A Thallium-Contaminated Drinking Water Supply in an Abandoned Mining Area: an Environmental Health Hazard

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Abstract Sulphide ores in abandoned mine sites from the southern Apuan Alps (Italy) are known to carry significant thallium levels. In September 2014, thallium contamination was found in the tap water distributed in Valdicastello Carducci Village (southern Apuan Alps) (from 2 to 10 μg/L). The thallium-contaminated water that fed the aqueduct of this area originates from a spring located very close to the abandoned mining sites. In the present study, to assess the impact of thallium exposure in the inhabitants who used the contaminated tap water, thallium was quantified in hair, urine and saliva samples.

Key words Thallium, Human Contamination, Biomonitoring, Water Pollution, Abandoned Mines

Introduction

Thallium (Tl) is a non-essential, highly toxic element. Its poisonousness to mammals is considered comparable to that of mercury, cadmium or lead (Rodriguez-Mercado et al. 2013).

The ingestion of Tl-contaminated drinking water represents the most likely pathway of exposure for humans. The U.S. Environmental Protection Agency (EPA) poses a maximum concentration level (MCL) of 2 μg/L for drinkable water. Hence, contamination processes of waters and soils by Tl may have serious consequences for human health.

A recent geological study (Biagioni et al. 2017) showed the presence of Tl at high concentrations (up to 37 μg/L) in a groundwater spring that fed the aqueduct of Valdicastello Carducci village and part of the aqueduct of Pietrasanta town (southern Apuan Alps). The source of Tl has been identified in the Tl-bearing pyrite ores occurring in the area. The spring is indeed located between two abandoned mines, in an area characterized by the widespread occurrence of baryte, pyrite, magnetite, hematite, and iron hydroxide mineralizations (Biagioni et al. 2017). Recent geological studies show Tl concentration levels up to ≈600 μg/g in the pyrite ores of the study area (D'Orazio et al. 2017). Pyrite ores are subjected to both biotic and abiotic oxidation processes releasing Tl and other metals (e.g. Fe, As, Sb, Pb, Zn, Cd etc.) into the aquatic environment. Acid drainages from the abandoned mining tunnels typically contain 200-1000 μg/L of Tl, while some very acidic (pH = 1.5-2.0) water ponds inside the tunnels can reach even more extreme Tl levels, up to 9000 μg/L.

In September 2014 a substantial Tl contamination was also found in tap water distributed in Valdicastello Carducci village and in part of Pietrasanta town and in October 2014 local authorities replaced the contaminated spring with a Tl-free source. A geochemical survey of the contaminated spring is currently in progress in order to assess the origin of Tl contamination in the spring.

The goal of our work was to assess the impact of Tl exposure as a result of tap water contamination in Valdicastello Carducci and Pietrasanta. For this purpose, we quantified Tl levels in 45 saliva, 150 urine and 318 hair samples from the population living in the contaminated area and thallium values found in biological samples were correlated with Tl concentrations found in tap water. Thallium concentrations in the different matrices was measured by inductively coupled plasma—mass spectrometry (ICP-MS). Urine and hair represent convenient matrices due to their straightforward sample collection, sufficient quantities for analysis and ethical approval for sampling. The exposure to metals and metalloids is reflected in elevated concentrations in the hair, which provides informations about long-term exposure, while urine was chosen as model matrix indicative of short-term exposure (Gil et al. 2015).

Methods

Sampling

In the studied area the drinking water was supplied by a spring (Molini di Sant'Anna) located very close to an abandoned mining site (Fig. 1). Water samples were collected from six public tap fountains (Fig. 1), which are representative of the water distributed in each single house in the area considered.

Water samples were collected without filtering and acidified with 1% HNO_3.

A total number of 150 subjects provided a urine sample. Urine samples were frozen at –20 °C. Before the analysis, the samples were defrosted, centrifuged (5000 rpm for 10 min) and diluted 1: 10 with 2% HNO_3.

A total number of 318 subjects provided a hair sample. Hair samples with a length ranging between 3-15 cm were collected, cut in pieces and mixed. Considering that the hair growth is about 1-1.5 cm/month, Tl quantitation in hair evidenced an average exposure of 2-7 months. About 200–300 mg of hair from each sample were weighed into Teflon vessels, washed three times with 1:1 acetone/ultrapure water and pre-digested for 1 h at room temperature with HNO_3 (6 mL, 69 % w/w) and H_2O_2 (2 mL, 30 % w/w). Then, the vessels were placed in the microwave oven for the digestion (up to 200°C). After cooling at room temperature, samples were quantitatively transferred into 50-mL flasks and diluted with ultrapure water up to 50 mL. Samples were stored at room temperature.

Instrumentation and method

A quadrupole ICP-MS Agilent model 7700 (Agilent Technologies) equipped with a collision cell system was used for water and biological sample analysis. A solution of 10 µg/L iridium in 2% HNO_3 was used as internal standard.

Samples and standards were analyzed in triplicate. The limit of detection (LOD), based on the mean of the blank samples from all runs plus three times its standard deviation, was 2 ng/L for aqueous samples. To evaluate the accuracy a water sample certified for Tl (NIST1640A) was analyzed. The certified concentration of Tl reported for was 1.619 ± 0.016

µg/L, and the concentration that we found was 1.61 ± 0.08 µg/L. In addition, for the urine samples, the method was validated analyzing a certificate sample of lyophilized urine (NIST 2670, certificate Tl concentration = 5.417 ± 0.064 µg/L). The Tl concentration value found was 5.34 ± 0.11 µg/L (n=6, RSD% 2.06). The LOD for urine was 20 ng/L. Currently, hair reference materials certified for Tl are not commercially available. Thus, the commercially available hair European Reference Material ERM-DB001 certified for seven metals and metalloids (As, Cd, Cu, Hg, Pb, Se, Zn) was spiked with Tl in order to evaluate the matrix effect. We spiked the certified material before the digestion procedure with 250 µL of Tl standard solution (final concentration 81.0 ng/g). We found a Tl concentration of 79.6 ± 4 ng/g, corresponding to a recovery of 98.3% (6 replicates, RSD% 5.5%). The LOD for hair was 0.6 ng/g. Hair washing, digestion, and ICP-MS analysis were repeated three times for 7 samples, to estimate the reproducibility of the entire procedure. The maximum relative standard deviation obtained was 11%.

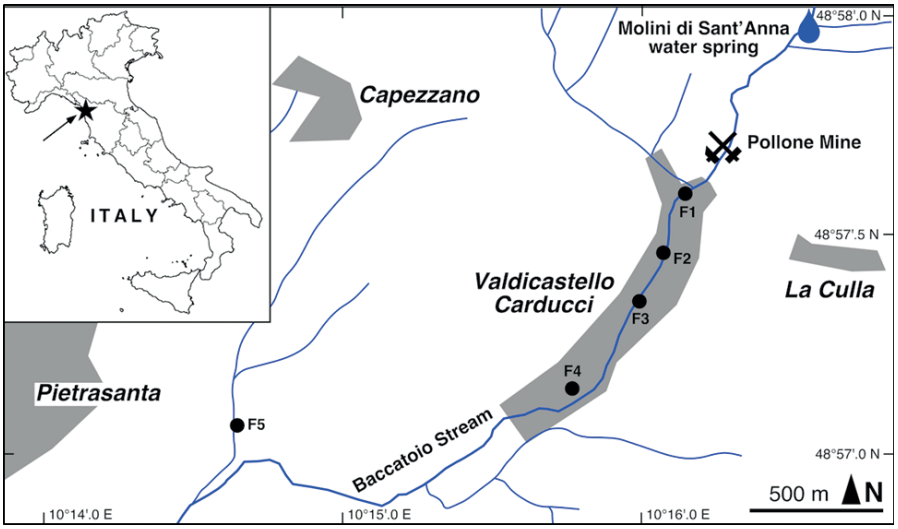

Figure 1 *Sketch map showing the localities cited in this work. F1 to F5 are the public fountains whose water was analyzed for this study (fountain F6 is located close to the Pietrasanta cemetery, outside the map); Molini di St'Anna is the contaminated spring that fed the aqueduct.*

Results

Figure 2 shows thallium concentrations measured in tap water from Valdicastello and Pietrasanta in September 2014. Water analysis revealed Tl concentrations ranging from 1.77 to 10.1 µg/L. The Tl contamination level in tap water was higher in upper Valdicastello > medium> lower ≈ Pietrasanta.

Until September 2014, the drinkable-water distribution system of Valdicastello Carducci (and, thus, also the public fountains F1 – F5) was fed by a single water spring which lies within the abandoned mining area (Molini di Sant'Anna, see Fig. 1). The same spring also fed about 10% of the drinkable water distribution system of Pietrasanta (public fountain

F6). This spring was found heavily contaminated by Tl (from 5 to 37 µg/L). On October 3rd, 2014 local authorities excluded the contaminated spring from the distribution system.

Fig. 3 shows the frequency distribution relative to thallium concentrations measured in urine samples sampled in October 2014. The 36% of the examined population (N=150) had Tl urine concentrations below 0.4 µg/L, the 49% between 0.4–1 µg/L and in the 15% of the population Tl exceeds 1 µg/L. Tl concentration ranged from 0.046 to 5.44 µg/L, with a mean value of 0.74 µg/L ± 0.67 µg/L. The maximum Tl concentration (5.14 µg/L) is 600 times higher than the Tl urinary mean value reports for European Union.

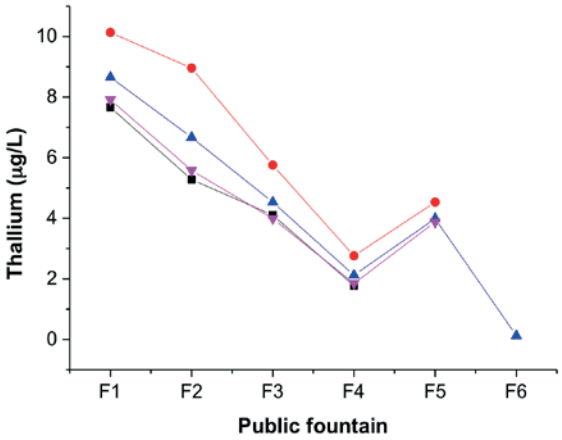

Figure 2 *Levels of Tl measured in tap water collected during four sampling in September 2014 from public fountains in Valdicastello and Pietrasanta (F1-F2: up part of the village; F3-F4: middle part of the village; F5: down part of the village; F6 located in Pietrasanta)*

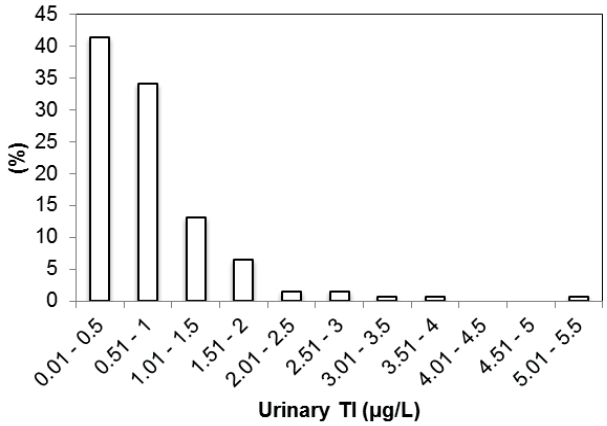

Figure 3 *Frequency histograms of the raw data set of Tl concentration (µg/L) found in the urine of 150 subjects.*

Thallium concentration found in saliva sample was between 0.03 to 3.48 µg/L, while salivary Tl level found in unexposed subject was below 0.04 µg/L. To the present day, there are not reference values for Tl in saliva.

Fig. 4 shows the frequency distribution relative to thallium concentrations measured in hair samples sampled in October 2014. Thallium levels in hair (N = 318) ranged from 1 to 498 ng/g, with a mean value of 41 ng/g ± 68 ng/g.

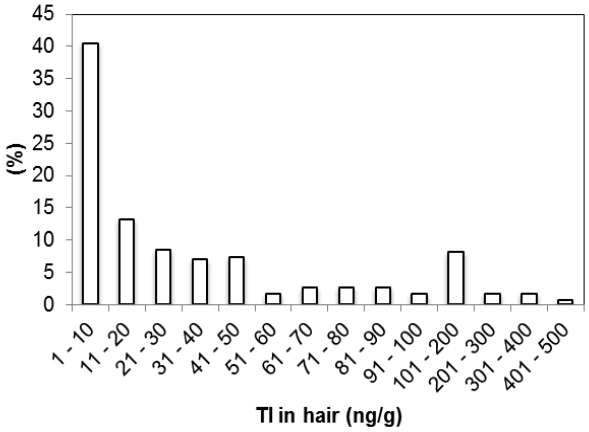

Figure 4 *Frequency histograms of the raw data set of Tl concentration (ng/g) found in the hair of 318 subjects.*

By providing the data of Tl concentration found in hair and urine samples according to the residence of the subjects, the upper area of Valdicastello emerged as the major area of exposure (data not shown). This trend is analogous to that found in the tap water, where the fountains in the upper area of Valdicastello were the most contaminated by thallium (Fig. 2). This suggests a correlation between Tl levels found in hair and urine and Tl concentration in tap water.

Conclusions

Thallium is an emerging pollutant. The widespread use of Tl, and its subsequent release into the environment, has led to an increase in Tl levels in several ecosystems and trophic chains, increasing its exposure to humans and other living organisms. Moreover, its presence, with other potentially toxic metals, close to mines, has been demonstrated. As no regulation exists from EU Authorities, this issue has to be carefully considered.

The present study investigates the accumulation of Tl in a population living in the southern Apuan Alps (Italy) where drinking water was contaminated by thallium. Hair, saliva and urine are suitable matrices for non-invasive exposure assessments in human population. Our findings indicate that people resident in the contaminated area of Valdicastello Carducci and Pietrasanta significantly accumulated Tl in their hair, urine and saliva compared

to the reference values of Italian population and to the values of unexposed people. About 50% of urine samples had a thallium concentration value above 0.5 mg/L; about 70% of hair samples had a thallium concentration > 10 ng/g. The high values of thallium found in hair samples suggest a long-term exposure.

References

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