XRF Quick-Scan Mapping for Heavy Metal Pollutants in SuDS: A Methodological Approach

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Abstract: Sustainable urban drainage systems (SuDS) such as swales are designed to collect, store and infiltrate a large amount of surface runoff water during heavy rainfall. Stormwater is known to transport pollutants, such as particle-bound heavy metals, which are known to often accumulate in the topsoil. In this study, a portable XRF instrument is used to provide in situ spatial characterization of soil pollutants. The method uses portable XRF measurements of heavy metals along profiles with set intervals (1 meter) to cover the swale with cross-sections, across the inlet, the deepest point and the outlet. Soil samples are collected, and the In-Situ measurements are verified by the results from laboratory analyses. Stormwater is here shown to be the transporting media for the pollutants, so it is of importance to investigate areas most prone to flooding and infiltration. This quick scan method is time and cost-efficient, easy to execute and the results are comparable to any known (inter)national threshold criteria for polluted soils. The results are of great importance for all stakeholders in cities that are involved in climate adaptation and implementing green infrastructure in urban areas. However, too little is still known about the long-term functioning of the soil-based SuDS facilities.

Keywords: portable X-ray fluorescence spectrometer (XRF); heavy metals; lead (Pb), zinc (Zn); copper (Cu); topsoil; sustainable urban drainage systems; SuDS; LID; BMPs; WSUD; GI; SCMs

1. Introduction

In urban and densely populated areas, surface runoff can carry material residue produced by daily human activity and has been identified as an important pathway for pollutants that enter receiving water bodies [1,2]. Sustainable urban drainage systems (SuDS, also called green infrastructure (GI), best management practices (BMP), low impact development (LID), water sensitive urban design (WSUD), ecosystem-based adaptation (EbA) and nature-based solutions (NBS) and more [3]) are constructed to receive, store and infiltrate surface water to restore the groundwater balance and to remove pollutants, such as lead, zinc and copper [4]. An increased pollutant load in urban stormwater degrades water quality, therefore knowledge of the characteristics of the pollutants is needed—vital knowledge that can be incorporated management and maintenance [5]. With climate change, a higher proportion of rainfall will become surface runoff [6], which in turn will result in increased peak flood discharges and subsequently degraded water quality [7].
As Tedoldi et al. [8,9] point out, few studies have carried out systematic mapping of the horizontal distribution of pollutants in SuDS. Studies by amongst others Jones and Davis [10] and Tedoldi et al. [8,9], show that the concentration of heavy metals are in the uppermost 0–12 cm of the soil in SuDS and decrease with depth, down to 90–100 m [8,10]. Investigation of SuDS constructions such as swales (Figure 1) by means of laboratory analysis of soil samples is costly and time-consuming. The high cost of soil analysis is the main reason the investigation of the environmental-technical functioning of rainwater facilities has not been systematically conducted on a large scale. Past research indicates that contamination is restricted to the upper 10 to 30 cm of soil [9]. In the quick scan method, a portable X-ray fluorescence spectrometer (XRF) measures a range of elements, including heavy metals. Portable XRF measurements are an established method for analyzing metals and other elements [11–13], and in cases where low detection levels are not required, time-consuming and costly laboratory analyses could be viewed as superfluous.

This paper proposes a methodology for mapping heavy metals, including lead (Pb), zinc (Zn) and copper (Cu), in situ in topsoil in SuDS. This study was conducted in the Netherlands where SuDS has been used for over a decade and is part of a national study [14]. A portable XRF device has been used that can give immediate results in the field. In general, in situ analysis of the degree of pollution in the topsoil may ensure quick follow-up actions, like soil remediation. In situ XRF measurements provide quick and cost-efficient analyses for heavy metal mapping.

The cost estimate for implementing SuDS usually includes installation but not management, monitoring or maintenance. Therefore, the analytical results are of great importance for all stakeholders in cities that are involved in the implementation and maintenance of green infrastructure for climate adaptation. Since swales (Figure 1) are the most common construction built for storing stormwater and infiltrating surface water in the Netherlands, more knowledge is needed on the long-term pollution levels in the soil. Therefore, this field-based study in the Netherlands aims to establish a methodology using in situ measurements by a portable XRF instrument that are quick and cost-efficient.

**Figure 1.** (A): Principle sketch of a swale. (B): Demonstration of in situ XRF measurements at every 1 meter along a profile across the swale. For the measuring results to be comparable with lab results for
soil samples, the vegetation is removed to measure directly on the topsoil (0–3 cm). The instrument is pointed on the topsoil and each measurement is read for 60 s.

2. Materials and Methods

The proposed approach for mapping SuDS in this study used swales as pilot facilities (Figure 1). The in situ XRF measurements are of topsoil (0–3 cm). Soil samples were collected at the same locality (also 0–3 cm) for lab analysis and quality control. Swales vary in shape and design from small swales along roads in residential areas (1–2 meters wide) to large swales (5–7 meters wide). Figure 1 shows the principles of a swale, commonly a depression in the ground with grass vegetation, an inlet for stormwater and outlet for surplus water. Further, swales are constructed with layers of filtering media according to Woods Ballard et al. [2]. The three pilot locations used in this study and more than 250 other Dutch swale locations are mapped in the open source webtool www.climatescan.org [15]. In the webtool the general characteristics of the sample area, photos and description were gathered at each location, where this research is available with description, images and videos.

The research results from this applied methodological approach will help national water authorities to control and improve the water quality in accordance to the EU Water Framework Directive [16]. In addition, the results will help improve national and international guidelines for the design, construction and maintenance of SuDS, the importance of which has been recognized by several stakeholders from water authorities and municipalities attending two recent national workshops [17].

This study focuses on the heavy metals lead (Pb), zinc (Zn) and copper (Cu) due to their prevalence in stormwater and their toxicity at high concentrations [5]. The threshold values for these heavy metals in soils, by Dutch regulations, are provided in Table 1.

| Metals  | National Background Concentration ppm (mg/kg) | Target Value ppm (mg/kg) | Intervention Value ppm (mg/kg) |
|---------|---------------------------------------------|-------------------------|---------------------------------|
| Lead (Pb) | 85                                             | 85                                    | 530                               |
| Zinc (Zn) | 140                                            | 140                                  | 720                               |
| Copper (Cu) | 36                                              | 36                                    | 190                               |

2.1. Portable XRF

Spectrometry is a method to detect elements, first established by Goldschmidt [19]. The portable XRF instrument was originally invented in the 1970’s to locate lead-containing pipes in buildings. Its functionality with multiple elements was further used to map lead in paint [20] and investigating metal contamination in soil and sediments [21–23]. The portable XRF instrument has further been developed and used for mapping soil and waste contamination [11,24]. Today, one of the main uses of the portable XRF instrument is characterization of polluted soils [12,13] and other types of contamination, such as heavy metals in organic matter, i.e., plants and algae [25,26].

2.2. Instrument Description

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. The portable XRF instrument determines the chemical composition by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of unique set characteristic fluorescent X-rays, like a fingerprint. [27]. The analyses cover the element content from magnesium (Mg, 12) to uranium (U, 92) in the periodic table [27,28]. The detection limit for each element varies, and the limits for the elements in focus for this study are given in Table 2.

This method for in situ mapping of pollutants in the topsoil of swales was carried out with portable XRF, with focus on heavy metals in soil. Two XRF instruments; Thermo Scientifíc™ Niton™
XL3t GOLDD+ XRF Analyzers (#SN67136) and Thermo Scientific Niton XL3t GOLDD XRF Analyzers (#SN36372c) were used to provide comparisons between readings and to improve quality control. The instruments were set for soil analysis and every reading with the instruments were executed for minimum 60 s for reliable results [28]. The instruments were calibrated with standard reference samples [27] and with Dutch soil standard samples. The latter are samples made from a batch of thoroughly analyzed soil, according to the national background values (Table 1) and following the national regulations for contaminated soil [18].

### Table 2. Detection limit per element used in this study for portable XRF and ICP-MS [27,29,30].

| Metals     | Portable XRF ppm (mg/kg) (ThermoFisher) | ICP-MS ppm (mg/kg) (Mineral Laboratories) | ICP-MS ppm (mg/kg) (Mineral Laboratories) |
|------------|----------------------------------------|--------------------------------------------|--------------------------------------------|
| Lead (Pb)  | 1                                     | 0.1                                        | 0.5                                        |
| Zinc (Zn)  | 4                                     | 1                                          | 1                                          |
| Copper (Cu)| 5                                     | 0.1                                        | 0.2                                        |

#### 2.3. In Situ Measurements with Portable XRF

Measurements were collected at a systematic interval; in this study, 1 meter intervals were used. To investigate the chemical background concentration of the topsoil, measurements were, for each cross-section, collected on the outside or along the rim of the swale crossing over to the other side, as demonstrated by the measuring tape in Figures 1 and 2. Such measurements will provide the background value and weather any build-up contamination is present in the swale. The profiling was executed as cross-sections from the inlet, the deepest part of the swale and further away from the inlet. The profiling approach is shown in Figure 2 and the method was applied to three locations in this study (Figures 2–4), demonstrating the profiling methodology and results.

![Figure 2](image-url) The swale at Heiloo is approximately 70 metre long and 4 metre wide. Three profiles with measurements at each meter were conducted with two different XRF instruments, XL3t#SN67136 and XL3t#SN36372c. Two soil samples for ICP-MS analysis was collected at the same locations at the mid-point of profile 3 for comparison. The soil samples were collected in a Rilsan® bag and a glass jar. A sandblasted stainless-steel spade was used for collecting the soil samples.
Figure 3. The swale at Limmen is approximately 70 metre long and 5 metre wide. Four profiles with measurements at each meter was collected with two different XRF instruments. Two soil samples for ICP-MS analysis was collected at mid-point of profile 1.

Figure 4. The swale at Almelo municipality, is approximately 40 metre long and 10 metre wide. Two measurement profiles with measurements at each meter were collected with XRF instruments.
XL3#SN67136 at P1 and XRF instruments XL3t#SN36372c at P2. A soil sample for ICP-MS analysis was collected at mid-point of Profile 2.

2.4. Soil Sampling for Quality Control

In order to provide quality control of the in situ XRF measurements, at least one soil sample was collected at every location to be analyzed in using inductively coupled plasma mass spectrometry (ICP-MS) in a laboratory. The samples were collected either at the inlet or at the deepest point of the swale. The sample collection followed the EuroGeoSurveys Geochemistry Expert Group Sampling protocol [31].

The soil samples were collected of the topsoil (0–3 cm) with a small, sandblasted, stainless steel garden spade and stored in contaminant-free glass container and RILSAN® bags for ICP-MS lab analysis (bottom right photo in Figure 2). The soil samples were dried for 18 days at 26 Celsius (min 26 °C–max 29 °C), then sieved using a 2 mm plastic sieve before sent for lab analysis. ICP-MS is a type of mass spectrometry which is known for its ability to detect metals with high precision and low detection limits (Table 2). The soil samples with metals were dissolved in acid (Aqua Regia Digestion). Then, the digestion liquid was analyzed with an ICP-MS instrument, as described by Flem et al. [32]. In the lab, the soil samples were then each measured with the portable XRF (XL3#SN67136) five times. The sample material was blended before each measurement to determine the heterogeneity of the sample material.

2.5. Data Collection at Locations

The three locations from the study are described here, providing examples for the method. Detailed characteristics of each swale studied are given in Table 3.

| Location (Municipality/Street) | Heiloo Jan Boltenhof | Limmen Zonndauw | Almelo Ter Kleef |
|-------------------------------|----------------------|-----------------|-----------------|
| Areal use                     | Residential          | Residential     | Residential     |
| Year of construction          | 1999                 | Approximately 2000 | 2002            |
| Estimated storage             | 20 mm                | 15 mm           | 10 mm           |
| [volume m³/connected area m²] |                      |                 |                 |
| Type of infiltration test     | Observation *        | Observation *   | Long term monitoring |
| Infiltration rate (m/day)     | >0.3 m/day *         | >0.3 m/day *    | 0.15-0.49 m/day |
| Soil type                     | Sandy soil           | Clay/organic soil | Sandy soil      |
| More information              | https://climatescan.or g/projects/135/detail | https://climatescan.or g/projects/3/detail | https://climatescan.org /projects/941/detail |
|                              |                       |                 |                 |

*Observation/interview by municipality.

2.5.1. Heiloo

The swale at Heiloo municipality is located in a residential area in the north-western part of the Netherlands (https://climatescan.org/projects/135/detail). This swale is a grassy field, approximately 70 metre long and 4 metre wide with car parking along each side (Figure 2). The surface water inlet is not from one point, but all along both sides. The outlet is located at the north-western point of the swale. Measurements from this swale were collected with two portable XRF instruments (#SN67136 & #SN36372c) used at each of the three profiles for comparable results. Profile 1 (P1) is close to the south-eastern end of the swale, profile 2 (P2) is 10 metre from P1 and profile 3 (P3) is 40 metre from P1 (Figure 2). Duplicate measurements were taken, first on top of vegetation and then in direct contact with topsoil after the removal of vegetation. This was conducted to determine the influence of
vegetation on the results. Further, it was decided to continue measurements only on topsoil because results from in situ topsoil measurements could be correlated to laboratory analysis of soil samples.

2.5.2. Limmen

The swale at Limmen is located in a residential area in the northwestern part of the Netherlands (https://climatescan.org/projects/3/detail). It is a large swale that measures approximately 70 metre long and 5 metre wide (Figure 3). The swale is surrounded by local roads and provides aesthetic effect by creating a park-like setting with grass vegetation. The swale has a clear outer rim, where the grassy field is kept short while the central part of the swale has taller vegetation (Figure 3). The part with tall vegetation is commonly flooded by surplus stormwater, and the deepest part is without vegetation due to frequent water cover. This swale has a one-point inlet at the eastern side and a one-point outlet at the western side. The measurements at the swale were conducted along four profiles with an interval of 10 meters between the profiles. The XRF measurements were conducted from left (south) to right (north) as shown in Figure 3. Profile 1 was measured with two portable XRF instruments (#SN67136 & #SN36372c, Figure 3) to enable comparison of the different instruments.

2.5.3. Almelo

The swale at Almelo municipality is located in a residential area in the eastern part of the Netherlands (https://climatescan.org/projects/941/detail). This swale is a grassy field, approximately 40 metre long and 10 metre wide with residential homes along the northern side and a street at the southern side (Figure 4). The surface water inlet is located at two points, connected to the gutter from a house on the northern side and located at the starting point (0 m) of each profile. The outlet is at the western point of the swale (Figure 4). Two measurement profiles, located 20 metre from each other, were conducted with two portable XRF instruments, #SN67136 at Profile 1 and XRF instruments #SN36372c at Profile 2.

3. Results and Discussion

3.1. Results Heiloo

At the Heiloo location three parallel profiles were measured at a 0, 10, and 30 metre distance (Figures 2 and 5A–C) where all profiles were measured by the two XRF instruments (#SN67136 & #SN36372c). To test out the influence of vegetation, all profiles at location Heiloo were executed with measurements on top of vegetation and directly on soil with vegetation removed, scraped off or just below roots.

The results from all profiles shown in Figure 5A–C indicate that lead (Pb) concentrations are lower in the vegetation than on topsoil. For Zinc (Zn) and Copper (Cu) the results are not so consistent. This is coherent with the findings of lead in vegetation by Zimdahl [33]. Other elements such as sulphur (S), calcium (Ca), potassium (K), chromium (Cr) show the opposite relation and are prone to be elevated in vegetation. Heavy metals appear to be accumulated in the topsoil, which is the media that people are exposed to [2,5,8–10]. Therefore, the uppermost topsoil (0–3 cm) is of interest for this study, and no more measurements on vegetation were conducted.

The results from Heiloo shown in Figure 5A–C do not reveal a consistent pattern. As shown for profile 3, the concentration of Pb from the laboratory analyses on the soil sample (ICP-MS, red dots in Figure 5C) is lower than that in the portable XRF in the field but matches the result from the XRF measured in the lab (marked with X in Figure 5C). The lack of consistency of the pattern, as is found in the two other locations Limmen and Almelo, is most likely due to the lack of clear water inlet and little water being discharged into the swale. There were no signs of the swale being frequently flooded since the swale was evenly vegetated (Figure 2). All values measured for lead, zinc, and copper are below the national intervention value (Table 1).
Figure 5. The profiles at location Heiloo were measured with two different portable XRF instruments, on top of vegetation (green lines) and on topsoil (black and grey lines) where vegetation is removed. Elements in graphs from top to bottom: Pb—Lead, Zn—Zinc, and Cu—copper. See Figure 2 for
location of profiles. (A). Results from profile 1, closest to the inlet (B). Results from profile 2, 10 metres from profile 1. (C). Results from profile 3, 40 metres from profile 1. Two soil samples were collected at midpoint of swale (deepest point) for quality control of method. Results from the soil samples are marked with red dots for ICP-MS analysis and X for the repetitive portable XRF measurements.

3.2. Results Limmen

At the Limmen location, four parallel profiles with 10 metre intervals were measured (Figures 3 and 6A–C). The profiles were measured from one side of the swale to the other, and the results show that for lead and zinc values are low on both outside rims of the swale and increase in the middle of the swale (Figure 6A, B). Values are highest close to the inlet and at the deepest point of the swale, in profile 1 and 2 (Figure 6A, B). For lead and zinc, there is a build-up in the middle part, where the swale is most frequently flooded. This does not apply to copper (Cu), which has no consistent pattern as shown in Figure 6C. The values from the soil sample by lab ICP-MS are higher than in situ XRF measurements (red dots in Figure 6A–C). The lab measurements on the soil sample by the portable XRF (XL3#SN67136) are on the same level as the lab analysis, as shown in Figure 6A–C, marked with X. Values of lead and copper are close to the national background values, but all values measured at Limmen are below intervention levels (Table 1).
Figure 6. Results for lead, zinc and copper from location Limmen. Four profiles were measured on topsoil, where profile 1 was measured with two different portable XRF instruments for comparison. P1 is a cross-section covering the inlet at 0 m, P2 cross-cut the deepest part of the swale at 10 m, where P3 and P4 are located at 20 and 30 m, respectively. The location of the profiles is shown in Figure 3. Two soil samples were collected at the midpoint of the swale in profile 1, close to the inlet for quality control of method. Results from the soil samples are marked with red dots for ICP-MS analysis and X for the repetitive portable XRF measurements. (A). Results for lead (Pb). (B). Results for zinc (Zn). (C). Results for copper (Cu).
3.3. Results Almelo

At the Almelo location, two parallel profiles separated by 20 metre were measured (Figures 4 and 7). This swale is different from those in Heiloo and Limmen, which have a trench shape, where the side facing the residential homes slopes gradually towards the mid-point, while the opposite side extends flat towards the road (Figure 4). The inlet points are positioned at the end of numerous residential gutters, which are the starting point of profile 1 and 2. This is reflected in the results, Figure 7, where the highest metal concentrations in the soil are close to the inlet and decrease further away from the inlet. Copper (Cu) differs from this trend, as the highest concentration is located at the mid-point (Figure 7). The values from the ICP-MS analysis of the soil sample (taken from profile 2) resemble the result from the portable XRF. The values measured for lead, zinc, and copper in this swale are close to or higher than the national background value, but below the intervention values (Table 1).

Figure 7. Results from Almelo. Both profiles start at an inlet (0 m). Profile 1. Profile 1 and 2 are situated approximately 20 metre apart. The soil sample, marked with red dots analyzed by ICP-MS and X for repetitive readings in lab with portable XRF instrument, was collected at mid-point of profile 2. Elements in graphs from top to bottom: Pb—Lead, Zn—Zinc and Cu—copper.
This study shows that the highest concentration of pollutants is close to the inlet(s), based on the portable XRF measurements, which is consistent with the findings of Jones and Davis [10] and Tedoldi et al. [9]. Jones and Davis [10] and Tedoldi et al. [9] also observe that the spatial distribution of pollutants varies over a short distance and can vary greatly within SuDS. The variation of spatial distribution of pollutants in swales is confirmed in this study, where great variations over short distances (1 meter) can be observed. The distribution of the pollutants is controlled by the pathways of the water in the swale, with highest measured values close to the inlet and at the deepest point of the swale, where the occurrence of surplus water is most frequent and has the longest duration. Since the water flow path controls the distribution of the pollutants it is important to locate the profiles in such manner that it covers the inlet and the deepest part of the swale, as exemplified in Figures 2–4. These results confirm that stormwater is a significant contributor of pollutants to SuDS, as shown by Boogaard et al. [5].

This study has focused on the occurrence of heavy metals in the topsoil layer and should be followed up by sampling at greater soil depths and vertical profiling, as demonstrated by Ingvertsen et al. [34], Jones and Davis [10] and Tedoldi et al. [9]. These studies show that heavy metals are trapped in the uppermost layers of the soil, and the concentration decreases with depth in the uppermost 0–30 cm, with the highest concentration in topsoil [9,10,34], as heavy metals in stormwater are prone to be particle-bound [5].

Soil samples were collected and analyzed according to Demetriades and Birke [31], which is a common standard procedure for geochemical mapping as shown by Flem et al. [32]. The variations in the different elements, especially copper (Cu), demonstrate the importance of control samples of soil with laboratory analysis, such as ICP-MS. The use of portable XRF for in situ measuring in the field is increasing and as is evidence of the tool’s reliability, most notably Radu and Diamond [24], Bull, Brown and Turner [35], Turner and Solman [36], Rincheval, Cohen and Hemmings [25] and Turner et al. [26,37]. Researchers analyzed many forms of media, including algae, bark, and soil, and all demonstrate that the results produced by the portable XRF were as reliable as those produced in laboratory, using methods, such as ICP-MS. Based on the comparative analyses presented in [24–26,35–37], we argue that in situ measurements with the portable XRF are valid as a quick-scan method for mapping heavy metal pollutants in SuDS. Radu and Diamond [24] have conducted an extensive study correlating portable XRF results with results from laboratory atomic absorption spectrophotometry (AAS), giving portable XRF credential as a predictable in situ measuring tool.

This work is part of a national study [14] where two national workshops on this research-based study contributed to the re-evaluation of the design or to new guidelines for design, management and maintenance of sustainable urban drainage systems, to improve the water quality of the receiving water bodies [17,38]. Portable XRF measurements provide a rapid in situ analysis of the concentrations of a range of elements, which can help lead to a rapid response to a hazardous waste situation. This has been also pointed out by Kalnicky and Singhvi [11]. The traditional soil samples and lab analysis are time-consuming as well as costly compared to in situ XRF measurements. Therefore, this suggested method using portable XRF provides a foundation to limit area for follow-up investigations including in-depth profiling, as demonstrated by Tedoldi et al. [8,9], Jones and Davis [10] and Ingvertsen et al. [34]. The values of the detected heavy metals described here are well below the Dutch threshold values for intervention for lead, zinc and copper (Table 1) and thereby the XRF quick scan analytical procedure could be used for water management and water quality control to comply with the Water Framework Directive [16] and the CIRIA-The SuDS manual [2].
4. Conclusions

This study presents in situ measurement of heavy metal pollutants in SuDS using portable XRF instruments at three pilot locations. This is a cost and time-efficient method that gives immediate results, as pointed out by Bernick et al. already in 1995 [22]. The instrument’s detection limits are well below threshold values which makes this method suitable for the purpose of evaluating the toxicity of SuDS soil. With this quick-scan method, traditional soil sampling and laboratory analyses become superfluous. This study thus suggests a method for a thorough chemical characterization of heavy metals of topsoil in SuDS.

Three swales have been investigated with the portable XRF method. The results confirm a substantial variation of spatial distribution of heavy metal pollutants; the storm-water inlet and volume control the distribution in swales.

When in the field, the measurement profiles should be adjusted according to the design of the SuDS, making sure that the profiles cover the inlet—the deepest section as well as the outer rim—to represent the highest and lowest possible values of built up of heavy metal pollutants. The measurements along the profiles should be executed systematically with a set interval. Control samples of soil should be collected and analyzed in the laboratory to validate the XRF quick scan.

This quick scan XRF mapping methodology of topsoil will indicate if the topsoil is polluted and whether the concentrations exceed national or international standards. If pollutant values are found above threshold values, a follow-up investigation with more detailed mapping, both with quick scan, soil samples on the surface and in depth, is recommended before clean-up is initiated.

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