in that Orange G did not adsorb appreciably to the tested soils (< 5 %), and the adsorption of Orange G increased with the amount of PlumeStop<sup>®</sup> spiked into a sample. Linear regressions were fit to the adsorption data for the experiments conducted with each of the seven different soils, and the regression parameters are presented in Table 3.2

*Table 3.2- The regression parameters and the coefficients of determination for the linear regressions of the results of experiments conducted with PlumeStop<sup>®</sup>-spiked soils*

Soil ID	Regression Parameters		
	$y = a*x + b$		
	a	b	$R^2$
Ottawa	98	3	0.985
MAAP	98	0	0.987
Dover	87	4	0.992
LSU	95	0	0.994
USU	85	2	0.989
NCS	95	4	0.991
Borden	101	1	0.989

The  $R^2$  values for the regressions were between 0.985 and 0.994, suggesting that there is a strong linear relationship between the removal of Orange G from a solution and the concentration of PlumeStop<sup>®</sup> in a sample. The slopes of each regression also fell within a similar range (i.e., 85 – 101), and differed by less than 18 %. The pH ranges observed in the PlumeStop<sup>®</sup> experiments were also similar to the values observed in the experiments with polymer-free CAC and ranged from 3.6 – 3.7 and 4.5 – 6.0. A statistical analysis was performed on the PlumeStop<sup>®</sup> data, to determine if the differences in Orange G removal at the low and high pH ranges were statistically significant. This analysis was similar to the one performed on the polymer-free CAC data

described in the previous section. Similar to the results of the statistical analysis performed on the polymer-free CAC data, the differences between the adsorption of Orange G to PlumeStop<sup>®</sup> at each CAC concentration were not statistically significant (Figure 3.9).

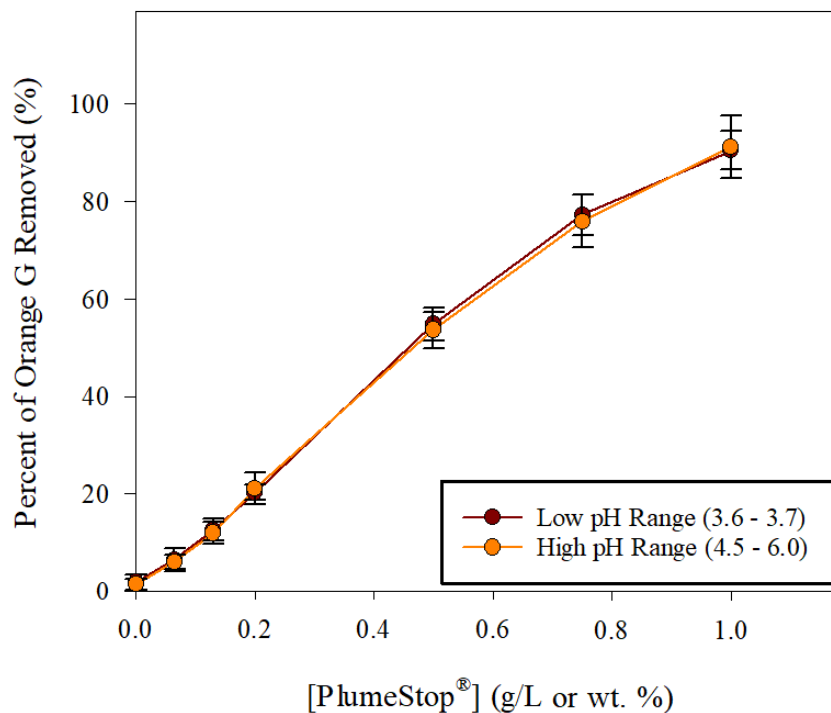


Figure 3.9- The relationship between the percent of Orange G removed and the concentration of the PlumeStop<sup>®</sup> in spiked soils, at a low pH range (3.6 – 3.7), and a high pH range (4.5 – 6.0)

All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of PlumeStop<sup>®</sup> ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of the PlumeStop<sup>®</sup> per mass of soil ranged between 0 – 1 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

The data of all the PlumeStop<sup>®</sup> soil experiments were therefore combined into a single data set, and a similar compilation of the polymer-free CAC data was performed. The results of these compilations are presented in Figure 3.10. The  $R^2$  values for both the PlumeStop<sup>®</sup> and the polymer-free CAC regressions were 0.987 and 0.990 respectively, indicating that for both materials, there

is a strong relationship between the amount of Orange G adsorbed and the concentration of CAC in a sample across a pH range of approximately 3.6 to 6.1.

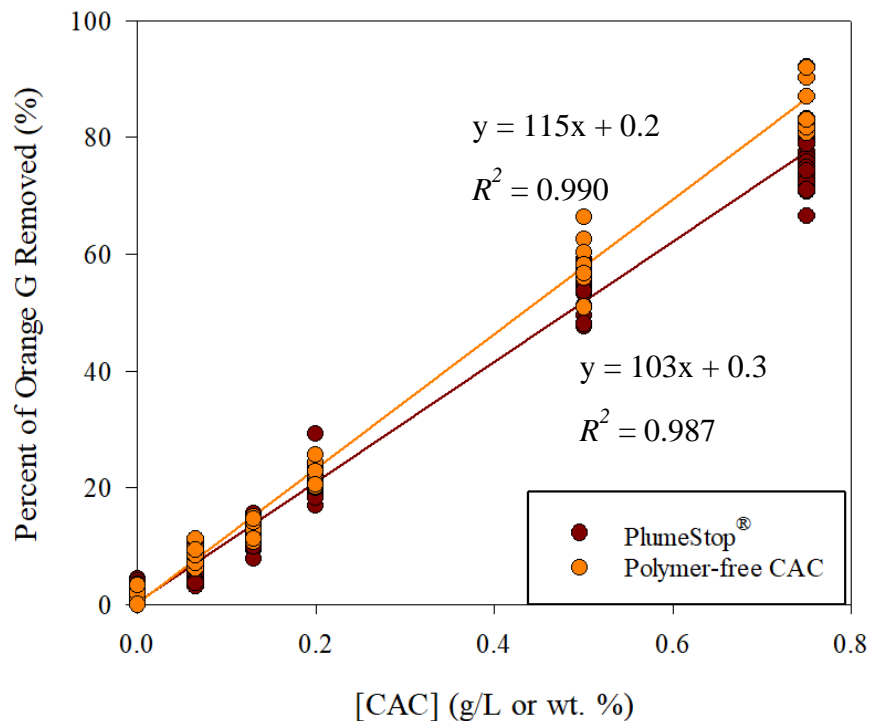


Figure 3.10- The relationship between the percent of Orange G removed and the concentration of polymer-free CAC or PlumeStop® in spiked soils, across all observed pH ranges (3.6 – 6.1)

Regressions have not been forced through the origin. The pH range for the PlumeStop® systems is between 3.6 – 6.0, while the pH range for systems containing polymer-free CAC is between 3.6 – 6.1 All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of CAC ranged between 0 – 0.75 g/L. With the concentration of soil being 100 g/L, the mass of CAC per mass of soil ranged between 0 – 0.75 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments with PlumeStop®-spiked soils were conducted in triplicate, whereas only one trial of the experiments with polymer-free CAC-spiked soils was completed, due to the limited amount of soil available. All data points are provided on the figure.

As the y-intercept values of the two regressions were minor (< 0.3 % of tracer removal) and would round to zero, the regressions were adjusted and forced through the origin. The regression curves with this adjustment are presented in Figure 3.11. The  $R^2$  values of the regressions range from 0.993 to 0.995, indicating that the adjusted regressions represent a strong relationship

between the amount of Orange G adsorbed and the concentration of CAC in a sample across a pH range of approximately 3.6 to 6.1.

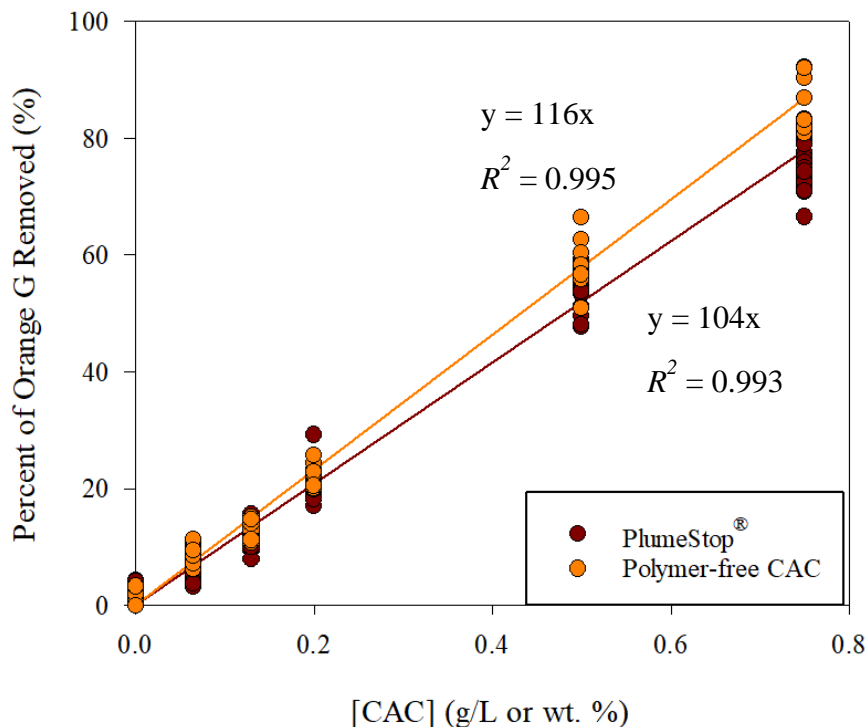


Figure 3.11- The relationship between the percent of Orange G removed and the concentration of polymer-free CAC or PlumeStop® in spiked soils, across all observed pH ranges (3.6 – 6.1), with regressions forced through the origin

The pH range for the PlumeStop® systems is between 3.6 – 6.0, while the pH range for systems containing polymer-free CAC is between 3.6 – 6.1. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of CAC ranged between 0 – 0.75 g/L. With the concentration of soil being 100 g/L, the mass of CAC per mass of soil ranged between 0 – 0.75 wt. %. Thus, these two CAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments with PlumeStop®-spiked soils were conducted in triplicate, whereas only one trial of the experiments with polymer-free CAC-spiked soils was completed, due to the limited amount of soil available. All data points are provided on the figure.

The regression equations presented in Figure 3.10 and Figure 3.11 were compared to ensure that forcing the equations through the origin would have a minimal impact on the regression slope. Using the lowest and highest tested CAC concentrations (0.065 and 0.75 wt. %), the predicted amount of Orange G removed from the system was estimated via the regression equation with a

y-intercept of zero, and with an intercept of greater than zero. The analysis was conducted for both the polymer-free CAC and the PlumeStop<sup>®</sup> regressions. In both cases, the percent error of the Orange G removal predicted by the adjusted regression was less than 3.5 %, compared to the value predicted by the original equation. For example, using the PlumeStop<sup>®</sup> regression derived in Figure 3.10, at an AC concentration of 0.065 wt. %, the predicted percent of Orange G removal would be approximately 7 %. Using the regression derived in Figure 3.11, at a PlumeStop<sup>®</sup> concentration of 0.065 wt. %, the predicted amount of Orange G removal would be approximately 6.8 %. The percent error between these values (i.e., the percent error in the predicted Orange G removal after forcing the regression through the origin) is approximately 2.9 %. This error was considered minimal, and as such, the regressions that were forced through the origin were considered to be acceptable representations of the relationship between the amount of Orange G adsorbed and the concentration of CAC in a sample across a pH range of approximately 3.6 to 6.1.

Overall, less Orange G adsorption was observed in the PlumeStop<sup>®</sup> systems than in the polymer-free CAC systems. This indicates that the polymer present in PlumeStop<sup>®</sup> diminishes the adsorption of Orange G to CAC. This impact appears to be limited, as the slopes of the regression lines for the two CAC materials differ by approximately 11 %. It should be noted, however, that these findings were based on the experiments utilizing two different CAC suspensions. As a result, there could be differences between the materials in addition to the presence of the polymer. As discussed in Section 3.2.1, there are a wide variety of factors which can impact the properties of AC, from the type and origin of the source material utilized in the activation process, to the activation and treatment methods, to the processes used to mill and crush AC particles to CAC sizes [38] [39]. These processes can impact the pzc and other properties of a given material (e.g., the surface functional group of AC, the pore size distribution), which in turn can also affect the

adsorption of Orange G on polymer-free CAC and PlumeStop<sup>®</sup>. However, further investigation into the role of the polymer and these other properties on Orange G adsorption was considered to be outside the scope of this work.

### **3.2.5 Relationship between the percent of Orange G removed and the concentration of PAC in AC-spiked soils**

The results of Orange G adsorption to PAC in the presence of seven different soils are presented in Figure 3.12. For these experiments, the initial concentration of Orange G was raised from 100 mg/L to 150 mg/L. This is because in the previous experiments wherein the concentration of Orange G was 25 mg/L, almost all (i.e., > 90 %) of the Orange G was removed in the systems containing PAC at concentrations of 0.5 g/L or above (Figure 3.3). Thus, increasing the initial concentration of Orange G was deemed necessary, as this would enable the quantification of PAC concentrations greater than 0.5 g/L (i.e., 0.5 wt. %).

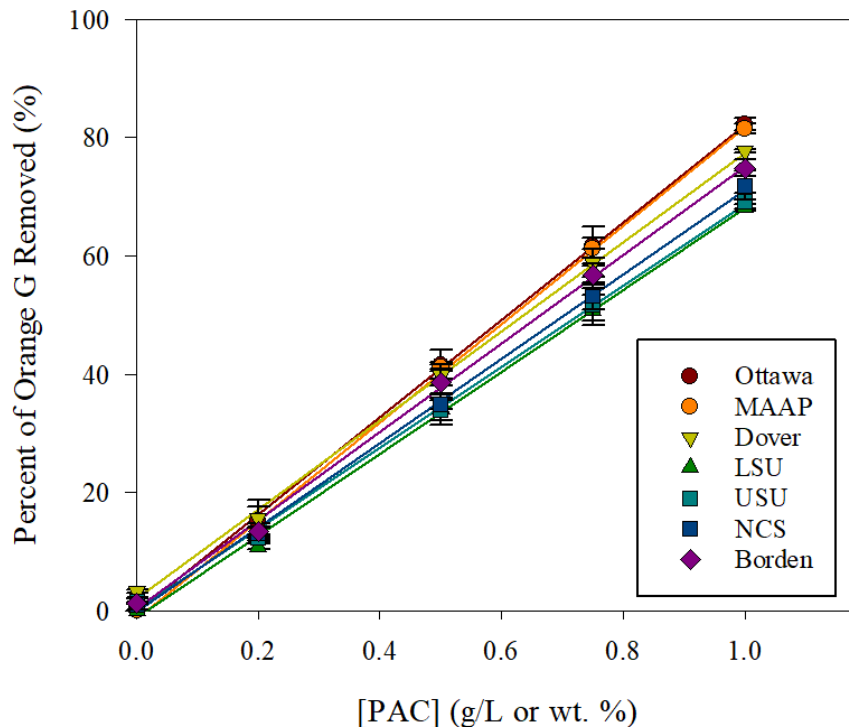


Figure 3.12- The relationship between the percent of Orange G removed and the concentration of the PAC in seven spiked soil samples

Linear regressions of the experimental results are shown in the figure. The parameters of these linear regressions are provided in Table 3.3. The pH range for the experiments is between 3.5 – 6.1. All solutions contained 150 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of PAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of PAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two PAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

It was observed that, similar to the results of the experiments with the CAC materials, the removal of Orange G increased with the concentration of PAC in a sample. Orange G did not adsorb appreciably to the tested soils (< 3 %), and the adsorption of Orange G increased with the amount of PAC spiked into a sample. Linear regressions were fit to the adsorption data for the experiments conducted with each of the seven different soils. The parameters of the linear regressions are presented in Table 3.3.

Table 3.3- The regression parameters and the coefficients of determination for the linear regressions of the results of experiments conducted with PAC-spiked soils

Soil ID	Regression Parameters		
	$y = a*x + b$		
	a	b	$R^2$
Ottawa	82	0	1.00 (Rounded from 0.9996)
MAAP	83	-1	0.998
Dover	75	2	0.999
LSU	69	-1	0.998
USU	69	0	0.998
NCS	71	0	0.999
Borden	75	0	0.998

The y-intercept of the MAAP and LSU regressions were slightly negative, with values of -1 %. As discussed in Section 3.1.1, negative values of Orange G removal are theoretically not possible. However, since the method would be used to quantify PAC concentrations between 0.2 and 1 wt. %, and the Orange G removal values in this range are positive, these negative intercepts were considered acceptable at this stage of method development. The  $R^2$  values for the regressions were between 0.998 and 0.9996, suggesting that there is a strong linear relationship between the removal of Orange G from a solution and the concentration of PAC in a sample.

The pH ranges observed in the PAC experiments were similar to the values observed in the experiments with polymer-free CAC and PlumeStop<sup>®</sup> and ranged from 3.5 – 3.7 and 4.7 – 6.1. A statistical analysis was performed on the PAC data, similar to the one performed on the polymer-free CAC and PlumeStop<sup>®</sup> data, described in Section 3.2.3 and 3.2.4. To perform the statistical

analysis, the data collected from the seven soil experiments was combined, to generate an average value and standard deviation of the percent of Orange G removed at each tested PAC concentration, from 0.2 to 1 wt. %. The MAAP, Dover, and Ottawa systems were utilized for the low pH range (i.e., 3.5 – 3.7), and the LSU, USU, NCS, and Borden systems were utilized for the high pH range (i.e., 4.7 – 6.1). These results are shown in Figure 3.13.

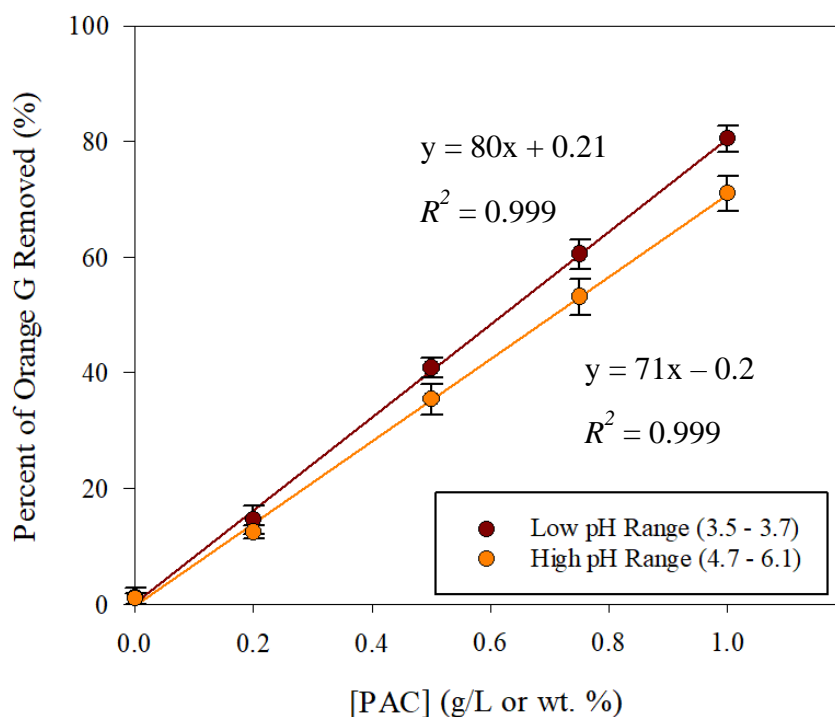


Figure 3.13- The relationship between the percent of Orange G removed and the concentration of the PAC in spiked soils, at a low pH range (3.5 – 3.7), and a high pH range (4.7 – 6.1)

Regressions have not been forced through the origin. All solutions contained 150 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of PAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of PAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two PAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments were conducted in triplicate, and the average percent of Orange G removed along with one standard deviation (i.e., error bar) are presented.

The differences between the adsorption of Orange G to PAC at the low and high pH ranges were determined to be statistically significant, across PAC concentrations of 0.2 to 1 wt. %. This indicates that, unlike in the experiments with the polymer-free CAC or PlumeStop<sup>®</sup> materials, there

is an influence of pH on the adsorption of Orange G to PAC. The adsorption was higher in the systems with a low solution pH (MAAP, Ottawa, and Dover, pH of 3.5 – 3.7) than in the systems with a higher solution pH (LSU, USU, Borden, or NCS, pH of 4.7 – 6.1).

These results are consistent with the hypothesis originally proposed in Section 3.2.1, that as the pH of a system decreases, the adsorption of anionic Orange G will increase. This hypothesis was contrary to the results of the experiments with PlumeStop<sup>®</sup> and polymer-free CAC. This was attributed to the varying effects that pH and ionic strength can have on adsorption [16]. For the polymer-free CAC and PlumeStop<sup>®</sup> systems, it was hypothesized that the impact of ionic strength on adsorption could have counteracted that of pH, causing the variation in the adsorption of Orange G across the pH range of 3.6 – 6.1 to not be statistically significant. As previously stated in Section 3.2.3, an increase in ionic strength can increase or decrease the adsorption of an anionic compound like Orange G, depending on the surface charge of a given adsorbent [16]. This is important to note as the surface charge of a material is impacted both by the pH of a system, and the pzc of the material itself. As the observed pH ranges in experiments with all three AC materials were similar (approximately 3.5 – 6.1), it was hypothesized that the pzc of the PAC utilized in experiments was different from the pzc of the two CAC materials (polymer-free CAC and PlumeStop<sup>®</sup>), and therefore the surface charges of the PAC and CAC across the pH range of 3.5 to 6.1 could have differed, leading to varying impacts of ionic strength on the adsorption of Orange G. However, without knowing the pzc of the materials, it is difficult to determine the effects of ionic strength across the pH range in each system.

Given that the difference in the adsorption of Orange G at the low and high pH range was statistically significant, the data was not combined into a single regression line describing the relationship between the percentage of Orange G removed and the PAC concentration in the soil

samples. Instead, the regressions were left as two separate trends, one for each pH range (Figure 3.14). Additionally, similar to the adjustments made to the final polymer-free CAC and PlumeStop<sup>®</sup> regressions, (Figure 3.11), the regressions developed for the PAC system were adjusted, and forced through the origin of the plot. The results of these adjustments are presented in Figure 3.14. The  $R^2$  value of these regressions were 0.997 and 0.998, indicating a strong relationship across the pH ranges of 3.5 – 3.7, and 4.7 – 6.1, respectively. The predicted removal of Orange G in both the original and adjusted regression was calculated for each pH range, at the lowest and highest PAC concentrations of 0.2 and 1 wt. %. The percent error of the adjusted regressions was less than 1.5 %, and as this error was considered minimal, the regressions that were forced through the origin were considered to be acceptable representations of the relationship between the amount of Orange G adsorbed and the concentration of PAC in a sample.

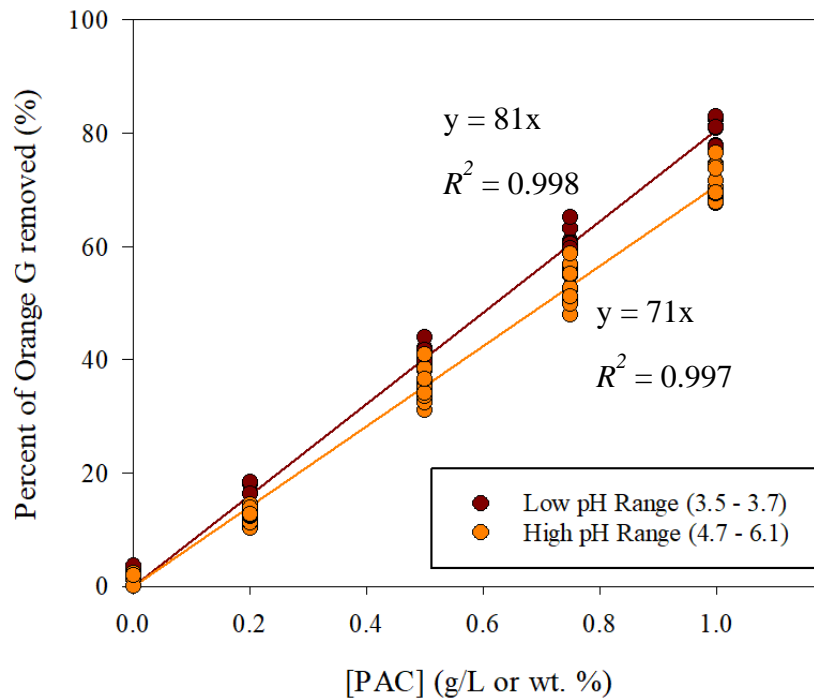


Figure 3.14- The relationship between the percent of Orange G removed and the concentration of PAC in spiked soils, across the observed low (pH 3.5 – 3.7) and high (pH 4.7 – 6.1) pH ranges, with regressions forced through the origin. All solutions contained 150 mg/L Orange G, 100 mM HCOOH, and 100 mM HCOONa. The concentration of PAC ranged between 0 – 1 g/L. With the concentration of soil being 100 g/L, the mass of PAC per mass of soil ranged between 0 – 1 wt. %. Thus, these two PAC concentrations (i.e., g/L and wt. %) can be presented on the same x-axis. Experiments were conducted in triplicate, and all data points are provided on the figure.

To utilize one of the developed regressions in the field, the pH of the solution within an experimental vial containing a soil core sample could be measured following shaking. Based on the resulting value the appropriate regression could be selected to estimate the concentration of PAC within the sample. This process was used to select a linear regression for validation sample set 4, and the regression was then used to back-calculate the concentration of PAC in this validation sample set (Section 3.3.4).

### 3.2.6 Visual appearance of experiment vials as a basis for estimating AC concentrations

During the experiments with PAC, polymer-free CAC, and PlumeStop<sup>®</sup>, it was noticed that the visual appearance of the test suspension could provide a qualitative/semi-quantitative estimate of the AC concentration in a soil sample. First, it was observed that the experiment vials containing the Orange G solution, soil, and one of the three AC materials were often black in colour, compared to the vials containing no AC, which often appeared orange in colour (Figure 3.15 to Figure 3.17). The exception to this visual appearance was the samples that contained Dover or NCS. The suspensions containing AC and these two soils tended to have a brown colour, and qualitative indications of the presence of AC in these vials were less distinct, especially when the AC concentration was less than 0.5 g/L (Figure 3.18 to Figure 3.20).

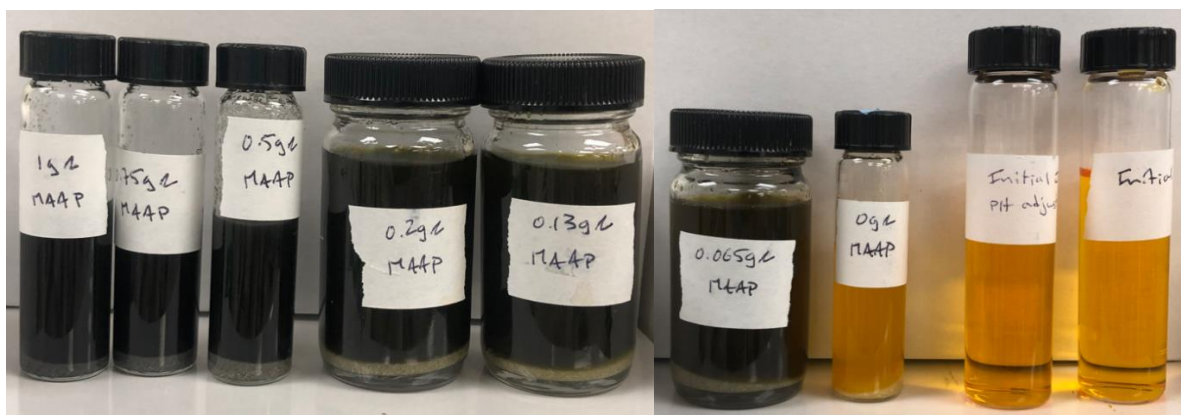


Figure 3.15- An image of the vials used in an experiment with polymer-free CAC-spiked MAAP

All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of MAAP spiked with polymer-free CAC. The concentration of polymer-free CAC ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., MAAP) and the concentration of polymer-free CAC (e.g., on the far left, 1 g/L). The pH of the MAAP system in experiments with polymer-free CAC was between 3.6 – 3.8. The first 7 samples from the left contained MAAP, while the two vials on the right were control vials, and as such, did not contain soil. From left to right: samples with 1, 0.75, 0.5, 0.2, 0.13, 0.065, and 0 g/L of polymer-free CAC, and two control vials.



*Figure 3.16- An image of the vials used in an experiment with PlumeStop<sup>®</sup>-spiked Borden. All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of Borden spiked with PlumeStop<sup>®</sup>. The concentration of PlumeStop<sup>®</sup> ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., Borden) and the concentration of PlumeStop<sup>®</sup> (e.g., on the far left, 1 g/L). The pH of the Borden systems in experiments with PlumeStop<sup>®</sup> was between 4.5 – 5.9. From left to right: samples with 1, 0.75, 0.5, 0.2, 0.13, 0.065, and 0 g/L of PlumeStop<sup>®</sup>.*



*Figure 3.17- An image of the vials used in an experiment with PAC-spiked Ottawa*

*All vials contained 150 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of Ottawa spiked with PAC. The concentration of PAC ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., Ottawa), as well as the concentration of PAC (e.g., on the far left, 1 g/L). The pH of the Ottawa systems in experiments with PAC was between 3.5 – 3.7. The first 5 samples from the left contained Ottawa, while the vial on the right was a control vial, and as such did not contain soil. From left to right: samples with 1, 0.75, 0.5, 0.2, and 0 g/L of PAC, and a control vial.*



Figure 3.18- An image of the vials used in an experiment with polymer-free CAC-spiked Dover

All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of Dover spiked with polymer-free CAC. The concentration of polymer-free CAC ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., Dover) and the concentration of polymer-free CAC (e.g., on the far left, 1 g/L). The pH of the Dover system in experiments with polymer-free CAC was between 3.6 – 3.7. The first 6 samples from the left contained Dover, while the vial on the right was a control vial, and as such did not contain soil. From left to right: samples with 1, 0.75, 0.5, 0.2, 0.13, and 0 g/L of polymer-free CAC, and a control vial.



Figure 3.19- An image of the vials used in an experiment with PlumeStop®-spiked NCS

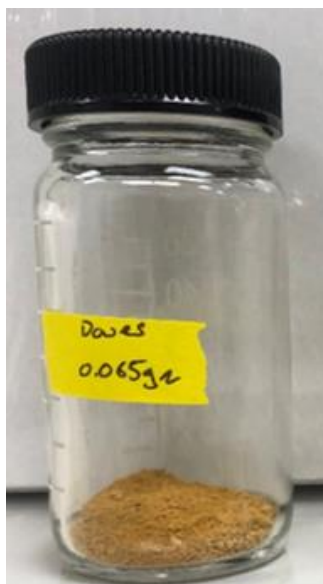
All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of NCS spiked with PlumeStop®. The concentration of PlumeStop® ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., NCS) and the concentration of PlumeStop® (e.g., on the far left, 1 g/L). The pH of the NCS systems in experiments with PlumeStop® was between 5.6 – 6.0. From left to right: samples with 1, 0.75, 0.5, 0.2, 0.13, 0.065, and 0 g/L of PlumeStop®.



Figure 3.20- An image of the vials used in an experiment with PAC-spiked Dover

All vials contained 150 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of Dover spiked with PAC. The concentration of PAC ranged between 0 – 1 g/L. The vials were labelled with the soil type present (i.e., Dover) and the concentration of PAC (e.g., on the far left, 1 g/L). The pH of the Dover systems in experiments with PAC was approximately 3.6. From left to right: samples with 1, 0.75, 0.5, 0.2, and 0 g/L of PAC.

The brown colour of the suspension in the experiments with Dover and NCS could be attributable to the presence of fine particles, as well as the colour of Dover. As shown in Table 2.2, the reported effective grain size ( $d_{10} = 0.003$  mm) of Dover is 20 – 50 times lower than that of the other tested soils ( $d_{10} = 0.065 - 0.15$  mm). Likewise, the reported effective grain size ( $d_{10} = 0.0009$  mm) value of the original NCS soil (i.e., prior to crushing) was approximately 70 – 170 times lower than that of the other tested soils. As not all the fines had been settled when the photos were taken, the colour of the fines could have masked the black colour of the AC particles. Additionally, Dover has a strong orange colour, similar to that of the Orange G solution (Figure 3.21), which could be further masking the black colour of the AC particles.



*Figure 3.21- An image of a vial containing Dover*

It was also observed that in the experiments with 1 g/L polymer-free CAC, nearly all Orange G was removed from the solution, resulting in a clear, colourless filtrate (Figure 3.22). As such, a colourless filtrate would indicate that the polymer-free CAC concentration in a sample is equal to or greater than 1 wt. %.

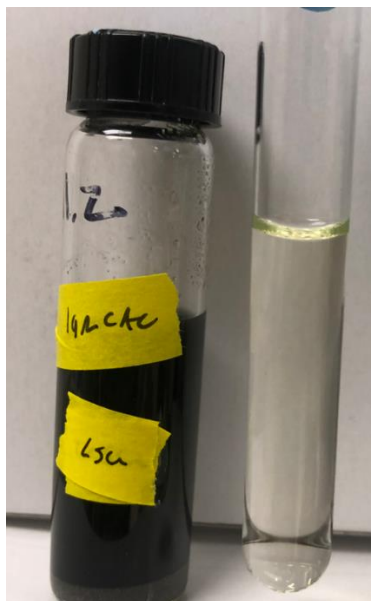


Figure 3.22- An image of a vial used in an experiment with polymer-free CAC-spiked LSU (left), and the colourless filtrate of the suspension (right)

The vial contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of LSU spiked with polymer-free CAC. The concentration of polymer-free CAC in the vial was 1 g/L. The vial was labelled with the soil type present (i.e., LSU) and the concentration of polymer-free CAC. The pH of the LSU systems in experiments with polymer-free CAC was approximately 5.3 – 6.0.

In the vials containing 1 g/L of PlumeStop<sup>®</sup>, Orange G was not completely removed at the end of the experiment and so the filtrates of these suspensions were not colourless, as shown in Figure 3.23. These results mean that if the Orange G were to be completely removed from an experiment vial (i.e., if a colourless filtrate were to be observed), then the AC concentration in a sample containing PlumeStop<sup>®</sup> would be greater than 1 wt. %. Therefore, the complete removal of Orange G from a system containing polymer-free CAC or PlumeStop<sup>®</sup> would indicate AC concentrations above the tested range, i.e., greater than 1 wt. %. This observation could also be applied to the PAC systems, in which approximately  $71 \pm 3.0$  % (pH 4.7 – 6.1) and  $80 \pm 2.2$  % (pH 3.5 – 3.7) of Orange G was removed from experimental vials containing soil samples with a PAC concentration of 1 wt. %. If Orange G were to be completely removed from a suspension containing PAC, the filtrate of the suspension would be clear, indicating a PAC concentration of > 1 wt. %.

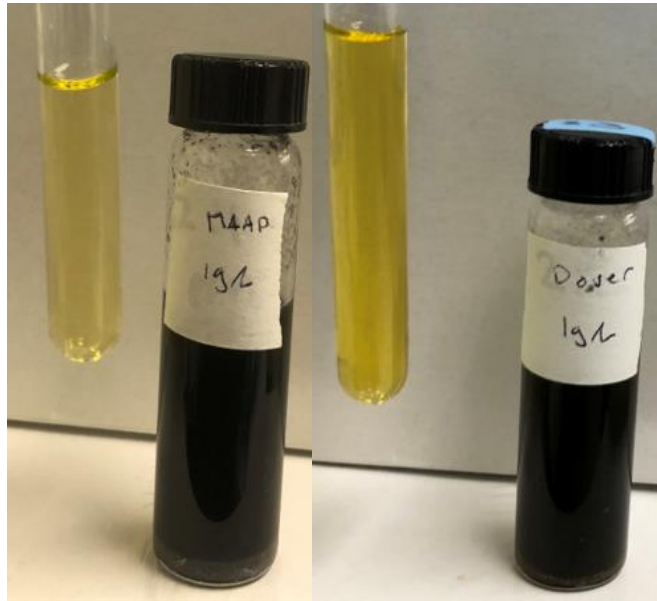


Figure 3.23- An image of vials used in an experiment with PlumeStop<sup>®</sup>-spiked MAAP (left), and PlumeStop<sup>®</sup>-spiked Dover (right)

The filtrates of each suspension are shown to the left of each vial. The vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of MAAP or Dover, spiked with PlumeStop<sup>®</sup>. The PlumeStop<sup>®</sup> concentration was 1 g/L. The vials were labelled with the soil type present (i.e., MAAP or Dover) and the concentration of PlumeStop<sup>®</sup>. The pH of the MAAP and Dover systems in experiments with PlumeStop<sup>®</sup> was 3.6 – 3.7.

To summarize, there are several visual observations during the tracer analysis that can provide indications regarding the presence and/or the concentration of AC in a sample. These observations can be made by inspecting the colour of a suspension within an experimental vial, or the colour of the filtered solution. A black suspension indicates the presence of AC in a sample, while an orange suspension indicates that little to no AC is present. Additionally, a colourless filtrate (i.e., a filtrate in which all Orange G has been removed from solution), indicates that the concentration of AC in a sample is above 1 wt. %. When applying the tracer analysis in the field, these visual observations could be used to provide additional information with respect to the concentration of AC in a sample, alongside the quantitative values developed from the analysis. This qualitative analysis also offers an improvement over the current visual inspection method in examining the colour of

solid material in soil cores, as the distinct colour change in the vials in the presence of AC (i.e., from orange to black), as well as the distinct difference between the Orange G solution and a colourless filtrate, can help to make clearer indications with regards to the presence or concentration of AC in a sample.

### 3.3 Phase 3 - Method validation

#### 3.3.1 Validation sample set 1: APTIM column experiments containing PlumeStop®

Prior to the analysis of samples via the tracer method or a TOC analysis, the validation samples were visually inspected. Photos of the validation set 1 samples are presented in Figure 3.24 and Figure 3.25.



*Figure 3.24- An image of the validation set 1 samples taken from Column 1  
From left to right: Col-1-1, Col-1-2, Col-1-3, Col-1-4, Col-1-5, Col-1-6.*



*Figure 3.25- An image of the validation set 1 samples taken from Column 2  
From left to right: Col-2-1, Col-2-2, Col-2-3, Col-2-4, Col-2-5, Col-2-6.*

The black colour of the Column 1 samples was suspected to be due to the presence of CAC in the samples. The brown colour of the Column 2 samples indicated the presence of little to no CAC, which was expected, as this column was used as a control in APTIM's experiment and was not

injected with PlumeStop<sup>®</sup>. As the colour of the Col-1-6 sample appeared to be grey rather than black, the concentration of CAC in the soil was predicted to be between that of the other Column 1 samples and the Column 2 samples.

Following visual inspection, the concentration of CAC in each sample was determined using the developed tracer analysis. A small amount of the soil (approximately 2 – 3 g) from each validation sample was used in the analysis, and the amount of Orange G adsorbed was calculated using Equation 1. As previously stated in Table 2.3, validation sample sets 1 – 3 contained PlumeStop<sup>®</sup>, which is a CAC product that contains a polymer additive. Previous experiments (Figure 3.11) had demonstrated that this additive could potentially inhibit the adsorption of Orange G to CAC. The polymer is expected to degrade and/or wash away post-injection, but the time required for this to occur is unknown, and therefore the concentration of polymer present in the samples was similarly unknown. As a result, the CAC concentrations in the samples from these validation sets were determined in the tracer analysis using the regression developed with both PlumeStop<sup>®</sup> and polymer-free CAC (i.e., utilizing regressions derived with stocks containing theoretically the maximum and minimum concentrations of the polymer). The resulting values were then averaged, and the range between the two values was utilized as the potential error.

The CAC concentrations in the validation set 1 samples determined via the tracer analysis are presented in Figure 3.26.

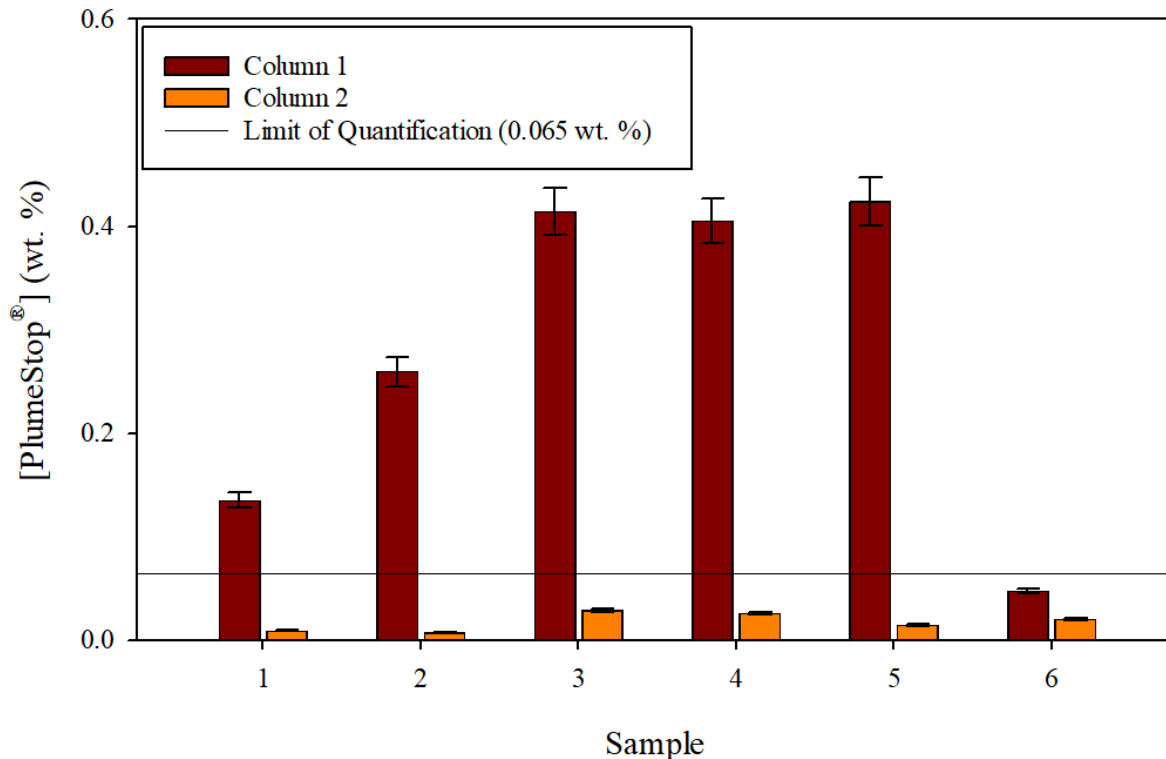


Figure 3.26- The PlumeStop® concentrations in the validation set 1 samples measured by the tracer analysis. The pH range for the experiments is between 3.6 – 3.7. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. PlumeStop® concentrations were derived using both the developed PlumeStop® and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The black line represents the quantification limit of the developed tracer analysis (0.065 wt. %). This limit is based on the lowest CAC concentration utilized in the experiments with the spiked soils (i.e., the experiments in Phase 2).

The concentrations of CAC in the Column 1 samples were higher than those of the Column 2 samples, as expected. The removal of Orange G in the Column 2 samples is attributed to the adsorption of Orange G to the soil. This adsorption is equivalent to the presence of less than 0.031 wt. % CAC, which is more than twice lower than the quantification limit of the tracer method.

Based on the tracer method, the sample that contained the highest CAC concentration was Col-1-5 ( $0.42 \pm 0.02$  wt. %), while the sample that contained the lowest CAC concentration was Col-1-6 ( $0.048 \pm 0.003$  wt. %). The CAC concentration of Col-1-6 was lower than the quantification limit of the tracer analysis, and as such, there could be a high uncertainty associated with this

value. Additionally, the two values are consistent with the relative difference in the visual appearance of these samples, i.e., the Col-1-6 sample was grey and the Col-1-5 sample was black.

The visual appearance of the suspension colours is consistent with the observations noted in previous experiments (detailed in Section 3.2.6); that is, the colour of the suspension can be used to indicate the presence of CAC (Figure 3.27 and Figure 3.28). The vials containing the Column 2 samples appeared orange, indicating little to no CAC, while the vials containing the Column 1 samples appeared black, indicating the presence of CAC above 0.065 wt. %. This is consistent with the fact that Column 1 was injected with PlumeStop<sup>®</sup>, while Column 2 was used as a control.



*Figure 3.27- An image of the vials used in the tracer analysis of validation set 1, Column 1 samples. All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. The vials were labelled with the sample number (e.g., on the far left, Col-1-1). The pH of the solutions in the vials was between 3.6 – 3.7. The first 6 samples from the left contained validation set 1, Column 1 samples, while the 2 vials on the right were control vials, and as such did not contain soil. From left to right: samples Col-1-1, Col-1-2-, Col-1-3, Col-1-4, Col-1-5, Col-1-6, and two control vials.*



Figure 3.28- An image of the vials used in the tracer analysis of validation set 1, Column 2 samples. All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. The vials were labelled with the sample number (e.g., on the far left, Col-2-1). The pH of the solutions in the vials was between 3.6 – 3.7. The first 6 samples from the left contained validation set 1, Column 2 samples, while the 2 vials on the right were control vials, and as such did not contain soil. From left to right: samples Col-2-1, Col-2-2, Col-2-3, Col-2-4, Col-2-5, Col-2-6, and two control vials.

It was observed that even though the CAC concentration in sample Col-1-6 ( $0.048 \pm 0.003$  wt. %) was lower than the quantification limit of the tracer method ( $0.065$  wt. %), the colour of the suspension in the vial containing Col-1-6 was still darker than that of the Column 2 samples. This indicates that even if the CAC concentration of a sample is below the quantification limit of the tracer method, the presence of CAC can be visually determined during the tracer analysis. It is important to note that quantitative assessment of the CAC concentration based on visual observation may not always be reliable, as it is prone to the bias of the inspector. For example, based on the author's assessment, the black colour of the vials containing both the Col-1-1 and Col-1-4 samples appeared to be similar in intensity. However, the CAC concentration of Col-1-1 was approximately three times less than that of Col-1-4 ( $0.14 \pm 0.01$  wt. % and  $0.41 \pm 0.02$  wt. %, respectively). As such, it is recommended that the primary focus of the developed tracer method remain on the quantitative concentrations of AC derived from pre-established relationships, and

that qualitative observations of the colour of suspensions within vials simply be used as an additional indication of the presence or high concentration (i.e., < 1 wt. %) of AC in a sample.

The CAC concentration values determined by the tracer method were compared to those measured by TOC analysis (Figure 3.29 and Figure 3.30).

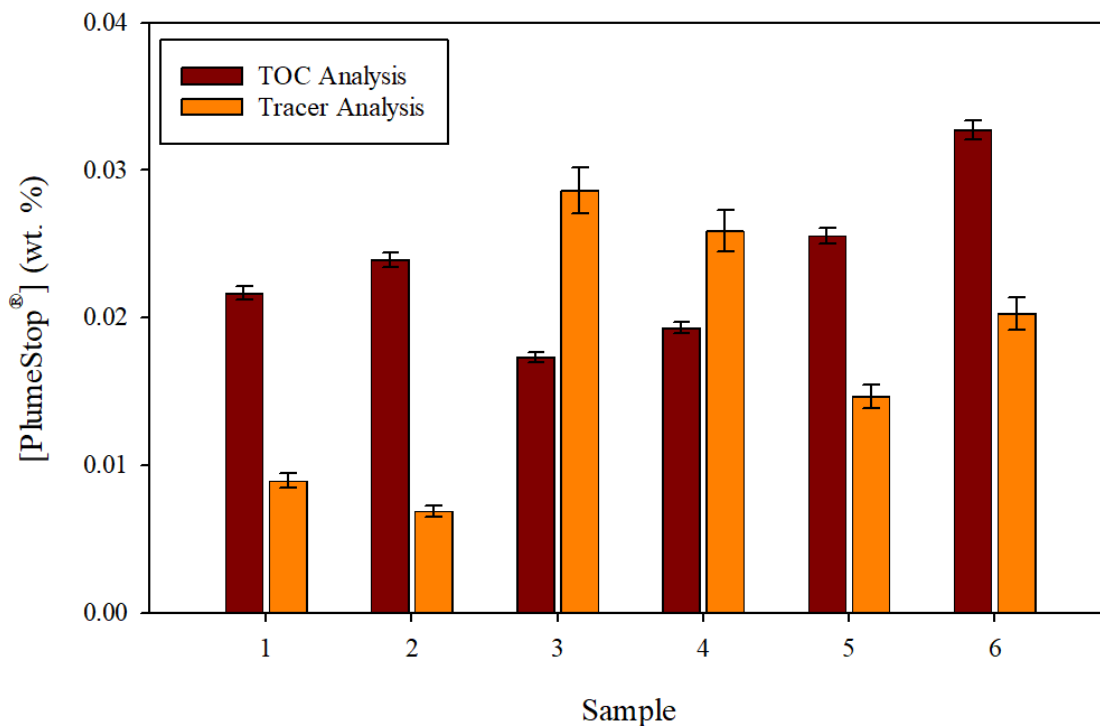


Figure 3.29- The PlumeStop<sup>®</sup> concentration in the validation set 1, Column 2 samples measured by the tracer and TOC analyses

The pH range for the experiments is between 3.6 – 3.7. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. In the tracer analysis, PlumeStop<sup>®</sup> concentrations were derived using both the developed PlumeStop<sup>®</sup> and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

The amount of Orange G adsorbed in the tracer analysis with the Column 2 samples was equivalent to CAC concentrations below the quantification limit of the method (0.065 wt. %). As Column 2 had not been injected with PlumeStop<sup>®</sup>, the removal of Orange G within the tracer analysis was attributed to adsorption to soil. The organic carbon content of the soil also appeared

to vary between samples. Based on the results of the tracer analysis, the organic carbon content of the samples ranged from  $0.007 \pm 0.0004$  to  $0.029 \pm 0.002$  wt. %. Likewise, the organic carbon content of the Column 2 samples, based on the results of the TOC analysis, ranged from  $0.017 \pm 0.0003$  to  $0.033 \pm 0.001$  wt. %.

For the Column 1 samples, the CAC concentrations derived from the tracer analysis range from  $0.048 \pm 0.003$  to  $0.42 \pm 0.02$  wt. %. The concentration of CAC in the column appears to increase from the column bottom to the center, and then decrease towards the top of the column.

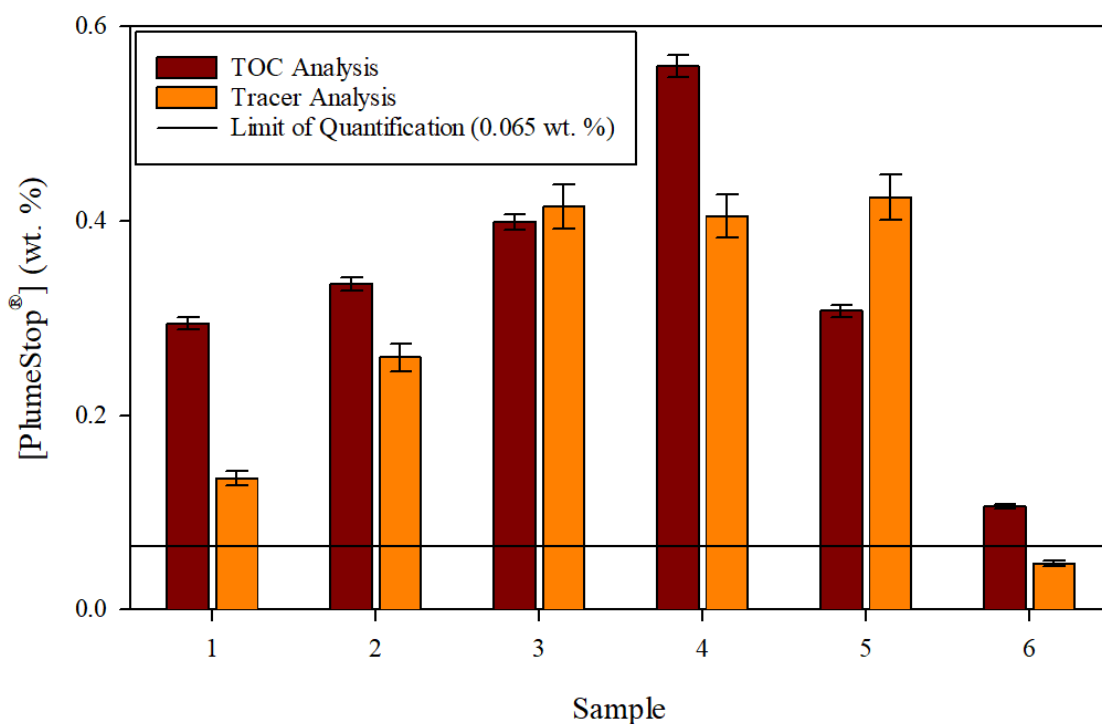


Figure 3.30- The PlumeStop<sup>®</sup> concentration in the validation set 1, Column 1 samples measured by the tracer and TOC analyses

The pH range for the experiments is between 3.6 – 3.7. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. In the tracer analysis, PlumeStop<sup>®</sup> concentrations were derived using both the developed PlumeStop<sup>®</sup> and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

As mentioned above, the CAC concentrations derived from the tracer analyses for the Column 2 samples and the Col-1-6 sample were below the method's limit of quantification. As such, the CAC concentrations derived from the tracer method were not considered to be reliable, and therefore were excluded from comparative analysis with the CAC values derived from the TOC method. For the remainder of the Column 1 samples, i.e., Col-1-1 to Col-1-5, the values derived via the tracer and TOC analyses differed by between 4 and 32 %, with the exception of Col-1-1, in which the percent difference between the derived concentrations was 74 %.

There are several explanations for the difference between the CAC concentrations derived from the TOC and the tracer analysis. Firstly, these differences could be due in part to the fact that two different portions of the soil sample were used for the tracer and the TOC analyses. In particular, although soil samples appeared to be homogeneous based on visual inspection (Figure 3.24, Figure 3.25), there could be quantitative differences in the AC concentrations throughout the soil. For example, upon removing soil from samples Col-1-5 and Col-1-6, darker soil was observed towards the base of the sample jar, and a dark colour bled out into the standing water present in the sample (Figure 3.31). This indicates that the CAC could have been distributed somewhat heterogeneously within the soil or mixed with the standing water in the samples.



*Figure 3.31- An image of the Col-1-5 (left) and Col-1-6 (right) samples from validation set 1, after soil had been removed from the sample containers*

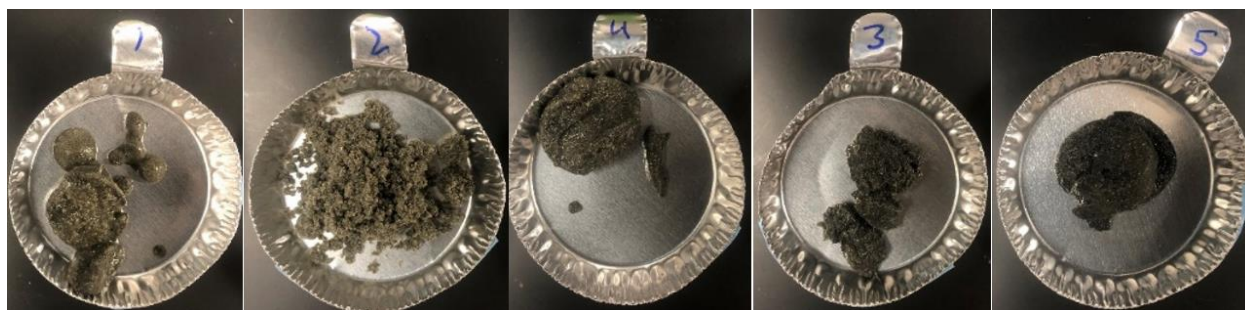
Secondly, the difference between the CAC concentrations obtained by the tracer and TOC analyses could be because the CAC concentrations in the tracer analysis were derived using the linear regression equations developed using fresh CAC. The CAC present in the validation set 1 samples had been aged for a period of approximately 3 months, and as such it is possible that the adsorption of Orange G to the aged material differed from the adsorption to fresh CAC. The presence of co-contaminants (i.e., PFAS) within the samples could also have impacted the adsorption of Orange G. In the column experiment originally completed by APTIM, PFAS-contaminated groundwater had been passed through column 1. Due to competitive sorption, these pre-sorbed contaminants could have suppressed the adsorption of Orange G by CAC, resulting in an underestimation of the CAC by the tracer method. Additionally, the AC concentrations were derived using pre-established relationships between Orange G adsorption and the concentration of a given stock of polymer-free CAC and PlumeStop<sup>®</sup> in a sample. However, the adsorption of the tracer to two different AC materials, or even between two different batches of the same AC product, could differ. Therefore, the developed regressions may not have been fully representative of the adsorption of Orange G to the PlumeStop<sup>®</sup> material utilized in the Column experiment performed by APTIM.

Finally, the higher CAC concentrations determined by the TOC method could also be due to the fact that all carbon measured via TOC analysis was attributed to CAC. As the soil sample can also contain organic carbon, this assumption could have caused the CAC concentrations measured by the TOC analysis to be greater than those measured by the tracer method. Note that this overestimation cannot simply be corrected by subtracting the results of the TOC analysis on the Column 1 samples by the background organic matter, because there is no single concentration value of background organic matter that could be used for this subtraction. As mentioned above,

the organic carbon content of Column 2 samples ranged from  $0.017 \pm 0.0003$  to  $0.033 \pm 0.001$  wt. %.

### 3.3.2 Validation sample set 2: Regenesis column experiments containing PlumeStop®

Photos of the validation set 2 samples are presented in Figure 3.32 below. The photos were arranged so that the intensity of the black colour in the samples increases from left to right.



*Figure 3.32- An image of the validation set 2 samples  
From left to right: Sample PS-1, PS-2, PS-4, PS-3, and PS-5.*

All samples appeared to be light to dark brown in colour, and it was predicted that the darkest sample, PS-5, would have the highest AC concentration. The tracer and TOC analyses were performed on the samples, and the CAC concentration values obtained from these analyses are shown in Figure 3.33.

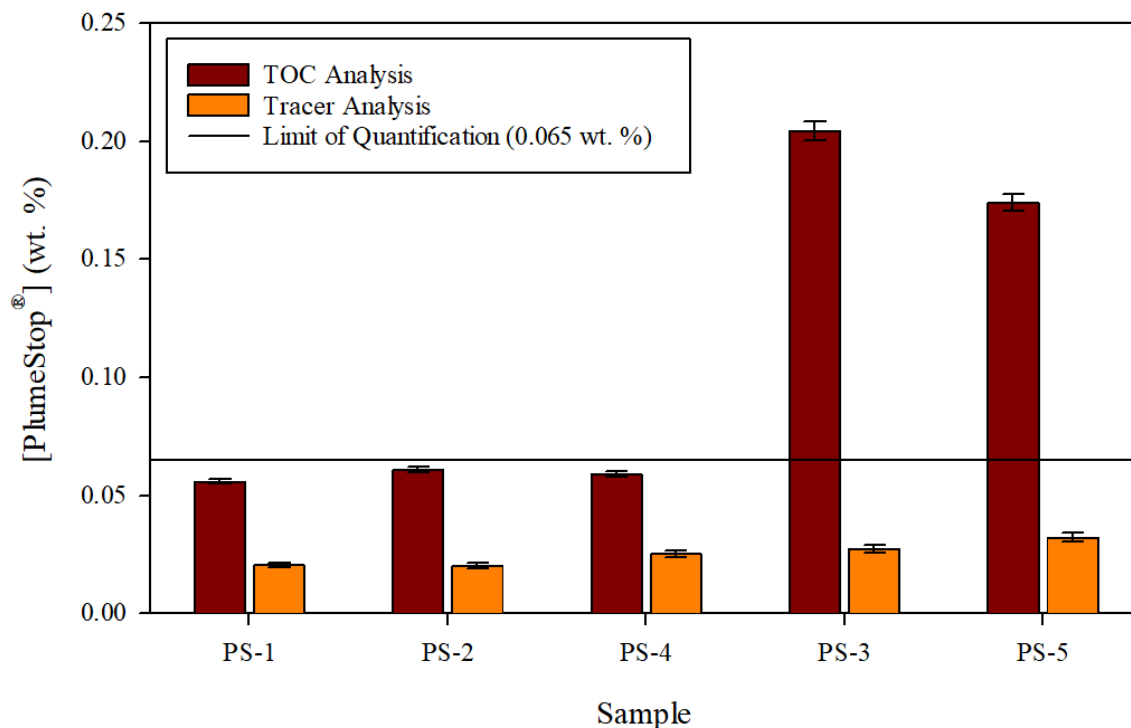


Figure 3.33- The PlumeStop<sup>®</sup> concentrations in the validation set 2 samples, measured by the tracer and TOC analyses. The pH range for the experiments is between 3.6 – 3.7. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. In the tracer analysis, PlumeStop<sup>®</sup> concentrations were derived using both the developed PlumeStop<sup>®</sup> and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

For all five samples, the CAC concentrations derived from the tracer analysis ranged from approximately  $0.020 \pm 0.001$  to  $0.032 \pm 0.002$  wt. %, which were below the quantification limit of 0.065 wt. %. For samples PS-1, PS-2, and PS-4, the CAC concentrations measured by TOC analysis ranged from approximately  $0.056 \pm 0.001$  to  $0.061 \pm 0.001$  wt. % and were also less than the quantification limit of the tracer analysis. However, the results of the TOC analysis indicate that the CAC concentrations in samples PS-3 and PS-5 ranged from approximately  $0.17 \pm 0.003$  to  $0.20 \pm 0.004$  wt. %. These concentrations were approximately 2.5 – 3 times higher than the quantification limit of the tracer analysis.

The colour of the suspensions observed within vials during the tracer analysis were also consistent with the observations made in the experiments that were discussed in Section 3.2.6. A photo of the vials used in the tracer analysis of the validation set 2 samples is presented in Figure 3.34. The colour of the suspensions in all vials containing validation set 2 samples appeared to be dark, which indicates the presence of CAC in the samples. However, the vials containing samples PS-3 and PS-5 appeared to be slightly darker than the vials containing samples PS-1, PS-2, or PS-4, which could indicate that the concentration of CAC in PS-3 and PS-5 was higher than in the other three samples. These visual observations are consistent with the results of the TOC analysis, in which the derived concentrations of CAC in samples PS-3 and PS-5 were greater than the CAC concentrations in the other three samples. This could indicate that tracer analysis could have underestimated the CAC concentrations for samples PS-3 and PS-5.



Figure 3.34- An image of the vials used in the tracer analysis of validation set 2 samples

All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. The vials were labelled with the sample number (e.g., on the far left, PS-1). The pH of the solutions in the vials was between 3.6 – 3.7. From left to right: samples PS-1, PS-2, PS-4, PS-3, and PS-5.



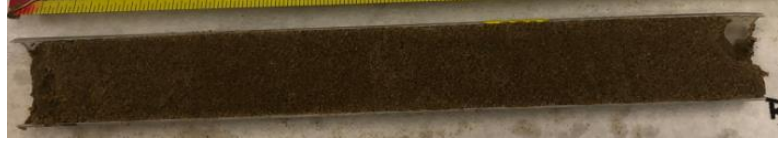
The exact reason for which the results of the TOC and tracer analyses varied (particularly in the case of samples PS-3 and PS-5) is unknown. As discussed in the previous section, the differences in CAC concentrations could be due to differences between the PlumeStop<sup>®</sup> material used in Regenesi's column experiments, and the polymer-free CAC and the PlumeStop<sup>®</sup> material used in this work (these materials were used to develop linear relationships between the amount of Orange G adsorbed and the concentration of AC in a sample, as discussed in Section 3.2.3 and 3.2.4). The Regenesi experiments were also conducted for a period of three years. As such, the CAC present in the column was aged. As discussed in Section 3.3.1, the adsorption of Orange G to the aged and fresh material could have differed, particularly with the presence of contaminants, such as PFAS. The presence of these co-contaminants could have inhibited the adsorption of


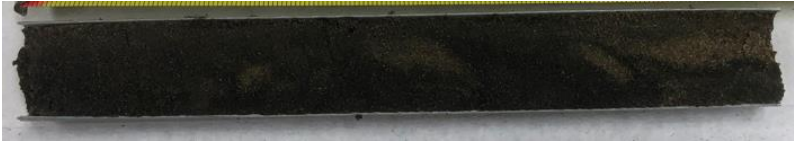

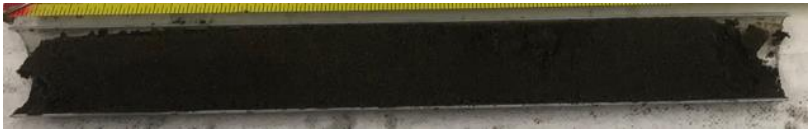
Orange G to CAC in the tracer analysis, resulting in underestimation of CAC concentrations in samples. Additionally, the differences in the concentration values could also be due to the heterogeneous distribution of CAC within samples. Finally, all of the carbon measured via the TOC analysis was attributed to the presence of AC, rather than SOM, which could have resulted in an overestimation of the AC concentrations derived from the TOC analysis.

### 3.3.3 Validation sample set 3: Regenesis soil cores containing PlumeStop®

Following a visual inspection of the soil cores, photos of the opened cores were taken and are presented in Table 3.4. The samples were arranged from what appeared to be the lightest to darkest colours, and each core was assigned a sample ID, from A to F.

*Table 3.4- Images of the soil cores from validation sample set 3*

Sample ID	Photo of Core
A	
B	
C	

C2(1) and C2(2)	 <table border="1" data-bbox="581 443 1317 646"> <tr> <td data-bbox="581 443 943 646">           C2(1) sampling range             (Approximately 1 – 6” from the top of the core segment)         </td> <td data-bbox="943 443 1317 646">           C2(2) sampling range             (Approximately 6.5 – 9” from the top of the core segment)         </td> </tr> </table>	C2(1) sampling range  (Approximately 1 – 6” from the top of the core segment)	C2(2) sampling range  (Approximately 6.5 – 9” from the top of the core segment)
C2(1) sampling range  (Approximately 1 – 6” from the top of the core segment)	C2(2) sampling range  (Approximately 6.5 – 9” from the top of the core segment)		
D			
E			
F			

The colour of the soil within the opened cores ranged from brown to black. Upon visual inspection, it was suspected that CAC was present within the large, black patches of soil in the C2, D, E, and F cores. The distribution of CAC in cores E and F appeared to be homogeneous, while the distribution in core D appeared to be somewhat heterogeneous. The results of the tracer and TOC analyses performed on the samples are shown in Figure 3.35.

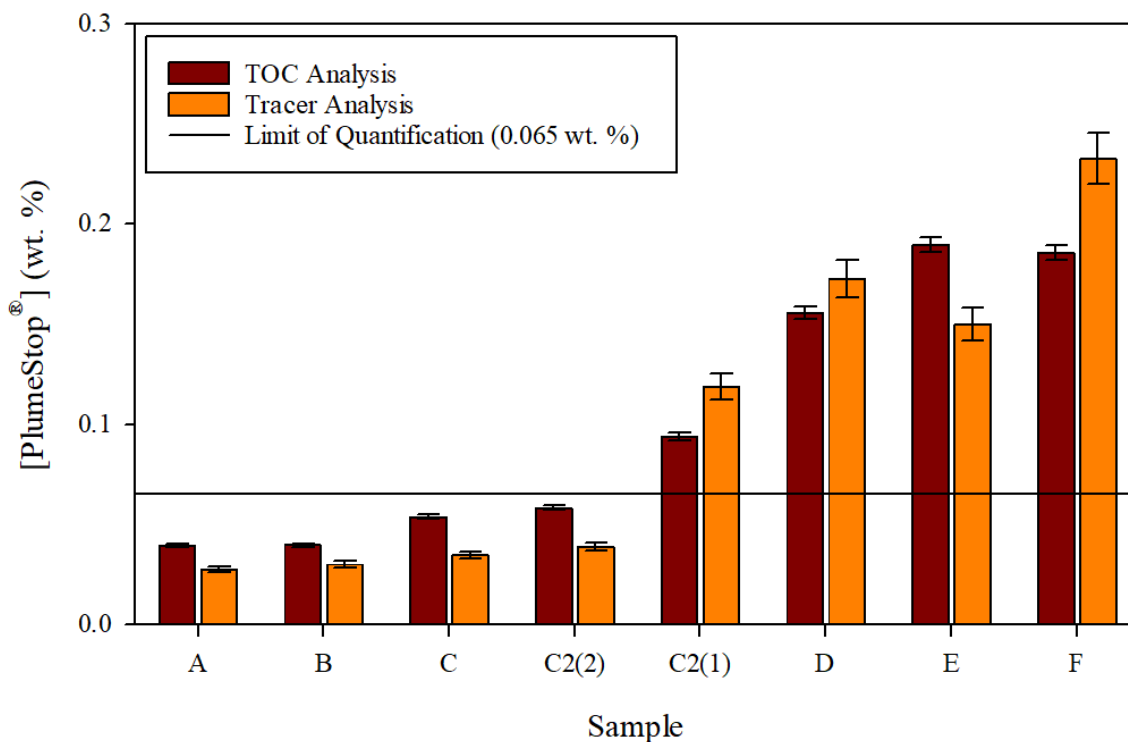


Figure 3.35- The PlumeStop® concentration in the validation set 3 samples, measured by the tracer and TOC analyses. The pH range for the experiments is between 3.6 – 4.5. All solutions contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. In the tracer analysis, PlumeStop® concentrations were derived using both the developed PlumeStop® and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

For samples A, B, C, and C2(2), the concentration of CAC derived from the tracer analysis ranged from  $0.028 \pm 0.002$  to  $0.039 \pm 0.002$  wt. %, while the concentrations measured by the TOC analysis ranged from  $0.039 \pm 0.001$  to  $0.058 \pm 0.001$  wt. %. These values were lower than the quantification limit of the tracer method (0.065 wt. %), indicating there was little, if any, CAC present in the samples. Meanwhile, the CAC concentrations of the C2(1), D, E, and F samples were higher than the quantification limit of the tracer method. The CAC concentrations derived from the tracer method ranged from  $0.12 \pm 0.01$  to  $0.23 \pm 0.01$  wt. %, while the concentrations derived from the TOC analysis ranged from  $0.094 \pm 0.002$  to  $0.19 \pm 0.004$  wt. %. The observations made during the visual inspection of the samples are consistent with the CAC concentration

determined from the tracer and TOC analyses. That is, the darker the colour of a sample, the higher the concentration of CAC within the soil. For example, the predicted CAC concentrations of sample B (utilizing values from both the tracer and TOC analyses) were  $0.030 \pm 0.002$  and  $0.040 \pm 0.001$  wt. %, respectively, while the concentrations of sample F, which was a dark black soil, were  $0.23 \pm 0.01$  and  $0.19 \pm 0.004$  wt. %, respectively. Additionally, in samples A, B, C and C2(2), the CAC concentrations determined by the tracer method were below the method limit (0.065 wt. %), meaning that there is likely a higher uncertainty associated with these values. Finally, as discussed in Section 2.3.2, the core labelled as SC (sample A) was taken prior to CAC injection, while the CC cores were taken post-injection. Since sample A was not expected to contain CAC, the removal of Orange G in this system was attributed to Orange G adsorption to the soil, while the CAC concentration determined via the TOC analysis for this sample would represent the percent of organic carbon in the soil, rather than the concentration of CAC. As previously discussed in Section 3.3.1, the organic carbon content of soil could vary between samples, and therefore it is unknown whether the value derived from the TOC analysis of sample A is representative of the organic carbon content of the soil present in samples B to F. For the samples in which the CAC concentration derived from the tracer analysis was greater than the method's limit of quantification, i.e., 0.065 wt. %, the percent difference between the results of the tracer and TOC analyses was between 10 and 24 %. These samples included C2(1), D, E, and F.

The visual observations made during the tracer analysis also agreed with the quantitative CAC concentrations and were consistent with observations made in the previous experiments (Section 3.2.6). As shown in Figure 3.36, samples A, B, C, and C2(2) appeared orange during analysis, indicating that little to no CAC ( $<0.065$  wt. %) was present in samples. Samples C2(1), D, E, and F appeared black or murky brown, indicating that some CAC ( $>0.065$  wt. %) was present.

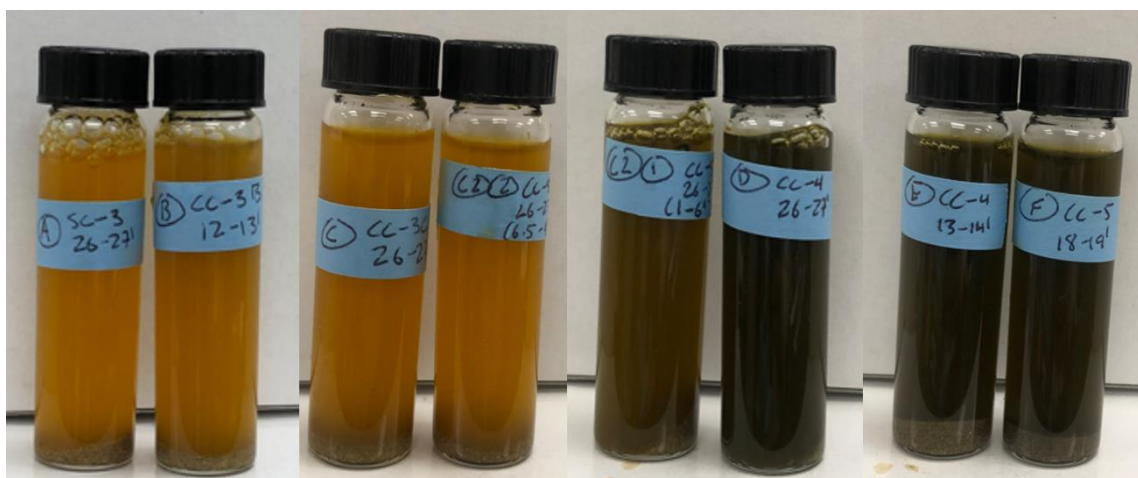













Figure 3.36- An image of the vials used in the tracer analysis of validation set 3 samples

All vials contained 100 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. The vials were labelled with the sample number (e.g., on the far left, A). The pH of the solutions in the vials was between 3.6 – 4.5. From left to right: samples A, B, C, C2(2), C2(1), D, E, and F.

### 3.3.4 Validation sample set 4: Borden soil cores containing WPC Calgon PAC

Photos of the opened soil cores, prior to subsampling, are presented in Table 3.5. Each sample was assigned an alphabetical ID, from A to L. Following visual inspection of the open cores, samples were then arranged from lightest to darkest colours. Samples A-H were observed to have the least amount of black-coloured soil, followed by samples K-J. Samples B-E were found to have the highest amount of black-coloured soil.

Table 3.5- Images of the soil cores from validation sample set 4

Sample	A	D	F	H
Photo				
Sample	K	G	I	J
Photo				
Sample	B	E	C	
Photo				

The distribution of PAC in soil cores appeared to be heterogeneous, compared to the distribution observed in the soil cores containing PlumeStop<sup>®</sup> (validation set 3 samples). This difference was expected, as it had been noted in a previous study that the distribution of CAC within an in-situ barrier can be more homogeneous than that of PAC [47]. Additionally, a black colour within the soil cores was used to indicate the presence of PAC. Upon visual inspection, it appeared as though little to no PAC was present in the soil cores, with the exception of samples B, C, and E. This is likely because the soil cores in this validation set were taken from a research site which was used to model the breakthrough of PHCs across a PAC barrier. As the goal of the research had been to observe the breakthrough of the PHC within the study time, the area was

underdosed with PAC, and target concentrations were set to approximately 0.33 wt. %. Higher PAC concentrations could be found at other field sites, where the purpose of an in-situ barrier is to immobilize contaminants in the subsurface, and therefore the PAC concentrations within the Borden samples are likely not fully representative of other field sites.

The results of the PAC concentration measured by the tracer and TOC analyses are shown in Figure 3.37. It should be noted that Figure 3.37 does not include the data collected for sample C. This is because the values collected during the tracer and TOC analysis with this sample are much higher than the concentrations of the other samples. During the tracer analysis, all the Orange G was removed from the solution. Therefore, sample C was determined to contain >1 wt. % PAC. The concentration of PAC in the sample, derived from the TOC analysis, was approximately 18 wt. %.

As previously discussed in Section 3.2.5, two regression curves, at two separate pH ranges, were developed to represent the relationship between the amount of Orange G adsorbed and the concentration of PAC in a sample (Figure 3.14). In the tracer analysis with the validation set 4 samples, the pH of the solution within the experimental vials was measured at 0, 5, and 20 minutes of shaking, and the values were found to range from 4.8 – 5.9 across a majority of the shaking time (i.e., 5 to 20 minutes). This pH range fell within that established for the high pH (4.7 – 6.1) curve shown in Figure 3.14. As such, this regression was utilized to derive the CAC concentrations in the tracer analysis of the validation set 4 samples.

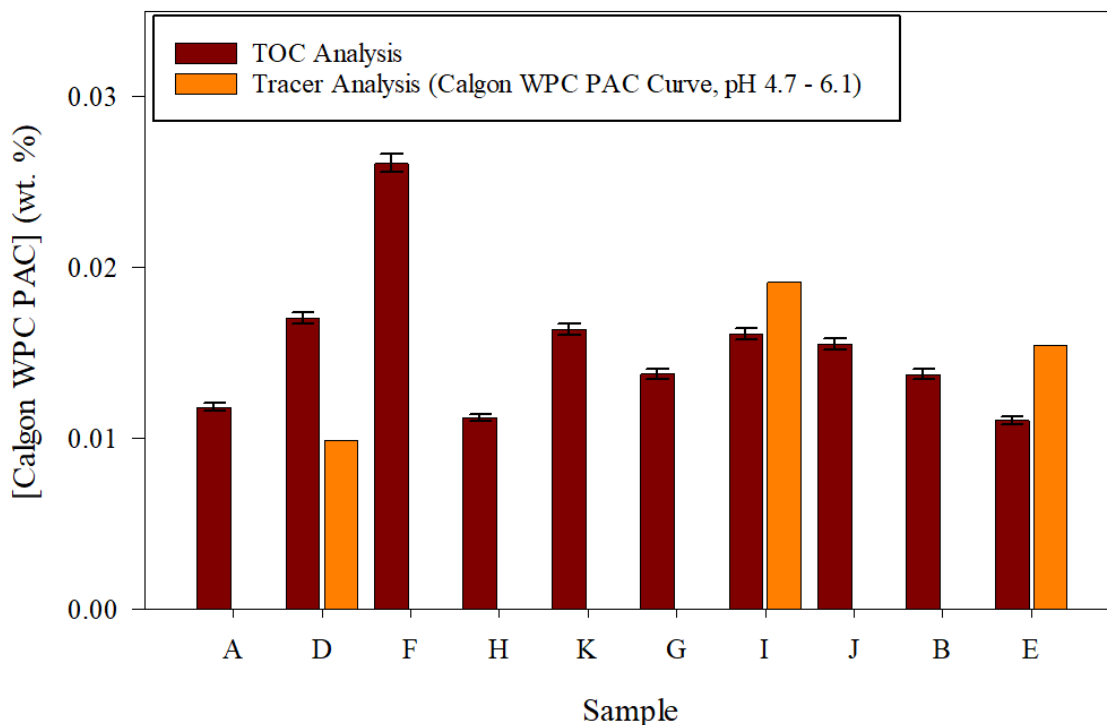


Figure 3.37- The PAC concentrations in the validation set 4 samples, measured by the tracer and TOC analyses (Sample C not included)

The pH range for the experiments is between 4.8–5.9. All solutions contained 150 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. An uncertainty value was not provided for the PAC concentrations derived from the tracer analysis, as the concentrations were derived from a single curve. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

In the tracer analysis, with the exception of samples C, D, I, and E, the Orange G adsorption was negative when calculated using Equation 1. As discussed in Section 3.1.1, this could be due to the presence of additional compounds (such as, for example, CDOM or dissolved iron [35]) in the filtrates of these samples. Thus, the percent adsorption of Orange G was set as zero, meaning that the concentration of PAC in a sample was also calculated to be zero. With the exception of sample C, the PAC concentrations derived from the tracer analysis ranged from 0 to 0.019 wt. %, while the PAC concentrations derived via the TOC analysis ranged from  $0.011 \pm 0.0002$  to  $0.026 \pm 0.001$  wt. %. However, as the CAC concentrations derived from all samples (i.e., samples A to

K) were outside the limits of quantification for the method (i.e., less than 0.2 wt. % or greater than 1 wt. %), there may be high levels of uncertainty associated with these values.

The results of the tracer and TOC analyses indicate a PAC concentration of  $< 0.027$  wt. % in all samples (with the exception of sample C). Dr. Neil Thomson's research group at the University of Waterloo has performed additional studies and analysis at the Borden site and has estimated that the TOC value of the soil could be approximately 0.3 mg/g, or 0.03 wt. % [48]. This indicates that although PAC was visually observed in the soil cores, it was not present in a concentration high enough to be detected by the TOC or the tracer analyses. This result enforces that although visual inspection can be used to identify the presence of AC in a soil core, it is possible that this method cannot provide reliable values regarding the concentration of AC in a sample.

Visual observations regarding the colour of the suspensions during the tracer analysis were again similar to those observed in previous experiments (Section 3.2.6) and are consistent with the quantitative values of the AC concentrations in the samples. During the tracer analysis, the vials containing all samples (with the exception of sample C) appeared orange in colour, indicating less than 0.2 wt. % of PAC would be present within the samples. This value (0.2 wt. %) is the minimum PAC concentration tested in the experiments with AC-spiked soils, and therefore the minimum concentration at which the colours of the suspensions were observed to be black in colour. It was observed that the vial containing sample C did appear black, and the filtrate of the suspension was clear (i.e., all Orange G was removed), meaning that the sample likely contained a PAC concentration of greater than 1 wt. %. The photos of the vials containing samples E and C are shown in Figure 3.38.



Figure 3.38- An image of two of the vials used in the tracer analysis of validation set 4 samples

The vial containing sample E is presented on the left, and the vial containing sample C is presented on the right. The colourless filtrate of the sample C vial is also provided. All vials contained 150 mg/L Orange G, 100 mM HCOOH, 100 mM HCOONa, and 100 g/L of a validation sample. The pH of the solution in the vial containing sample E was 5.3 – 5.8, and the pH of the solution in the vial containing sample C was between 5.7 – 5.9.

These observations indicate that while visual inspection of soil cores may not be able to provide reliable values of AC concentrations, the colour of the suspension in the vials used in the tracer analysis can indicate the presence of PAC and potential range (i.e., less than or greater than 0.2 wt. %) in a sample.

### 3.3.5 Final comparison of validation results and summary of validation findings

Following the individual testing of the validation sets, the results of the TOC and tracer analyses were compiled, and the AC concentrations derived from the TOC analyses were plotted against those derived from the tracer analyses on a scatter plot (Figure 3.39). Since AC concentrations outside of the quantifiable limits of the tracer analysis could have higher associated uncertainties, only samples for which the derived AC concentrations were within the method limits (i.e., 0.065 – 0.75 wt. % for PlumeStop<sup>®</sup> and polymer-free CAC, or 0.2 – 1 wt. % for WPC Calgon PAC) were included in this plot. The nine samples that fit this criterion all contained PlumeStop<sup>®</sup>, and included

Col-1-1, Col-1-2, Col-1-3, Col-1-4, and Col-1-5 from validation sample set 1, and samples C2(1), D, E, and F from validation sample set 3.

The experimental data points were compared to a linear line with a slope of 1. Values falling upon this line would indicate that the AC concentrations derived from the tracer analysis were equivalent to those derived from the TOC analysis. The 1:1 line was bounded with two additional linear lines, with slopes representing a given percent difference from the ideal value of 1. For example, for a given percent difference of 35 %, the slopes of the upper and lower bounds would be approximately 1.42 and 0.70, respectively. The results of the compilation are provided in Figure 3.39. The percent differences of the compiled samples were less than 35 %. The exception to this was the sample collected from Col-1-1, where the percent difference was 74 %. These results indicate that the tracer method may be able to provide results comparable to the quantitative analysis of TOC, particularly when AC concentrations are within the method limits (i.e., 0.065 – 0.75 wt. %, for samples containing CAC).

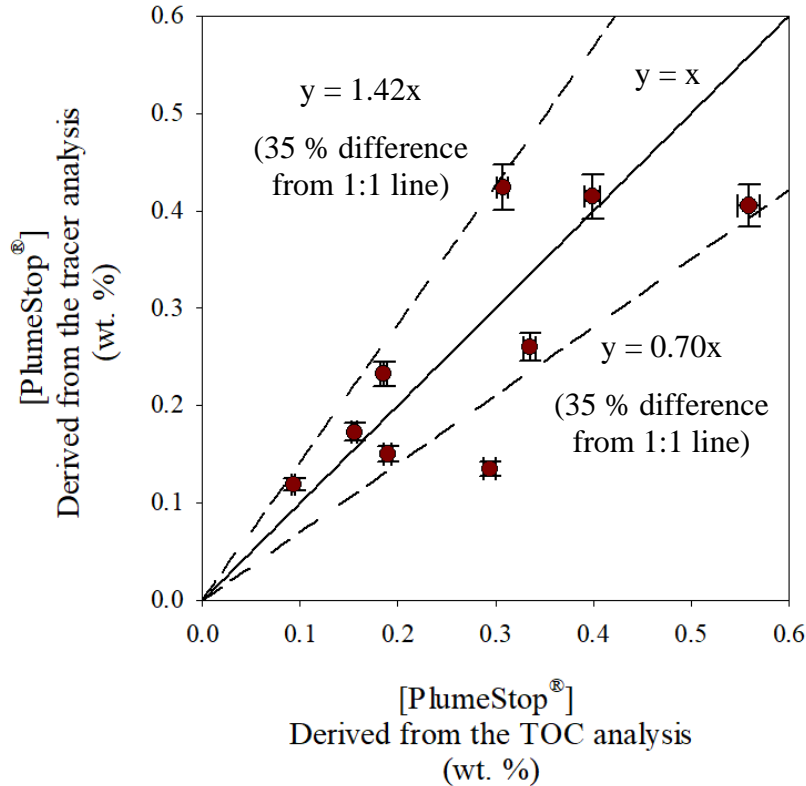


Figure 3.39- A comparison of the AC concentrations derived from both the tracer and TOC analyses. Only the results of tests with validation samples in which the AC concentration derived from the tracer analysis was within the limits of the method (i.e., 0.065 – 0.75 wt. % for CAC and 0.2 – 1 wt. % for PAC) have been plotted. This includes samples Col-1-1, Col-1-2, Col-1-3, Col-1-4, and Col-1-5 from validation sample set 1, and samples C2(1), D, E, and F from validation sample set 3. The solid black line represents a target regression with a 1:1 slope. The black dashed lines represent regressions with a 35 % percent difference from the target slope (i.e., with slopes of 1.42 and 0.70). In the tracer analysis, PlumeStop® concentrations were derived using both the developed PlumeStop® and polymer-free CAC curves. The average of the two values is presented, and the error bars represent the range of the two values. The uncertainty associated with the values derived from the TOC analysis was estimated by EIL to be 2 %.

In summary, the results of the validation tests indicate that the tracer method could be a useful tool for practitioners to determine AC concentrations in soil cores at a field site. Firstly, for eight of the nine analyzed samples for which the CAC concentration derived from the tracer analysis were within the method limits, the AC concentrations derived from the tracer analysis could be considered comparable (within 35 %) to those derived from a TOC analysis. Given that multiple

days can be required to perform a TOC analysis, *versus* the approximate time of 30 min required for the tracer method, the tracer analysis can provide AC concentrations in a much shorter time frame. Additionally, unlike the TOC analysis, the tracer method can be performed in the field. Thus, the tracer method could provide real-time or near real-time quantitative values of AC concentrations in soil cores, which would aid in decision-making during the AC injection process (i.e., with regard to whether the concentration of AC in a barrier can be considered sufficient and within design criteria, or if additional injections of AC are required).

Secondly, similar to the observations made during the Phase 2 experiments (method development), the results of the validation tests indicate that the colour of the suspension in a test vial can be used to provide additional information with regard to the presence or absence of AC, and the complete removal of Orange G from a system can indicate that concentrations of AC in a sample are high, and exceed the range that can be quantified by the method (>1 wt. %). This means that in addition to providing quantitative values of AC concentrations in samples, the developed tracer analysis can also provide an additional and improved method of visual inspection. The current estimation of AC concentrations via visual inspection of solid material in soil cores is a qualitative analysis that is prone to human error. For example, in validation set 4, although the presence of PAC was identified in several samples during visual inspection of soil cores, the results of the tracer and TOC analyses indicated that AC concentrations in samples were very low (<0.03 wt. %). However, the quantitative results of the tracer method agreed with the visual observations made during the analysis, where the colour of the suspension within the vials appeared orange, indicating the presence of little to no CAC (< 0.2 wt. %). This indicates that the stark contrast between the orange and black suspensions observed during the tracer analysis can help to indicate the presence or absence of AC in a sample and may be able to do so more clearly than the visual

inspection of solid samples within soil cores. Therefore, not only can the quantitative values of AC concentrations in samples provided by the developed tracer method decrease or remove the human bias associated with visual inspection of soil cores, but the colour of the suspension within a vial can offer clearer indications with regard to the presence or absence of AC.

## **Chapter 4 - Summary, Conclusions, Recommendations, and Future work**

The work presented in this thesis details the development of a rapid (less than 30 minutes per sample) and simple method that can be used to quantify the concentration of AC in soil cores. Such a method could provide real-time or near real-time information to practitioners regarding the distribution and concentration of AC in the subsurface, which would aid in decision-making during AC injection. Specifically, the concentration of AC measured by the tracer method would provide insights into whether AC concentrations in the subsurface are within design parameters, or if additional AC injections are required at a site.

The developed tracer method relies upon the adsorption of a tracer (Orange G) to AC particles in a soil sample. Orange G was selected as a tracer as this compound was shown to adsorb preferentially to AC over nine soils. Orange G absorbs light in the visible spectrum, and thus can be easily measured in the field using a portable spectrophotometer. Additionally, a 100 mM HCOOH/100 mM HCOONa buffer was selected to control the pH of the suspensions of AC-spiked soils between approximately 3.6 and 6. Following the tracer and pH buffer selection, linear relationships between Orange G adsorption and the concentration of AC in the soil samples spiked with three AC materials (polymer-free CAC, PlumeStop<sup>®</sup>, and PAC) were established. The coefficients of determination for the linear regressions were between 0.993 and 0.998, indicating a strong relationship between the amount of Orange G adsorption and the concentration of AC in a sample. It was also noted that the colour of the suspensions could be used to indicate the presence of AC in a sample. Generally, a black suspension will indicate the presence of AC, while an orange suspension will indicate little to no AC in a sample.

It should be noted that the regressions developed in this work were specific to the three tested AC materials (i.e., a single batch of PlumeStop<sup>®</sup>, polymer-free CAC, or WPC Calgon PAC). However, the adsorption of Orange G to two different AC materials, or even between two different batches of the same AC product, could differ. Additionally, the adsorption of Orange G can be impacted by both the ionic strength and pH of the solution. Solution pH can be impacted by the type of soil present in a sample, specifically, the soil's pH and buffering capacity. Therefore, prior to applying the tracer method at a field site during an AC injection, a regression curve should be developed to represent the adsorption of Orange G to the specific AC material used for the injection and using site-specific soil samples. Note that this process would also allow for flexibility in the method design, and for the method to be adjusted as needed. For example, the method could be adjusted to quantify a different range of AC concentrations, depending on the design targets of a given in-situ barrier. In this study, this approach could not be implemented prior to the validation portion of this work (i.e., Phase 3), as the exact PlumeStop<sup>®</sup> and WPC Calgon PAC batches present in the validation sample sets were not available. Therefore, the regressions developed in Phase 2 of this study were utilized to deduce the concentrations of AC within the validation samples.

The tracer method was validated using samples collected from two column studies and from soil cores collected from two field sites where AC had been injected. The AC concentrations in the samples were quantified using the tracer analysis and a TOC analysis. For eight of the nine tested samples for which the CAC concentration derived via the tracer analysis was within the tracer method limits, the percent difference between the AC concentrations derived via the tracer method and the TOC analysis was below 35 %. In the other sample, the percent difference was 74 %. These results indicate that the tracer method may be able to provide results comparable to a TOC analysis. Additionally, throughout the tracer analysis, qualitative observations made during

the visual inspection of vials containing the validation samples were consistent with those seen during method development experiments. The difference in the colour of the suspensions in the presence or absence of AC was generally clear and distinct (i.e., orange or black), meaning that the visual observations of the experimental vials could offer a method of visual inspection prone to less human bias than the current method of inspecting solid soil cores.

The results indicate that in this study, the AC concentrations derived from the tracer method could be considered comparable to the AC concentrations derived from a TOC analysis. Additionally, by utilizing the tracer analysis, AC concentrations can be derived in the field, and within approximately 30 minutes, which is a much shorter time frame than a TOC analysis would require. The tracer method can also provide quantitative values of AC concentrations, while the currently utilized field method of visual inspection can only provide qualitative observations, which are prone to human bias.

There are several areas of future work which could be useful for this research. First, the tracer analysis was developed for use with AC particles. However, in-situ adsorption barriers can be created with other types of amendments. An example is the potential use of ion exchange resins in the immobilization of PFAS in the subsurface [8]. As such, future work could consider adjusting the tracer analysis to be used with these other materials. Secondly, the method currently requires that soil cores be opened in the field. Once a core has been opened, it is difficult to package or transport it elsewhere. Therefore, if the tracer method could be performed without opening the core, additional flexibility could be provided to practitioners in the field, in that cores could be transported from the site and stored for later use, such as ex-situ characterization and analysis in a lab. This could potentially be done by adjusting the developed tracer method to a “push-pull” analysis, in which a small hole could be inserted into the sleeve of a soil core, and the tracer

solution could be injected into the core via a syringe. After allowing the Orange G to adsorb to AC within the soil, the syringe could be used to extract a portion of water from the core, which could then be used to determine the amount of Orange G adsorbed to AC within the soil [49] [50]. Finally, the method was validated using samples collected from field sites and column studies. However, these samples were collected and shipped to the University of Waterloo, where they were analyzed. Therefore, to ensure that the method can function as intended in the field, the method should be demonstrated at the site during an AC injection event.

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