Available online www.jsaer.com

Journal of Scientific and Engineering Research, 2018, 5(9):160-167

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Elemental Analysis of Rainwater Samples Using Total X-ray Fluorescence Spectroscopy (TXRF) in Western Sweden

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Abstract Trace elements (TE_S) uptake from rainwater was investigated to evaluate pollution in rainwater samples at two sites in Gothenburg of Chalmers University of Technology (CUT) and Sahlgrenska hospital (Sh), Sweden. Concentrations of zinc (Zn), cooper (Cu), potassium (K), sulfur (S), manganese (Mn), gallium (Ga) and rubidium (Rb) were determined in rain water, using TXRF (Total X-Ray Fluorescence). Analysis of the samples indicated an existing variation in all trace element concentration in rainwater of CUT and Sh. Mains water samples were found to contain significantly higher concentration of zinc and gallium, and significantly lower concentrations of cooper, potassium, sulfur, manganese and rubidium. The mean levels of the elements Zn and Ga on 19 April were higher (0.215, 0.506mg L^{-1}) and (0.560, 0.259 mg L^{-1}) at CUT and Sh respectively. While, the analysis on 23 April, revealed also elevated level of contaminants of Zn and Ga (0.483, 0.575 mg L^{-1}) and (0.390, 1.062mg L^{-1}) at CUT and Sh respectively. However, for the other metals Cu, K, S, Mn and Rb, there was little significant difference in the concentrations Cu (0.130 *vs* 0.043 mg L^{-1}), K (0.060 *vs* 0.007 mg L^{-1}), S (0.013 *vs* 0.005 mg L^{-1}), Mn (0.026 mg L^{-1} *vs* 0.016mg L^{-1}) and Rb (0.066 *vs* 0.018 mg L^{-1}) on 19 April for CHT and Sh respectively. Meanwhile, (0.044 *vs* 0.077 mg L^{-1}), (0.059 *vs* 0.004 mg L^{-1}), (0.026 *vs* 0.025 mg L^{-1}), (0.015 *vs* 0.006 mg L^{-1}) and (0.066 *vs* 0.030 mg L^{-1}) on 23 April at CUT and Sh respectively. Results showed that concentrations of the trace elements vary between the 20 samples. In general, the majority of analyzed samples were significantly below World Health Organization (WHO) limits. Furthermore, high concentration on 19 and 23 April of Zn and Ga were found in both regions compared with other trace elements were indicates a possible contribution from different anthropogenic sources and industrial activities.

Keywords Roof rainwater, Total reflection X-ray fluorescence, Trace elements, Pollution, Sweden.

1. Introduction

Both natural and human activities have affected the water quality of rain water region. Water is the most common and wide spread chemical compounds in nature which is a major constituent of all living creatures. The continuing increase of greenhouse gases in the atmosphere will cause climate change associated with an increased global temperature [1], and urgent warnings from the environmental scientists over the last few decades have increased general public awareness regarding pollution, global warming, and diminishing the fossil fuel emissions. The emission of fossil fuel combustion such as coal and human activities are having their influence on water quality through elevated level of contaminants [2, 3]. In addition, the increasing frequency of fog and haze events in the world has disrupted road and air travel and led to considerable spikes in pollution levels. European urban environments nonpoint source pollution is generated from anthropogenic emission such as constructions or transports [4]. Bio-energy with CO_2 capture and storage could make it possible to achieve negative greenhouse gas emissions [5], NO_2 [6] and SO_2 [7], generally remain in the atmosphere until they are scavenged by precipitation through dissolution by falling droplets. Trace elements play an important role in the life processes, some of the trace elements such as Mn, Cu, Zn and K are essential elements for human health to activate vital functions and biological processes, some of these elements are toxic for the human bio-system, and these toxic elements are present in the air, food and plants, because of increasing industrialization and associated pollution of the biosphere. Hence, it was crucial to conduct a research project on the contamination of TEs in rainwater buildings. Concentrations of trace elements in rain roof water can vary from location to location and from season to season due to variation in the nature and intensity of human activities.

Various techniques used for the elemental characterization of trace elements in rainwater are, inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), total reflection X-ray fluorescence (TXRF), etc. Concerning this issue, there have been many studies which discuss the comparison of the content of trace elements in rain fall water [8-10]. Also, researchers have demonstrated that heavy metals like Cu, Zn and Cd are common pollutants in wet weather and urban waterways [11]. The mean seasonal TDS values of different sub-catchments as well as some trace elements in Latnjavagge area (Sweden) have been calculated [12]. Previous studies for a Qasr Ahmad and Misurata city in Libya catchments have found the concentration of TDS, TH, Cl^-, Na, Mg, Ca and K in rainfall samples at Qsar Ahmad were higher due to the Iron and steel complex sited very near from this region [13]. Furthermore, several studied have dealt with the effect of the concentration of trace elements on the drinking water, A. Båez et al, were study the chemical composition of rainwater in Mexico [14] and Northern Jordan [15], Lubinga Handia made comparative study of rainwater, He found for both direct and harvested, was of a higher quality than water from other sources [16]. In South of Italy Paolo Madonia, et al were analyzed trace elements such as Zn, Cu, Mn, Al, Fe, and Rb by inductively coupled plasma mass spectrometry (ICP-MS) [17].

The main objectives of the present study were as follows: (1) to determine the levels of trace elements (TEs) in the Chalmers University of Technology (CUT) and Sahlgrenska hospital (Sh) at various buildings (2) to compare the levels of TEs with World Health Organization (WHO) for drinking water standards (3) to compare the TE content of Chalmers University of Technology and Sahlgrenska hospital on 19 and 23 April.

2. Materials and Methods

2.1. Sampling Site

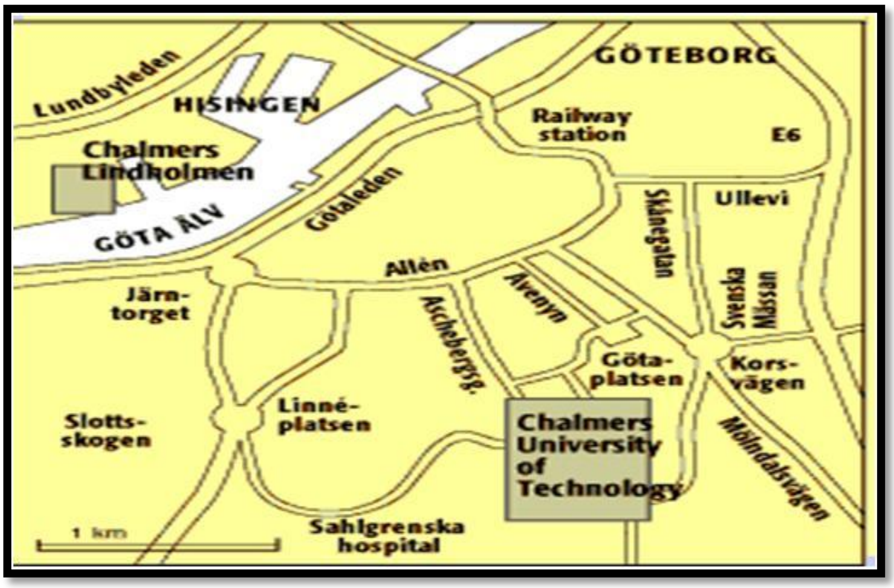

Figure 1: Sampling locations of Chalmers University of Technology (CUT) and Sahlgrenska hospital (Sh) containing roof rainwater analyzed within Gothenburg.

The City of Gothenburg (latitude ~ 58, longitude ~ 12) is Sweden's second largest city with a population of around ½ million, which can increase to 800,000 during the summer tourist season. The monthly average temperature ranges from 0 to 5°C in the winter to 25°C in the summer. The minimum temperature is -15°C in January and the maximum is 35°C in July. The history of city refers to the 350 years ago when King Gustav II Adolf found the *GreatLetter Patent* to Gothenburg in the year 1621. Also, Gothenburg has the largest and best equipped port in Scandinavia. Gothenburg is located on the North Sea, its position in the southwest coast of

Sweden, and a huge river which is called Göta Älv is running through that. There are two drinking water utilities and uses two surface water sources, the river Göta Älv is a source of freshwater for the city of Gothenburg, and a lake system Delsjön, both located at a higher altitude. Moreover, the most common roofing for both apartment buildings and detached houses in Sweden is concrete tile followed by clay tile. The impacts of roofing materials on the concentrations of metals in rainwater [18] finding resulting in significantly higher concentration of zinc. Two certain locations were investigated of a major trace elements in the rainfall water (see Figure 1). The first is Chalmers University of Technology (CHT) and the second is Sahlgrenska hospital (Sh), both the areas are located in close approximately (2-2.5 km) to the city center. Both places are lie at Baltic coast (Figure 2) in Gothenburg and in a residential and commercial areas with vehicular traffic whole day. The two areas were selected based mainly on the good quality of buildings roof to test the rainwater, where several roofs are considered. Samples were collected and analyses at different times during the rainy season. Trace metals (Zn, Cu, K, S, Mn, Ga and Rb) analysis was done at the chemistry laboratory of Swedish university using TRXF. Therefore the objective of investigating was to see whether it could make comparisons regarding of contamination and meet the high quality requirements for health drinking water.

Figure 2: Map of Sweden

2.2. Water Samples

Total Reflection X Ray Fluorescence is suitable for ultra-trace analyses for rain and drinking water [19]. TXRF is a method of excitation for energy dispersive x-ray spectral analysis. It is highly effective in micro and trace analysis of various kinds of samples, especially for environmental rain water [20]. In TXRF, a monochromatic x-ray beam falls on the samples at a very small angle, the instrumental conditions of excitation under grazing incident ($\theta < 0.1°$), less than the critical angle and gets totally reflected after touching the sample. The analysis of pure water samples leads to detection limits at the microliters / milligrams of the samples level. And, each element has its own straight line characterized only by the slope which called sensitivity. Figure 3 represents the experimental data of different sensitivities for many elements were obtained of elements with $Z > 11$ (Z=atomic number). In addition, since the λ and energy of the fluorescence radiation are specific for each element, TXRF analysis is possible because the concentration of each element can be calculated using the intensity of fluorescence radiation.

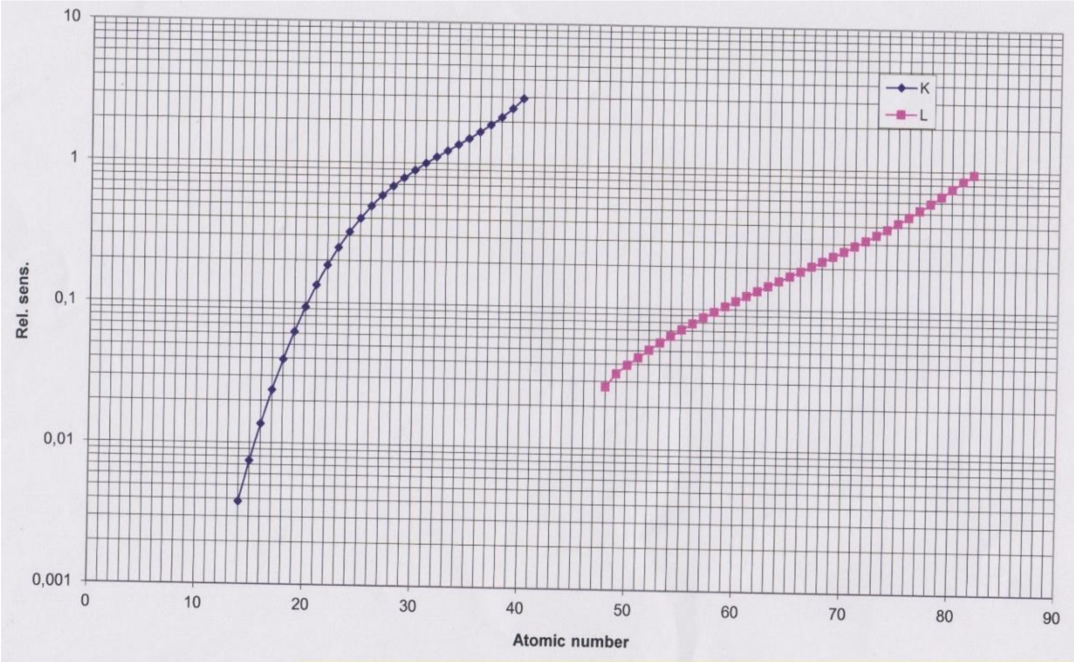

Figure 3: Relative sensitivity of elements for the two excitation modes

In the last two decade, total reflection X-ray fluorescence spectrometry (TXRF) has been shown to be a widely used multi element analytical technique for biological applications [21]. The TXRF technique has been applied to different kinds of samples, such as human serum [22], Soil [23], food [24], and others. Rainwater samples from roofs of residential building in Charmers University of Technology and Sahlgrenska hospital were collected using equipped with a high density polyethylene during rainy season on 19 and 23 April at sites shown in Figure 1. A total of 20 representative roof rain water samples were collected from buildingslocated at the selected sites in different locations at Chalmers University of Technology and Sahlgrenska hospital. Six set of samples were collected directly and these samples are (a) 1RA, B, C are based on 100 µl of sample volume. (b) 1CA, B, C are based on 150 µl of sample volume. (c) 1SA, B, C, D are based on 200 µl of sample volume. (d) 2RA, B, C are based on 200 µl of sample volume. (e) 2CA, B, C are based on 200 µl of sample volume. (f) 2SA, B, C, D are based on 200 µl of sample volume. All samples contains 20 ng analyzed directly with addition of gallium as an internal standard.

3. Results and Discussion

The predict concentration of any element can be determined by applied the simple equation (1), which concisely expressed as follows:

$$Cx = Ci \cdot \frac{Ix / Sx}{Ii / Si} \qquad (1)$$

where C indicates the concentration of the element x, I the net intensity of the spectral lines and S the relative sensitivity of analysis x or the internal standard i.

Results showed that seven trace metals (Zn, Cu, K, S, Mn, Ga and Rb) were detected in all water samples analyzed (20 samples) in this study; all of them are heavy metals except potassium (K). Selected trace elements in rainwater samples collected from different roof buildings from Chalmers University of Technology and Sahlgrenska hospital are summarized in Tables (1-4).

3.1. Chalmers University *versus* Sahlgrenska hospital

3.1.1. Zinc & Gallium Metals

All samples tested showed quantities of all of trace elements analyzed (Table 1 and 2). The concentrate the metals appeared to vary with metal and its location at the two regions on 19 April. In the investigated roof rainwater samples directly from Chalmers university buildings, the zinc metal varied between 0.04 and 0.39 with mean value of 0.22 and standard deviation of 0.13, while the gallium value ranged from 0.20 to 0.77 with a mean value of 0.51 and standard deviation of 0.21. While, the zinc of rainwater samples varied from 0.48 to 0.66 with mean value of 0.56 and standard deviation of 0.07, while the value of gallium ranged between 0.20 and 0.33 with a mean value of 0.26 and standard deviation of 0.05 in the Sahlgrenska hospital. All samples had high levels of Zn and Ga of both regions compared with other metals. Moreover, experimental studies established that high concentrations of some trace elements i.e. Zn, Cu and Mn, could disrupt body functions and have pathogenic effects in human respiratory organs [25].

3.1.2. Comparison of Cooper, Potassium, Sulfur, Manganese, and Rubidium Metals

The mean and standard deviation of the concentration Cu, P, S, Mn and Rb metals are also shown in Table 1 and 2. As we can see from Tables 1 and 2, there is a little significant difference between the mean and standard deviation values indicating that there are differences in the concentrations of the trace elements in the water samples analyzed in this study. Our results of Mean and Standard deviations of Cu (0.130, 0.067) *vs* (0.043, 0.002), K (0.060, 0.067) *vs* (0.007, 0.001), S (0.013, 0.001) *vs* (0.005, 0.001), Mn (0.026, 0.016) *vs* (0.016, 0.004) and Rb (0.066, 0.042) *vs* (0.018, 0.002) for both CUT and Sh respectively on April 19.For Cu,Mn, the allowed WHO limits in the drinking water are 2 mg L^{-1} and 0.4 - 0.5 mgL^{-1}[26], meanwhile for K, 20 mg L^{-1} [27]. Rb has no limit in drinking water by WHO, however, the metal was detected in all rainwater samples analyzed in this study. In addition, the mean concentrations of Zn and Ga metals follow the order, Ga > Zn and Zn > Ga at CUT and Sh respectively, while the standard deviation follow the order that Ga > Zn and Zn > Ga at CUT and Sh respectively. For Zn metal, the allowed WHO limit is 3 mg L^{-1}, while there is no limit for Ga in drinking water according to WHO limits, however, Ga was chosen as internal standard as it was not present in rainwater. Moreover, the possible reason for the highest Zn, Ga (see Tables 1 and 2) and Cu in some samples compared to other elements could be due to vehicles exhaust.

Table 1: Concentrations (mg L^{-1}) of trace elements in rainwater samples at Chalmers University on 19 April (values Max = maximum, Min = minimum, mean and standard deviation)

Samples	Zn	Cu	K	S	Mn	Ga	Rb
1CA	0.165	0.073	0.019	0.012	0.037	0.497	0.032
1CB	0.394	0.075	0.021	0.012	0.029	0.201	0.055
1CC	0.298	0.077	0.024	0.011	0.035	0.313	0.030
1RA	0.039	0.240	0.048	0.015	0.004	0.770	0.061
1RB	0.074	0.113	0.040	0.015	0.004	0.734	0.065
1RC	0.320	0.206	0.209	0.016	0.049	0.522	0.158
Mean	0.215	0.130	0.060	0.013	0.026	0.506	0.066
SD	0.134	0.067	0.067	0.001	0.016	0.205	0.042
Max	0.394	0.240	0.209	0.016	0.049	0.770	0.158
Min	0.039	0.073	0.021	0.011	0.004	0.201	0.030

1=Collected April 19, C=Chalmers roof samples, R=Rain and A, B, C, D = replicates.

Table 2: Concentrations (mg L^{-1}) of trace elements in rainwater samples at Sahlgrenska hospital on 19 April (values Max = maximum, Min = minimum, mean and standard deviation)

Samples	Zn	Cu	K	S	Mn	Ga	Rb
1SA	0.560	0.041	0.010	0.005	0.018	0.251	0.019
1SB	0.538	0.041	0.007	0.006	0.014	0.250	0.015
1SC	0.480	0.045	0.006	0.006	0.029	0.333	0.020
1SD	0.664	0.047	0.007	0.006	0.006	0.204	0.021
Mean	0.560	0.043	0.007	0.005	0.016	0.259	0.018
SD	0.066	0.002	0.001	0.001	0.004	0.046	0.002
Max	0.664	0.047	0.010	0.006	0.029	0.333	0.021
Min	0.480	0.041	0.006	0.005	0.006	0.204	0.015

1=Collected April 19, C=Chalmers roof samples, R=Rain and A, B, C, D = replicates

3.2. Chalmers University *versus* Sahlgrenska Hospital

3.2.1. Zinc & Gallium Metals

Table 3 and 4 summarize the concentrations of trace elements on April 23. The variation of Zn concentration in rainwater ranged from (0.104 to 1.095) with a mean value of 0.483, while Ga ranged between (0.215 and 1.086) with a mean value of 0.575 at CUT. Meanwhile, the concentration of Zn between (0.368 - 0.444) with mean value of 0.390 and Ga between (0.984 and 1.153) with mean value of 1.062, for Sh. According to Table 3, there was significant variation during different location samples, however in Chalmers and Sahlgrenska the highest mean of Zn and Ga metals were detected (0.483, 0.575) and (0.390, 1.062) respectively.

Table 3: Trace element concentrations in roof rainwater samples in Chalmers on 23 April in mg L^{-1}

Samples	Zn	Cu	K	S	Mn	Ga	Rb
2CA	0.104	0.059	0.020	0.050	0.022	1.086	0.053
2CB	0.142	0.071	0.022	0.045	0.023	0.975	0.046
2CC	0.110	0.059	0.024	0.039	0.018	0.924	0.034
2RA	1.095	0.017	0.072	0.010	0.008	0.252	0.085
2RB	0.594	0.031	0.113	0.007	0.012	0.322	0.095
2RC	0.855	0.027	0.105	0.007	0.010	0.215	0.088
Mean	0.483	0.044	0.059	0.026	0.015	0.575	0.066
SD	0.392	0.019	0.039	0.018	0.005	0.374	0.023
Max	1.095	0.071	0.113	0.050	0.023	1.086	0.095
Min	0.104	0.017	0.020	0.007	0.008	0.215	0.034

2=Collected April 23, R=Rain, C=Chalmers roof sample and A, B, C, D=Replicates

Table 4: Trace element concentrations in roof rainwater samples in Shilgrenska hospital on 23 April in mg L^{-1}

Samples	Zn	Cu	K	S	Mn	Ga	Rb
2SA	0.378	0.079	0.005	0.026	0.002	1.062	0.026
2SB	0.444	0.074	0.002	0.019	0.015	1.153	0.031
2SC	0.368	0.081	0.004	0.025	0.002	1.049	0.031
2SD	0.373	0.074	0.005	0.030	0.005	0.984	0.034
Mean	0.390	0.077	0.004	0.025	0.006	1.062	0.030
SD	0.030	0.003	0.001	0.003	0.005	0.060	0.003
Max	0.444	0.081	0.005	0.030	0.015	1.153	0.034
Min	0.368	0.077	0.002	0.019	0.002	0.984	0.026

2=Collected April 23, R=Rain, C=Chalmers roof sample and A, B, C, D=Replicates

3.2.2. Comparisons of Cooper, Potassium, Sulfur, Manganese, and Rubidium Metals

Variations of trace elements contents in the collected rainwater from the studied locations is shown in Table 4, all the trace elements cooper, potassium, sulfur, manganese and rubidium found in CUT and Sh were with few exceptions are lower than the other metals Zn and Ga studied /acceptable based on WHO [27].

The results indicated that concentrations all measured metals (except the amount of cooper in all samples 2SA, 2SB, 2SC and 2SD) were lower than other metals, however the highest mean concentrations of cooper, potassium, sulfur, manganese and rubidium were equal to 0.077, 0.004, 0.025, 0.006, and 0.030 mg L^{-1}

respectively. The concentrations of these metals are almost the same or less than the values reported in Table 3. Levels of cooper, potassium, sulfur, manganese and rubidium varied significantly between samples from sites with different roof buildings. Copper levels could be impacted by air pollution at some sites i.e., 2SA, 2SB, 2SC and 2SD, while potassium concentrations may have been impacted by the proximity of some sites to the Atlantic Ocean and Baltic Sea, and significantly low concentrations of manganese in all samples may be due to the agricultural use or from dirty roof buildings.

4. Conclusion

1. The variations in the concentrations of trace elements Zn, Cu, K, S, Mn, Ga and Rb in Chalmers University of Technology (CUT) and Sahlgrenska hospital (Sh) were investigated using Total X ray Fluorescence.
2. The studied water samples recorded to display elevated Zn and Ga concentrations above the other metals Cu, K, S, Mn and Rb.
3. Low detection limits were obtained for the metals Cu, K, S, Mn and Rb.
4. On 19 April, the trace elements were in the order of Ga > Zn > Cu > Rb > K > Mn > S for Chalmers University of Technology, while Zn > Ga > Cu > Rb > Mn >K > S for Sahlgrenska hospital.
5. On 23 April, the mean concentrations of trace elements were in the order of Ga > Zn > Rb> K > Cu > S > Mn, while, Ga > Zn > Cu> Rb > S > Mn > K for CUT and Sh respectively.
6. Results showed that all metal concentrations are significant different in the 20 samples analyzed in this study, this indicated that these 20 water samples are different from each other in terms of metal concentration, which confirms the locational variations of samples.
7. TXRF proved to be attractive and useful for trace elements analysis.

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