CONCENTRATION AND DISTRIBUTION OF ARSENIC, CADMIUM, LEAD AND MERCURY IN THE GROUNDWATER BODIES OF CYPRUS

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Abstract

The concentration of arsenic, cadmium, lead and mercury in Cyprus' groundwater bodies is monitored under the Water Framework Directive, 2000/60/EC and in relation to the Directive 2006/118/EC "on the protection of groundwater against pollution and deterioration". The concentration, range and distribution of these metals, from 98 monitoring stations, for the period 2007-2013 (991 samples), covering 19 groundwater bodies of Cyprus are being presented and discussed. Preliminary evaluation dictates that there aren't any severe pollution issues from arsenic, cadmium, lead or mercury in Cyprus' groundwater bodies. Elevated concentrations of these metals are usually periodical, not persistent and in the majority of cases bellow the corresponding drinking water standards. Nonetheless, further monitoring and investigation is needed especially in the cases of arsenic and lead to better understand contributing sources.

1. Introduction

The first integrated hydrogeological study in Cyprus was completed in 1970 (*United Nations, 1970*) in which all major aquifers of the island were investigated. In the 1980s an extensive hydrochemical study was carried out with only minor emphasis on heavy metals, however (*Wagner et. al. 1986 and Wagner et. al. 1987*). In 1990s and early 2000s several studies have investigated, among others, the concentration and distribution of heavy metals in groundwater of specific areas (*Constantinou et al 1997, Smith et all 1997, Constantinou 2004*).

For the purpose of the implementation of the Water Frame Directive 2000/60/EC, one river basin district was identified for the whole Cyprus. Furthermore, 20 groundwater bodies have been delineated (Republic of Cyprus, March 2005). The code and the name of the groundwater bodies are: CY_1 - Kokkinochoria, CY_2 - Aradippou, CY_3 - Kiti – Pervolia, CY_4 - Softades – Vasilikos, CY_5 - Maroni, CY_6 - Mari – Kalo Chorio, CY_7 - Germasogeia, CY_8 - Lemesos Town, CY_9 - Akrotiri, CY_10 - Paramali – Avdimou, CY_11 - Pafos, CY_12 - Letymvou – Giolou, CY_13 - Pegeia, CY_14 - Androlikou, CY_15 - Chrysochou – Gialia, CY_16 - Pyrgos, CY_17 - Central and Western Mesaoria, CY_18 - Lefkara – Pachna, CY_19 - Troodos and CY_20 - Pendadaktylos. Groundwater body CY_20 falls entirely in the area where the Goverent of the Republic of Cyprus does not have effective control (area occupied by Turkish troops) and therefore there are no available data. An integrated fresh water monitoring network has been developed (Republic of Cyprus, March 2007) consisting of 88 monitoring stations (85 wells and 3 springs) and threshold values have been assigned for all groundwater bodies, for all elements listed in the Part B, of the Annex II, of the Directive on the protection of groundwater against pollution and deterioration, 2006/118/EC, including arsenic, cadmium, lead and mercury.

In this paper, data on the concentration of trace metals arsenic, cadmium, lead and mercury, from 98 monitoring stations (95 groundwater and 3 surface water) for the period 2007-2013 (991 samples), covering 19 groundwater bodies of Cyprus are being presented and discussed. These metals are considered highly toxic and may be dangerous for both the environment and humans (WHO, 1993).

2. Methodology

Samples were collected twice a year, from a total of 98 monitoring stations (95 wells and 3 springs) through the period 2007-2013, covering 19 out of the 20 groundwater bodies of Cyprus. In total, 991 samples have been collected, 700 by the Cyprus Geological Survey and 291 by the Water Development Department staff. With some exceptions, the collected samples were filtered with 0.45μm filters and acidified on site with double distilled nitric acid and analyzed, among others, for arsenic, cadmium, lead and mercury, by the Cyprus State Laboratory. The lower detection limit(s) (LoD) was 0.3 μg/l for arsenic, 0.15 to 0.2 μg/l for cadmium, 1 to 1,5 μg/l for lead and 0,2 to 0,5 μg/l for mercury. For the purposes of statistical analysis, half of the corresponding LoD values were used in the cases where metal concentrations were below the LoD.

The data are presented in the form of tables, thematic maps, box and whisker plots and histograms. Thematic maps (Figure 1 to Figure 4) present metal average and maximum concentrations for each monitoring station separately for the whole of the monitoring period**.** Metal concentrations for each trace metal, from all monitoring stations, pertaining to each groundwater body, are presented in Table 1 and in the box and whisker plots (Figure 5 – Figure 8). The box part of a plot represents the interquartile range (IQR). The lower edge of a box is the 25^{th} percentile (Q_1) of the data and the upper edge of a box is the 75^{th} percentile (Q_3) of the data. IQR is the result of $Q_3 - Q_1$. The whisker part was created using error bars in excel. The upper whisker starts at (Q_3) and extends upward to Q_3+1.5(IQR) or the maximum value, whichever is lower. The lower whisker starts at (Q_1) and extends downward to Q_1-1.5(IQR) or the minimum value, whichever is greater. The box and whisker plot shows only the minimum and maximum outlier**.**

The averaged concentration values per station, their statistical analysis, distributions and ranges are also presented in Table 2 and in the form of histograms for the whole of the island (Figures 9 to 12).

3. Results

A total number of 991 samples were collected during the monitoring period, 953 of which were analyzed for arsenic, 991 for cadmium, 988 for lead and 936 for mercury. The maximum, average and median values are calculated, evaluated in this paper and presented in the following table, grouped by groundwater body (Table 1).

Table 1: Statistical data for AS, Cd, Pd and Hg, by groundwater body

GWB	Arsenic (As)				Cadmium (Cd)				Lead (Pd)				Mercury (Hg)			
	n	max	ave	med	n	max	ave	med	n	max	ave	med	n	max	ave	med
CY 1	48	9.49	3.11	2.01	50	0.78	0.16	0.14	51	7.72	0.98	0.75	49	0.30	0.15	0.10
CY 2	23	8.60	3.30	2.77	24	0.57	0.19	0.25	24	8.18	1.19	0.75	22	0.25	0.20	0.25
CY 3	38	10.47	1.85	1.17	40	0.82	0.20	0.15	41	12.03	1.51	0.75	39	0.30	0.17	0.10
CY 4	36	7.14	1.24	0.50	38	0.34	0.16	0.15	38	2.68	0.74	0.75	33	0.25	0.17	0.10
CY 5	28	5.59	1.38	1.11	28	0.71	0.19	0.25	28	8.32	1.10	0.75	28	0.25	0.19	0.25
CY 6	23	6.80	3.10	3.32	23	0.25	0.18	0.25	23	3.30	0.92	0.75	23	0.25	0.20	0.25
CY 7	35	1.50	0.54	0.50	37	0.71	0.16	0.10	37	4.64	0.63	0.75	35	0.25	0.16	0.10
CY 8	24	2.55	0.73	0.50	24	0.61	0.16	0.16	23	28.25	4.25	0.75	22	0.25	0.18	0.18
CY 9	83	4.06	0.92	0.50	88	1.31	0.17	0.15	87	13.56	1.11	0.75	81	0.40	0.17	0.10
CY 10	33	2.50	0.53	0.50	34	0.91	0.20	0.25	34	7.49	1.03	0.75	32	0.25	0.18	0.25
CY 11	73	8.37	1.25	0.50	75	0.84	0.15	0.08	75	5.71	0.75	0.75	74	0.25	0.16	0.10
CY 12	25	38.35	5.84	2.10	26	0.41	0.17	0.25	26	2.04	0.76	0.75	24	0.25	0.19	0.25
CY 13	33	6.70	2.05	1.08	34	0.56	0.16	0.20	32	8.90	1.21	0.75	34	0.30	0.18	0.25
CY 14	22	12.20	1.00	0.50	22	0.25	0.18	0.25	22	8.08	1.15	0.75	22	0.25	0.20	0.25
CY 15	35	6.01	1.46	1.12	37	0.49	0.15	0.08	37	5.04	0.84	0.75	35	0.25	0.16	0.10
CY 16	28	0.75	0.38	0.50	28	0.87	0.19	0.25	28	15.38	1.31	0.75	28	0.25	0.19	0.25
CY 17	108	47.75	3.08	1.33	113	1.53	0.14	0.08	114	17.21	1.49	0.75	103	1.00	0.17	0.10
CY 18	84	12.79	2.79	2.22	87	0.64	0.17	0.25	86	29.06	1.24	0.75	84	0.25	0.18	0.25
CY 19	174	2.96	0.53	0.50	183	2.57	0.18	0.10	182	35.08	1.44	0.75	168	0.40	0.17	0.10
All	953	47.75	1.71	0.50	991	2.57	0.17	0.15	988	35.08	1.23	0.75	936	1.00	0.17	0.10

The averaged concentration values per station, their statistics, distributions and ranges are presented in Table 2 and in the form of histograms for the whole of the island (Figures 9 to 12).

Table 2: Statistical data for averaged values, for each monitoring station

Element	As	Pb	Cd	Hg
Population	98	98	98	98
Minimum Value	0.15	0.46	0.02	0.10
Maximum Value	32.80	22.57	0.55	0.36
Range	32.65	22.11	0.53	0.26
Mean	1.90	1.40	0.17	0.18
Standard Deviation	3.63	2.33	0.06	0.04
Standard Error	0.37	0.23	0.01	0.00
Median	0.90	0.87	0.17	0.17
Sum	186.40	137.45	17.03	17.52
Sum of Squares	1633.54	719.38	3.35	3.28
Variance	13.19	5.43	0.00	0.00
Skewness	6.53	7.74	2.13	1.29
Kurtosis	51.02	66.64	10.79	3.91

The geographical distribution for the average and maximum concentrations of arsenic, cadmium, lead and mercury, for each of the 98 monitoring stations, for the whole of the monitoring period, are presented in the following thematic maps (Figures 1 to 4).

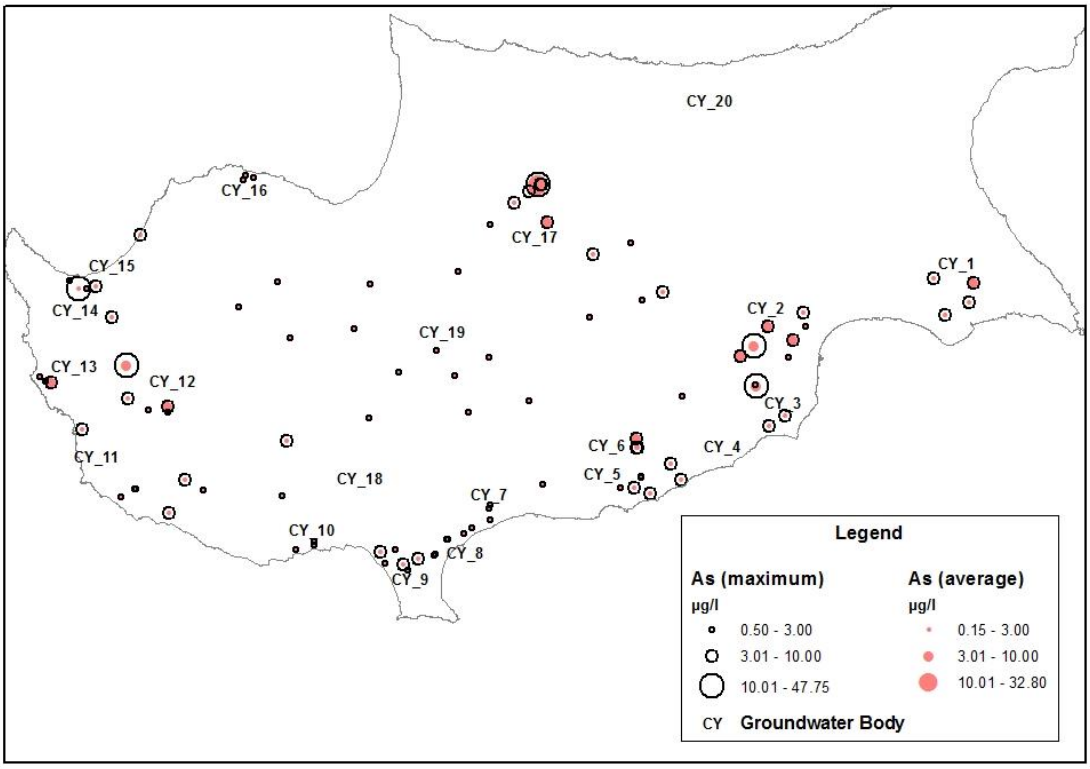

Figure 1: Arsenic concentration distribution in the groundwater bodies of Cyprus

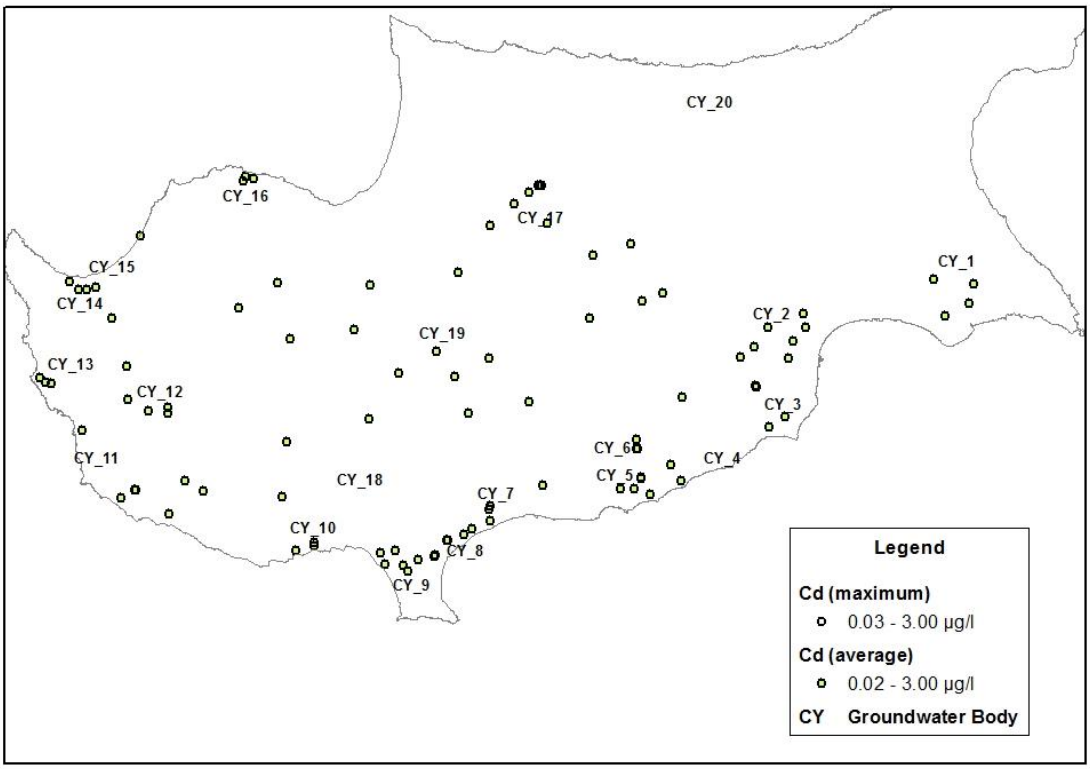

Figure 2: Cadmium concentration distribution in the groundwater bodies of Cyprus

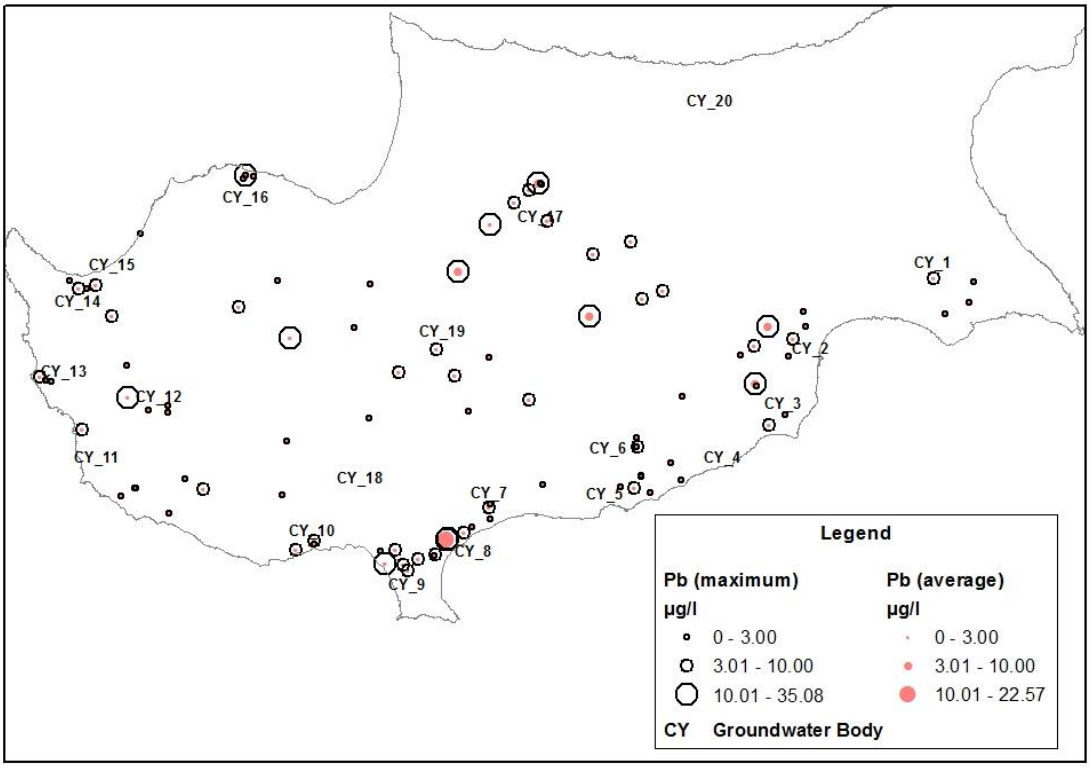

Figure 3: Lead concentration distribution in the groundwater bodies of Cyprus

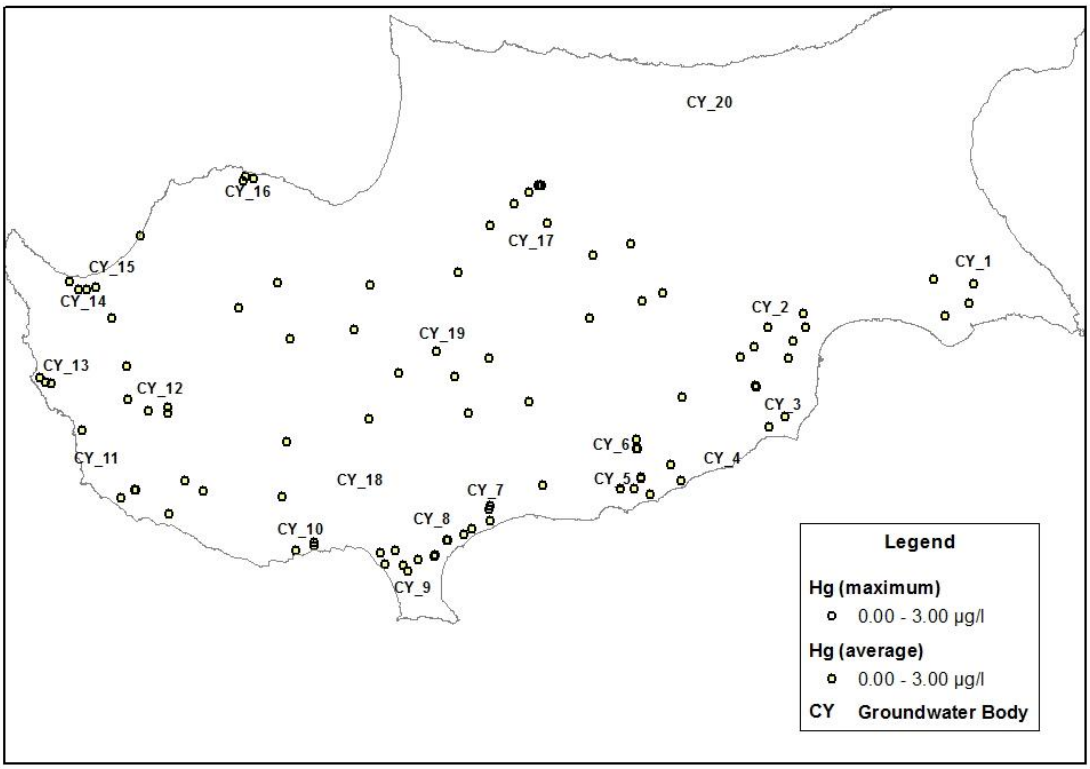

Figure 4: Mercury concentration distribution in the groundwater bodies of Cyprus

Metal concentrations for each trace metal, from all monitoring stations, pertaining to each groundwater body, are presented in the following box and whisker plots (Figures 5 to 8).

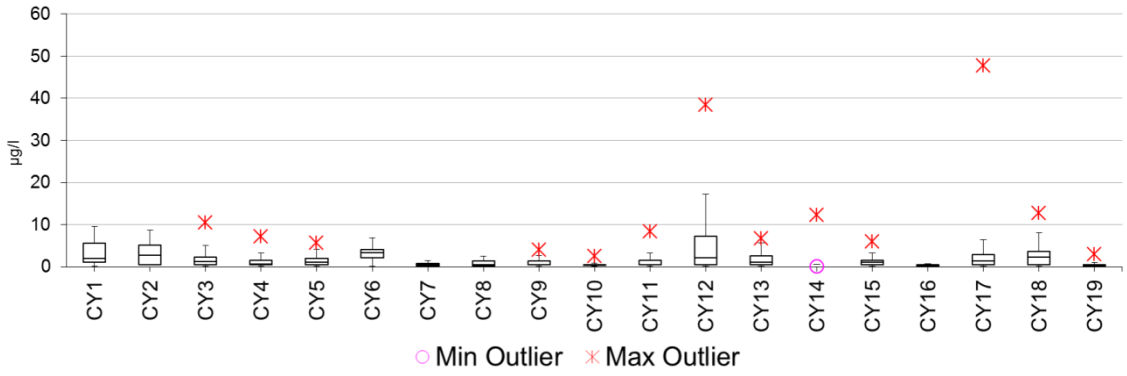

Figure 5: Box and whisker plot for arsenic concentration

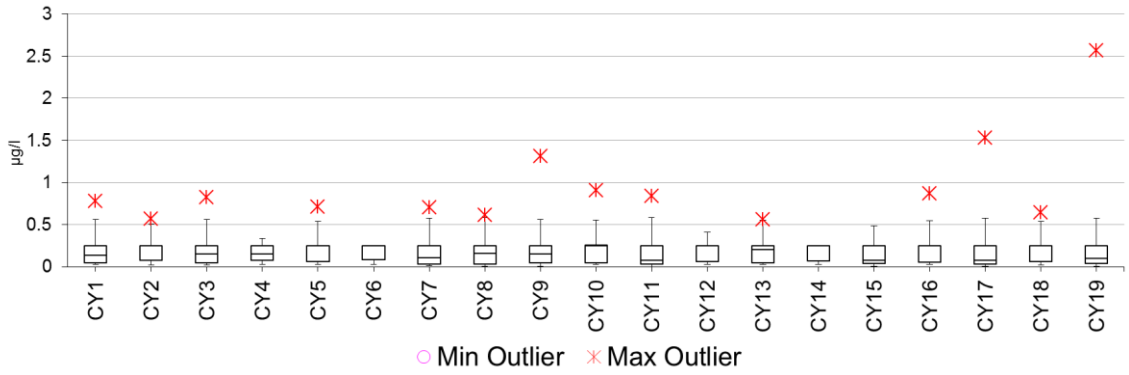

Figure 6: Box and whisker plot for cadmium concentration

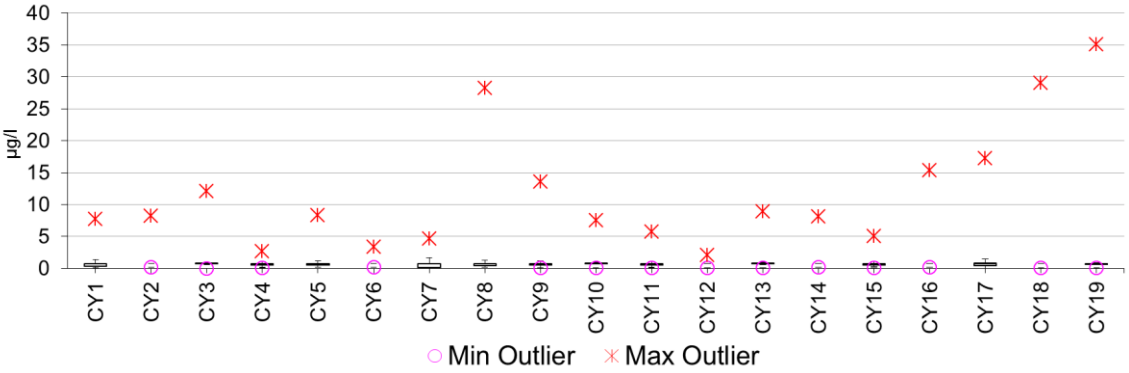

Figure 7: Box and whisker plot for lead concentration

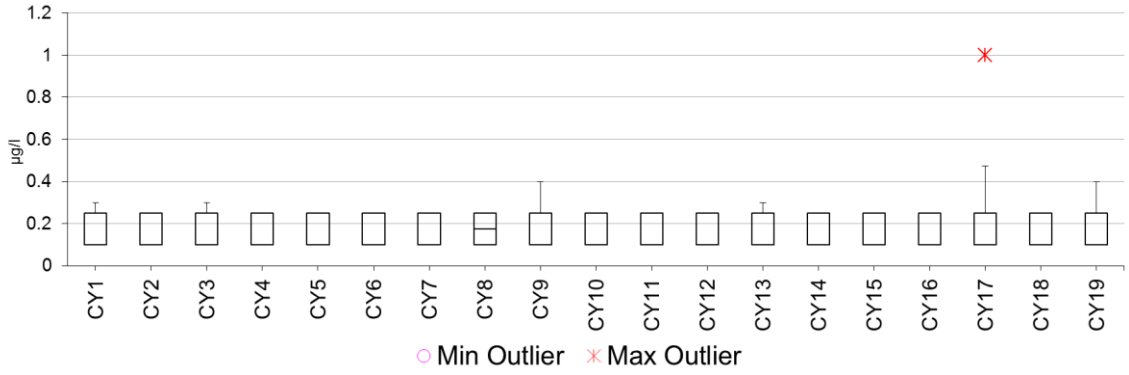

Figure 8: Box and whisker plot for mercury concentration

The averaged concentration values per station, their distributions and ranges are presented in the form of histograms for the whole of the island (Figure 9 to 12).

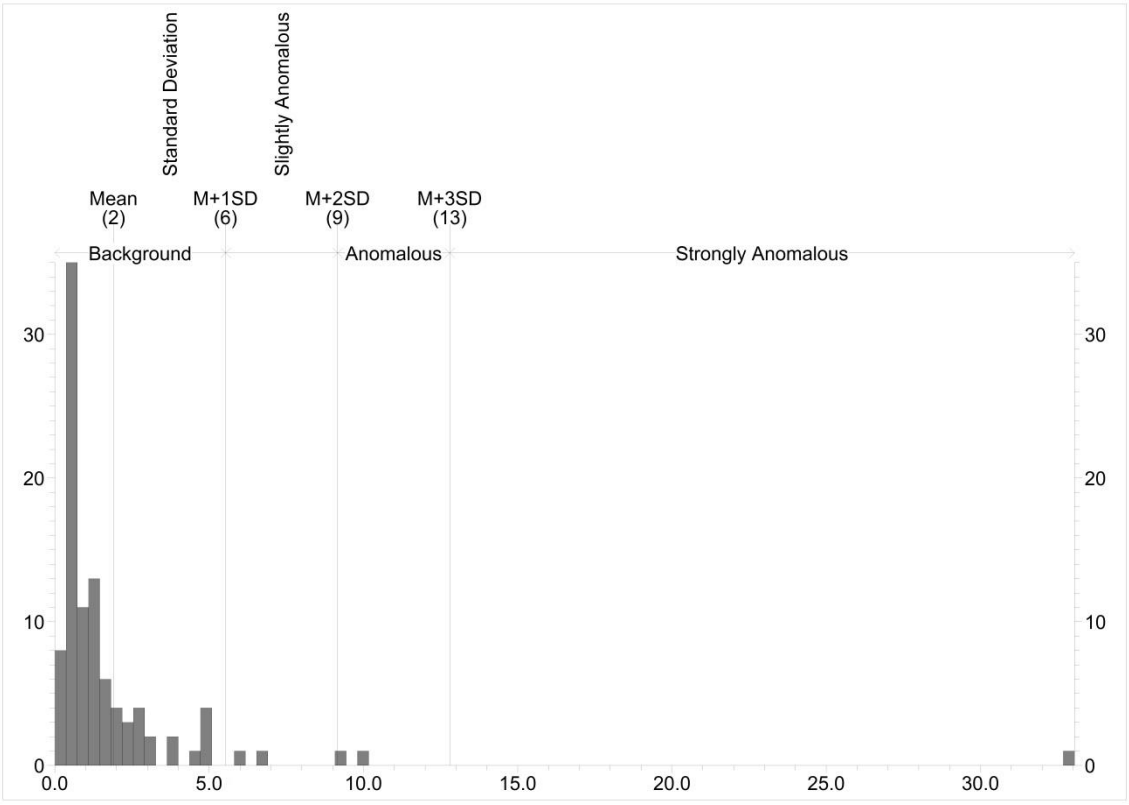

Figure 9: Histogram for arsenic concentrations in groundwater

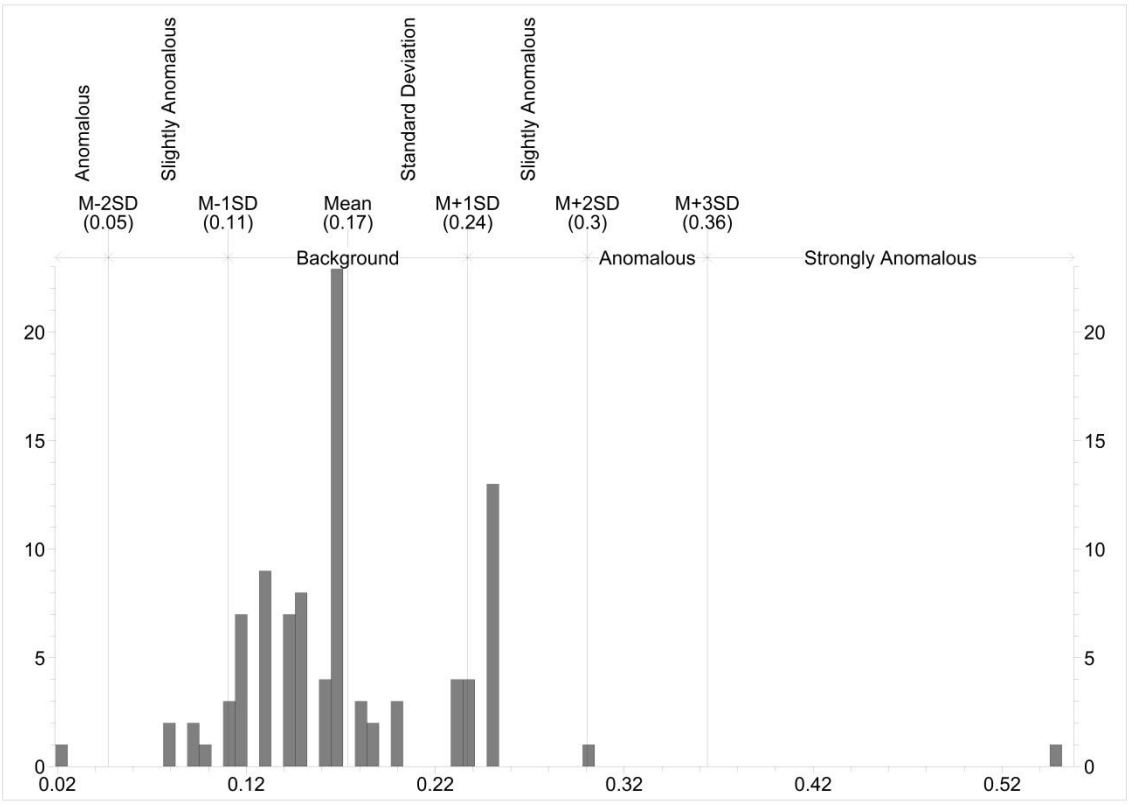

Figure 10: Histogram for cadmium concentrations in groundwater

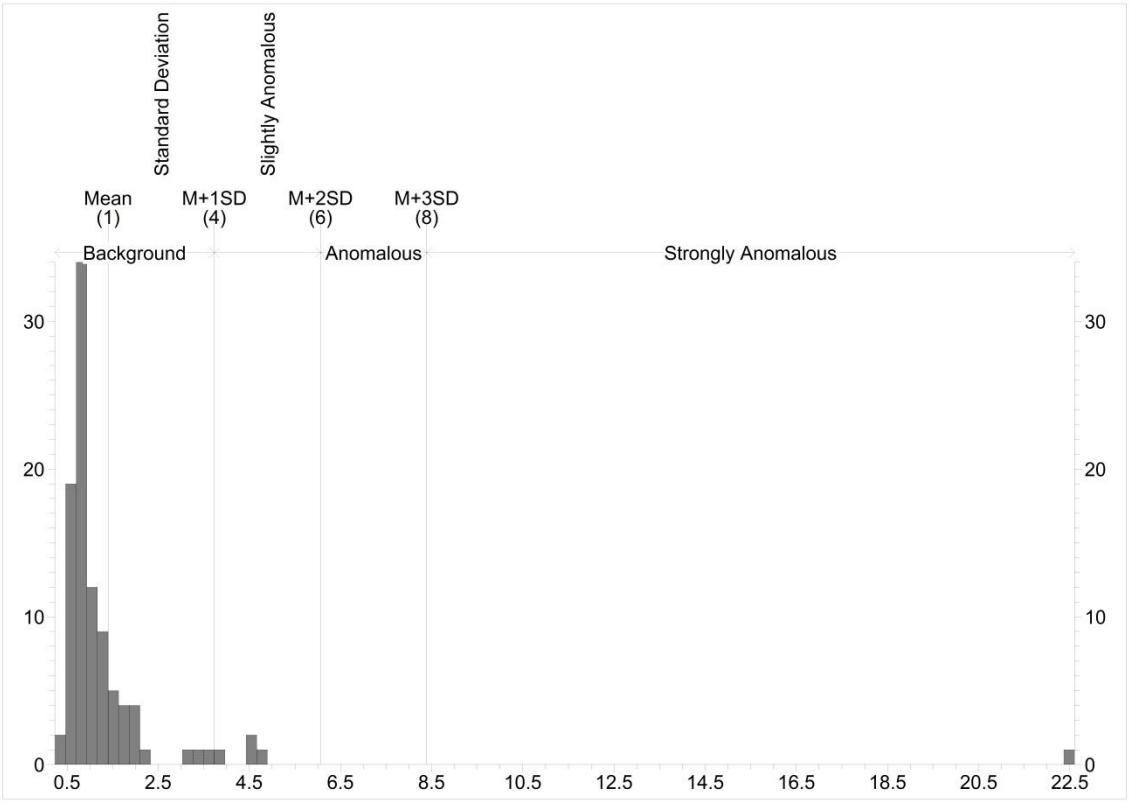

Figure 11: Histogram for lead concentrations in groundwater

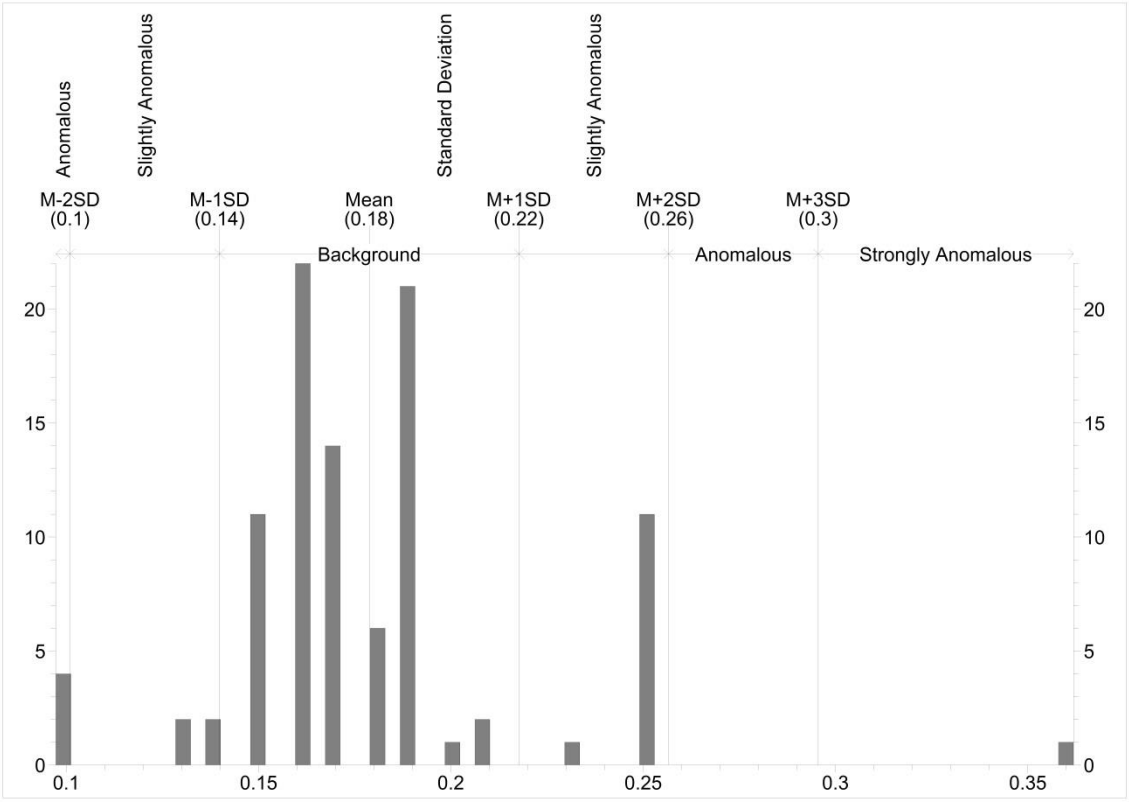

Figure 12: Histogram for mercury concentrations in groundwater

4. Discussion

The averaged values of the metal concentrations from the 98 monitoring stations are used as the bases for our interpretation here. The average arsenic concentration values in groundwater range from 0.15 to 32.8 μg/l (Table 1) whereas the mean and the standard deviation is 1.90 and 3.63 μg/l, respectively (Figure 1 & Figure 9). No discernible strong correlation exists between arsenic concentrations and the concentrations the other three trace metals. The distribution of arsenic concentration per groundwater body is shown in the box and whisker plots (Figure 5). With the exception of the gypsum aquifer (Constantinou, 2004) of CY 12, the ranges of arsenic concentration, in all other groundwater bodies, plot bellow the drinking water standard of 10 μg/l (Figure 5 & Table 1). However, groundwater bodies CY 1, CY 2, CY 6 and CY 12 exhibit a range of arsenic concentration close to or above standard one deviation of the averages (Figure 5). In addition, CY 3, CY 11, CY 14 and CY 17 show outliers above such standard deviation and in some cases above the drinking water standard. In the clastic aquifer CY 1, all 4 monitoring stations show periodical, not persistent slightly elevated arsenic concentrations. Although further monitoring and investigation is needed, the periodically slightly elevated arsenic concentrations in groundwater are most likely to be attributed to anthropogenic sources, namely agriculture and husbandry. In the gypsum aquifer of CY 2 only one of the three stations shows slightly elevated arsenic concentrations which is however periodical and not persistent. A similar situation applies for the gypsum aquifer of CY 12 (Figure 1 & Table 1). Arsenic mobilization from clay or organic rich layers in the gypsum aquifers may be possible and this process may contribute to the observed arsenic fluxes in these cases. Nonetheless, further monitoring and investigation is needed in order to reach to a safe conclusion. In the calcium carbonate matrix clastic aquifers of CY 6 and CY 18, the distribution of arsenic concentration is very close to or exceeding standard deviation of the averages. Although further investigation is needed a possible partial natural contribution from deeper groundwater percolation needs to be taken into account. In the case of the alluvium aquifer CY 3 (Constantinou, 2004) the distribution and range of arsenic values are below the standard deviation of the averaged and the slightly higher concentrations are only restricted to one station and thus considered outliers; nonetheless, pressures from urbanization, agriculture and seawater intrusion are exerted on this aquifer and might constitute contributing factors. In the case of the alluvial aquifer of CY 11, distribution and range of arsenic values are also bellow standard deviation of the averages. Outliers are only restricted to one station and they are not persistent. In the clastic aquifer of CY 17, the distribution of arsenic concentration is bellow standard deviation but a number of high values are seen in a specific area (Figure 1), with increased anthropogenic pressures such as poultry, husbandry, agriculture and urbanization thus rendering further monitoring and investigation necessary.

In conclusion, to a great extend the distribution of arsenic concentrations in Cyprus' groundwater bodies plot bellow the drinking water standard of 10 μg/l and in the majority of the cases bellow the standard deviation of the averages (Figure 1 & Figure 9). The sources of arsenic fluxes need to be further investigated although anthropogenic sources appear to be the primary contributor. Periodical, slightly elevated arsenic concentrations in gypsum aquifers may be naturally occurring and need to be further investigated.

The average cadmium concentration values in groundwater range from 0.02 to 0.55 μg/l whereas the mean and the standard deviation is 0.17 and 0.06 μg/l, respectively (Figure 2 & Figure 10). The distribution and range of cadmium concentration per groundwater body, shown in Figure 6, plot bellow 1 μg/l and bellow the drinking water standard of 5 μg/l; maximum values rarely excess 1 μg/l and they are thus considered as outliers. In conclusion, no real issues appear to exist with cadmium concentrations in Cyprus' groundwater.

The average lead concentration values in groundwater range from 0.46 to 22.57 μg/l whereas the mean and the standard deviation is 1.4 and 2.33 μg/l, respectively (Figure 3 & Figure 11). The distribution and range of lead concentrations per groundwater body, shown in Figure 7, plot bellow the drinking water standard of 10 μg/l and the one standard deviation of the averages. Seven groundwater bodies show maximum values above the drinking water standard and despite the fact that these values are generally not persistent and thus regarded as outliers, extreme

caution must be exercise in further monitoring and investigating possible pollution sources; of anthropogenic origin such as urbanization and possible direct infiltration.
The average mercury concentration values in groundwater range from 0.01 to 0.36 μg/l whereas the mean and the standard deviation is 0.18 and 0.04 μg/l, respectively (Figure 4 & Figure 12). The distribution and range of mercury concentrations per groundwater body, shown in Figure 8, plot within or bellow one standard deviation and no single value exceeds the drinking water standard of 1 μg/l. In view of the above, no real issues appear to exist with mercury concentrations in Cyprus' groundwater.
In conclusion, it appears that there aren't any severe pollution issues from arsenic, cadmium, lead and mercury in Cyprus' groundwater bodies. In addition, there is no any clear correlation of the concentration of these metals to geology. Elevated concentrations of these metals are usually periodical, not persistent and in the majority of cases bellow the corresponding drinking water standards. Nonetheless, further monitoring and investigation is needed especially in the cases of lead and arsenic to better understand contributing sources.

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6. References

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