

## Soil Contamination in Gartlage Area, Germany

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**Abstract:** Gartlage is the second smallest district of Osnabrück Germany. It is in direct vicinity to the city centre. There is a big wire and metal production factory (KME) in the area and the factory have been in operation since 1873. Main products are rolled copper and copper alloys, copper tubes, copper & brass rods and special products for the steel industry. The main strategy of KME factory for copper production is focusing on recycling of the products. Especially products made by copper are recycled back after main usage at homes, cars, computers and windmills with the help of scarp dealers. Although copper is recyclable and productive material, the wastes produced during the manufacturing process of copper may be harmful for environment and human kind. Smelting and refining operations are two mostly used copper manufacturing processes. Both may lead to different kinds of pollutants such as sulphur dioxide, particulate matter, flotation wastewaters, uncontrolled leachate, slurry sludge and slag. In this study, heavy metal pollution in Gartlage area of Germany was investigated. Several samples were taken from the area around KME factory and heavy metal analyses (copper and lead) were performed on these samples. Moreover, after the analyses, concentrations of copper and lead were compared with values in Federal Soil Protection Act. Thus, heavy metal pollution in the area was detected.

**Keywords:** *heavy metals, soil, contamination, copper, lead*

### Introduction

Soil contamination may be very serious when the health effects of the heavy metals are considered. Heavy metals are found in the environment by natural and anthropogenic sources. The natural emissions of heavy metals are mainly originating from earth crust. After a long-time period, these heavy metals enter the soil, air and water. Existence of heavy metals on the earth is in ore form with different chemical compositions. Heavy metals found in ore deposits may create pollution during mining activities by the help of the wind and flood (Duruibe et al., 2007).

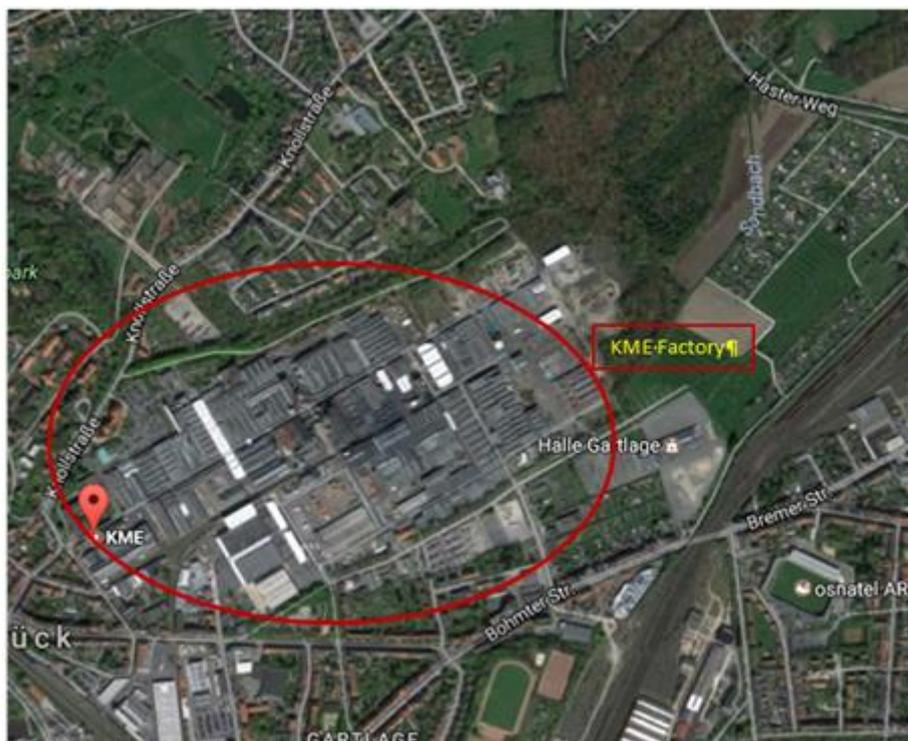
Main heavy metals which are extracted from ore deposits and create serious health problems are mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd) and arsenic (As) (Jarup, 2003). In this paper copper and lead are the focused heavy metals because in the area which is selected for measurement there is big wire and metal production factory (KME). In Figure 1, the map of Gartlage area and the location of KME Factory is given. KME mainly produce copper alloys, copper tubes, copper rods and several other products of metal industry (URL 1). During manufacturing of copper, four important steps are followed. First one is concentrating operation in which step dirt and clay material on the copper extracting from ores are removed. Crashing and flotation is applied to the copper ore for clean it from dirt. Second step is called as smelting operation. Main purpose is removal of iron and sulphur from the copper with several chemical operations. Two furnaces are used for smelting of the copper. In third step refining operation takes place. In this step copper is refined with the help of fire and electrode to provide 100% purification. The last step of copper manufacturing is casting. Copper is turned into the final product in this step (URL 2). However, several types of wastes may be produced by manufacturing of copper such as air pollution from smelting operation such as particulate matter (ash) containing lead, arsenic, cadmium, mercury, zinc and SO<sub>2</sub> emissions, water pollution from concentrating operation such as flotation wastewaters and leachate, and soil pollution from all steps such sludge and slag, leachate and ash (URL 3). As a result, the Gartlage area was assumed as a contaminated with pollutants (Cu and Pb) and this study was conducted to determine the situation.

Negative effects of copper on humans are kidneys cyst formation, swelling, hypertension, stroke, vomiting, melena, coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal distress.

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Also, it has some negative effect on plants. Plants may appear stunted, are usually bluish in colour, and eventually turn yellow or brown. Toxic copper levels reduce seed germination, plant vigour, and iron intake (URL 4). Furthermore, lead has some negative effects on human too such as anaemia, fatigue, headache, insomnia, hypotension, weight loss, gastrointestinal disorder, nervous system damage, kidney failure, stomach swelling (URL 5). Reducing the rate of photosynthesis, inhibiting respiration, encouraging an elongation of plant cells, effecting to the root by pre-mature aging are the negative effects of lead on plants (Greene, 1993). When these effects are considered, detection of these two heavy metals is significant.

In this study, soil contamination with copper and lead in the Gartlage area was investigated with experiments and the results were compared with the regulations.



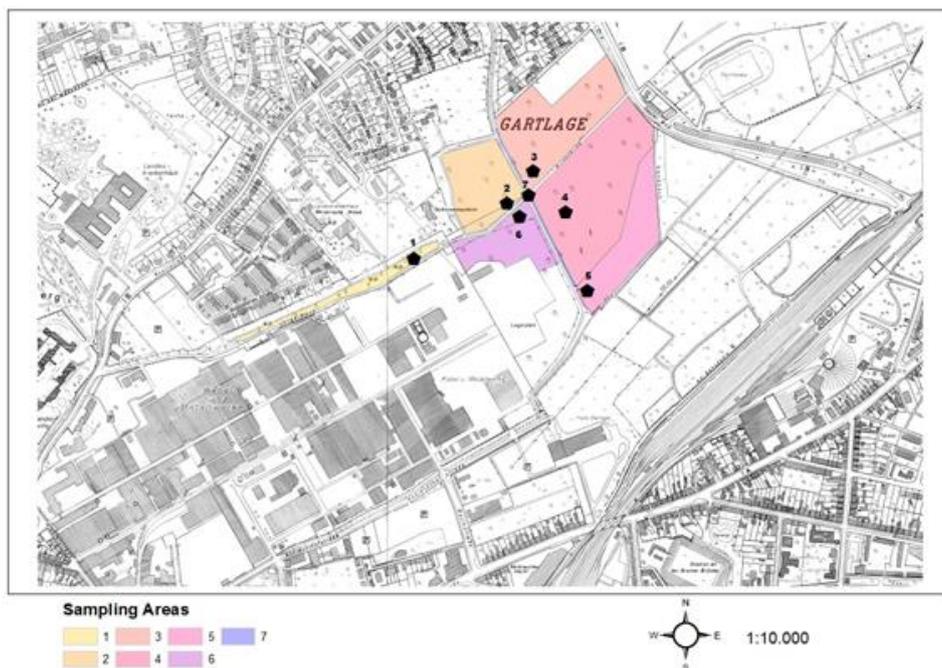
**Figure 1** Map of Gartlage Area (Google Earth, 2009)

### **Material and Method**

In order to understand the pollution in the area, several samples were taken from different points closest to the KME Factory. After sampling, some experiments were conducted for determine pollution concentrations. In this chapter, some information about sampling, experimentation and calculation is given.

### **Sampling**

Sampling areas were selected by main wind direction which is dominant in the area. When the location of KME Factory considered, main wind direction was determined as northeast. Seven areas were selected as a sampling area and some points are also determined within the vicinity of these areas for samples. In Figure 2 sampling areas are shown with different colours and sampling points are shown with black dots. Sapling areas one, two, three, four and six consist of trees and some small plants. In area seven there is a small water channel and sample was taken from the bottom mud. Furthermore, in area five there is an agricultural land. From these selected areas three samples were taken from the selected points and they are mixed with each other. Therefore, only one sample was taken from each area so seven samples were taken. However, from sampling area 1 one more sample were taken apart from other samples because it has darker colour which means high ash content than other three samples taken from area 1. Finally, they were packed separately and transported to the laboratory.



**Figure 2** Sampling Areas and Points

Besides, samples were taken with the help of shovel from the first horizon. The soil profile of the area consists of 5 horizons and overlay with leaves and needles at the top. It is clearly seen that in the first horizon there is presence of ash with black colour. The dominant soil texture of the area shows the similar properties with silt and loam which represents the soil including 70% of silt and not less than 20% of sand (URL 6). Moreover, fifth horizon includes iron minerals with reddish colour.



**Figure 3** Pictures of Experimental Steps

### Experimentation

Main Steps of experiment conducted on soil samples are given in the below and in Figure 3 the pictures of the experimental steps are given.

- Soil samples were dried in the oven at 40 °C for one week.
- Dried samples were sieved and big particles were separated from soil samples.

- Sieved samples were milled with Planetary Ball Mill PM 400 to get the soil particles to diameter of 100 μm. (After this step, 9<sup>th</sup> sample as a reference soil and 10<sup>th</sup> as a blank was investigated with other samples)
- Soil samples were weighted as 1 g for each put into the vessels and closed.
- 6 ml of 34% of HCl solution and 2 ml of 67% HNO<sub>3</sub> solution were added to the samples and they were shaken.
- Samples were left for digestion in one week.
- Samples were put in to the Ethos Plus Microwave Labstation and the system were adjusted to 900 W and 190 °C.
- Samples were cooled to 30-40 °C by the machine.
- With the help of filter papers, samples were filtered to remove soil particles.
- Atomic Absorption Spectrophotometer with FS95 Furnace Auto sampler and GF95 Graphite Furnace was used for measurements of Pb and Cu concentrations.

### Calculation of the Results

Calculation of the results taken from Atomic Absorption Spectrophotometer was made according to the formula given below:

$$\omega(X)_{Soil} \left[ \frac{mg}{kg} \right] = \frac{\beta(Y)_{Extract} \left[ \frac{mg}{L} \right] * F_D * V_{Extract} [ml] * F_{Stoich.}}{W_{Soil} [g]} \quad (\text{Formula 1})$$

$\omega(X)_{Soil}$  : Mass fraction wanted parameter X in soil (mg/kg soil)

$\beta(Y)_{Extract}$  : Mass concentration measured parameter Y in extract (mg/L extract)

$F_D$  : Dilution factor (with undiluted extraction solution=1)

$V_{Extract}$  : For extraction used volume of extraction solution in ml

$F_{Stoich.}$  : Stoichiometric factor (for conversion of different element forms; calculation as below)

$$F_{Stoich.} = \frac{n * M(Compound_{Wanted} X) \left[ \frac{g}{mole} \right]}{M(Compound_{Measured} Y) \left[ \frac{g}{mole} \right]} \quad (\text{Formula 2})$$

n : Number of atoms of wanted compound in the measured compound

M : Molar mass (g/mole)

$W_{Soil}$  : Weighted soil in extract in g

ASS gives the results of the Cu and Pb as mg/L. In order to convert it into mg/kg, Formula 1 was used and for the determination of stoichiometric factor Formula 2 was used.

### Example Calculation of Copper mass fraction in soil:

Measured value (with flame atomic absorption spectrometer) for Copper in Aqua regia extract: 4.2 mg Cu / 1 Aqua regia extract

$\beta(Y)_{Extract} = 4.2 \text{ mg Cu/l}$

$F_D = 10$  (The measured Aqua regia extract was diluted 1:10)

$V_{Extract} = 50 \text{ ml}$  (Volume of the Aqua regia Extraction solution)

$F_{Stoich} = 1$  (no calculation needed)

$W_{Soil} = 1.0023 \text{ g}$  (Weighted soil used for the extraction)

$$\omega(Cu)_{Soil} \left[ \frac{mg}{kg} \right] = \frac{\beta(Y)_{Extract} \left[ \frac{mg}{L} \right] * F_D * V_{Extract} [ml] * F_{Stoich.}}{W_{Soil} [g]}$$

$\omega(Cu)_{Soil} = 2095 \text{ mg/kg}$  (calculated value)

$\omega(Cu)_{Soil} = 2100 \text{ mg} \cdot \text{kg}^{-1}$  (reported value)

As seen in the example calculation, for all samples Cu and Pb concentrations were calculated as mg/kg and reported.

## Results

Results for copper and lead concentrations in the soil taken from 7 different areas were given in Tables 1 and 2. Evaluation of the results was made in accordance with the Federal Soil Protection Act of Germany. According to this act, two different limit values are found for Pb and one value for Cu. This act presents the precaution values for metals detected in soil with respect to different textures. Precaution value of copper is 40 mg/kg and precaution value of lead is 70 mg/kg. Furthermore, if there is a human contact in the area, 1000 mg/kg limit value is determined for lead (Federal Soil Protection Act, 1998). This value is only valid when the area is used as a park by humans. There is no limit value for copper with respect to human contact.

### For Copper (Cu)

When the results in Table 1 is compared with the regulatory value of Cu (40 mg/kg), it is clearly seen that the samples taken from all areas are higher than the precaution value of copper. Especially for the samples (Sample 1 and 8) taken from first area have the highest Cu concentrations. In addition, sample 6 has also very high amount of copper. These results are expectable when the location of first and sixth area considered because first area is the closest point to KME Factory and in sixth area there were no overlay of leaves and needles at the top.

**Table 1** Results of Cu Concentration in Soil

| Sample ID | Dilution-factor | $\beta(\text{Cu})$ [mg/L] | Extinction | Sample Weight | $\omega(\text{Cu})$ [mg/kg] |
|-----------|-----------------|---------------------------|------------|---------------|-----------------------------|
| 1         | 10              | 4.6                       | 0.2245     | 1.0027        | 2293.8                      |
| 2         | 10              | 1.4                       | 0.0750     | 1.0066        | 695.4                       |
| 3         | 1               | 8.9                       | 0.4253     | 0.9922        | 448.5                       |
| 4         | 10              | 0.88                      | 0.0509     | 1.0009        | 439.6                       |
| 5         | 1               | 6.1                       | 0.2979     | 1.0094        | 302.2                       |
| 6         | 10              | 2.1                       | 0.1085     | 1.0098        | 1039.8                      |
| 7         | 1               | 1.5                       | 0.0795     | 1.0027        | 74.8                        |
| 8         | 10              | 4.2                       | 0.2065     | 1.0178        | 2063.3                      |
| 9         | 1               | 0.75                      | 0.0448     | 0.9942        | 37.7                        |
| 10        | 1               | < 0.10                    | 0.0004     | 0.0000        | 0                           |

### For Lead (Pb)

According to the results given in Table 2, Pb concentrations in all areas are lower than the human contact limit value of Pb (1000 mg/kg) but the concentrations of the samples taken from first, second, third, fourth and sixth areas are higher than the precaution value (70 mg/kg) given in the act. Highest concentrations were detected in the areas third and fourth. This result is unexpected when the location of the sampling areas is considered.

**Table 2** Results of Pb Concentration in Soil

| Sample ID | Dilution-factor | $\beta(\text{Pb})$ [mg/L] | Extinction | Sample Weight | $\omega(\text{Pb})$ [mg/kg] |
|-----------|-----------------|---------------------------|------------|---------------|-----------------------------|
| 1         | 1               | 2.9                       | 0.0424     | 1.0027        | 144.6                       |
| 2         | 1               | 3.6                       | 0.0519     | 1.0066        | 178.8                       |
| 3         | 1               | 4.2                       | 0.0609     | 0.9922        | 211.7                       |
| 4         | 1               | 4.5                       | 0.0651     | 1.0009        | 224.8                       |
| 5         | 1               | 1.0                       | 0.0161     | 1.0094        | 49.5                        |
| 6         | 1               | 3.3                       | 0.0479     | 1.0098        | 163.4                       |
| 7         | 1               | 0.43                      | 0.0083     | 1.0027        | 21.4                        |
| 8         | 1               | 3.4                       | 0.0495     | 1.0178        | 167                         |
| 9         | 1               | 0.29                      | 0.0063     | 0.9942        | 14.6                        |
| 10        | 1               | <0.25                     | 0.0006     | 0.0000        | 0                           |

## Conclusions

Copper and lead pollution is very serious problem in Gartlage area according to the experimental results of this study. The amounts of Cu in the all sampling areas and the amounts of Pb in most of the sampling areas are higher than the standard values. Their concentration of the area should be decreased to the acceptable levels. Some precautionary actions may be taken by the government

because these two heavy metals could be very dangerous for the human, plants and other living organisms when the high amounts of exposure. It is clearly seen that the main source of Cu and Pb pollution in the area is the KME Factory. Due to the manufacturing operations such as concentrating, smelting and refining operations, copper and lead concentrations are getting higher. Main purpose of copper pollution in the area is ash produced by furnaces and especially in the points closest to the factory buildings copper concentrations were found higher. Lead is found in the ash, slag, sludge and leachate with small amounts. Main reason of lead pollution in the area could be leachate and other wastes of the factory when the results were commented.

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