

Entry to the Stockholm Junior Water Prize 2024

Investigation of Heavy Metal Contamination in Flood-Affected Agricultural Areas

A Case Study on Copper Levels in Soil and Crops

Anna Katharina Hinson (18)
and Benedikt Raimund Lamberty (18)

SUPERVISOR: Andrea Karlein
COUNTRY: Germany



Peter Joerres Grammar School Ahrweiler
Bad Neuenahr-Ahrweiler, Germany

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Abstract

In the summer of 2021 the Ahr River basin was impacted by severe flash flooding caused by unusually excessive rainfalls. After the flooding, elevated concentrations of the heavy metal copper were detected in several soil samples along the river. This contamination was presumably caused by copper-containing fungicides washed away from depots of organic vineyards.

This study investigates whether these concentrations are still elevated, to what extent crops absorb copper from the soil, and how strongly this affects plant growth. Furthermore, it examines whether increased copper levels can also be detected in viticulture, where the aforementioned fungicides are used.

To address these questions, experiments were conducted where radishes were planted and grown in soil artificially contaminated with varying concentrations of copper. Additionally, soil samples were taken from vineyards and the Ahr riverbank. Both these and the organic samples from the planting experiments were subsequently analyzed for copper using a spectrophotometer.

These experiments showed that copper concentrations in the soils along the Ahr River have returned to safe levels, posing no threat to agricultural use. No increased concentrations were found in viticulture either. Radishes absorb copper during growth and accumulate it up to a maximum saturation, which particularly affects their early growth phase. The copper intake caused by the consumption of radishes grown on contaminated soils, as they occurred after the flood, could exceed tolerable upper intake levels.

Contents

Abbreviations and Notation	3
Acknowledgements	4
Primary Content	5
1 Motivation	5
2 Research Questions	5
3 Theoretical Foundation — Spectrophotometry	5
4 Procedure	6
4.1 Spectrophotometric Analysis	6
4.2 Soil Samples from the Riverbank	8
4.3 Experiments with Plants	9
4.4 Soil Samples from Vineyards	10
5 Results	11
5.1 Computation of the Calibration Curve	11
5.2 Soil Samples from the Riverbank	11
5.3 Experiments with Plants	12
5.4 Soil Samples from Vineyards	13
6 Error Analysis	14
6.1 Growth Phase of the Planting Experiment	14
6.2 Propagation of Error in Calibration Curve Data	15
6.3 Propagation of Error in Copper Concentration Data	16
6.4 Apparent Errors without Explanation	17
6.5 Possibly Incorrect Assumptions	17
6.6 Discarded or Repeated Experiments	17
7 Conclusions	18
7.1 Contextualization of Copper Concentration in Radishes	18
7.2 Interpretations and Unresolved Phenomena	18
8 Summary	20
9 Outlook	20
Bibliography	21

Abbreviations and Notation

Remark. The following list of abbreviations and notations merely serves as a quick reference while reading. All abbreviations and symbols are either standard, introduced in the text or apparent in context.

1.23 The decimal point is used as the decimal separator.

A_λ Absorbance at the wavelength λ (cf. 3)

AI Adequate Intakes [3]

b , (\bar{b}) (Average) proportionality constant of the Lambert-Beer law (cf. 3, 4.1.4)

BCO Oxalic acid bis(cyclohexylidenehydrazide), also known as Cuprizone (cf. 4.1.2)

c Molar concentration

CBS Citrate buffer solution: a buffer solution to help keep the pH constant (cf. 4.1.2)

Citations Citations are written in square brackets.

CSS Copper stock solution: solution with known concentrations of copper ions (cf. 4.1.2)

d Width of a cuvette (cf. 3)

DM Dry matter: This abbreviation is often used after the unit of the mass fraction (e.g. 1mg/kg DM) to express the proportion of a substance in a mixture excluding water.

ϵ_λ Molar attenuation coefficient (cf. 3)

fig. Figure

I Intensity of light (cf. 3)

K_1 to K_5 Planting boxes labeled K_1 to K_5 sequentially with increasing copper concentrations

λ Wavelength

m Mass

M Molar mass

n A number or count of something, e.g. the germination rate (cf. 5.3.1).

$P \propto Q$ P is proportional to Q .

PS Photometer solution: a solution made to be spectrophotometrically analyzed (cf. 4.1.2)

PSS Photometer stock solution: photometer solution containing copper stock solution (cf. 4.1.2)

$Q_Y(X)$ Quantity or property Q of a substance X relative to the mixture or solution Y

ρ Density

SGDN Northern Structure and Approval Authority in Koblenz (cf. 1)

$\bar{\sigma}$ Average standard deviation

tab. Table

UI Tolerable Upper Intake Level [3]

Units The International System of Units, additionally: litre (l), day (d), minute (min).

w Mass fraction

Acknowledgements

Andrea Karlein Ms. Karlein, a teacher at the Peter Joerres Grammar School in Bad Neuenahr-Ahrweiler and head of the STEM department, is the supervising teacher of this project, which was originally submitted to the “Jugend forscht” contest in Germany. She assisted us in finding the topic and conducted experiments during the project week of the Peter Joerres Grammar School on the topic of water pollution of the Ahr River, which led us to our research questions. Anna Hinson was involved in some of the measurements of this series of experiments. Furthermore, experiments that needed to be conducted in the chemistry laboratory of the school were carried out under Ms. Karlein’s supervision after safety instructions on handling the chemicals used were given. She was also always available for any further questions.

Thomas Fetz Mr. Fetz is Benedikt Lamberty’s chemistry teacher and supervises a term paper on the same topic as this paper. He contributed his ideas in several meetings and was always available for questions.

Jessica Hartmann-Jetzek Ms. Hartmann is Anna Hinson’s advanced biology course teacher and supervises her term paper on the same topic. Several meetings allowed for an exchange of ideas.

Anonymous Winemaker An organic winemaker with vineyards in the Moselle Valley, who wishes to remain anonymous, allowed us to collect soil samples from his fields over the course of several days. He also shared his expertise on pest control in organic viticulture with us in an interview and remained available for further questions.

Large Language Models The *translation* of the original German version of this document [7] into English was partially assisted by the large language model “ChatGPT”. Therefore this paper might be flagged by software intended to detect texts written by artificial intelligence. However, this tool was only employed to translate the paper and not to write the original German version.

Anna Hinson and Benedikt Lamberty As the authors of this paper, we hereby declare that we have written it independently and have not used any sources or aids other than those indicated. Finally, we would like to sincerely thank everyone who helped us with this project!

Primary Content

1 Motivation

As the authors of this research paper, we were personally affected by the severe flash flooding in the Ahr Valley in 2021. After the flood, numerous newspaper articles and citizen initiatives in the Ahr Valley were concerned with flood-induced contamination of soils with environmental toxins [20]. Many garden owners had their soil tested or replaced the topsoil completely. Therefore, we were personally motivated to do further research on this topic and determine the actual threat posed by such contamination.

Since contaminants such as heating oil can be relatively quickly biodegraded in a natural environment and no other heavy metals besides copper were detected by a study of the Northern Structure and Approval Authority (SGDN) in Koblenz, which investigated the contamination with heavy metals at numerous locations along the Ahr River shortly after the flooding [19], we are focusing on the investigation of copper contamination. The elevated copper concentrations along the Ahr River were likely caused by copper-containing fungicides from organic viticulture, which were stored in warehouses along the Ahr that were affected by the flood [19].

2 Research Questions

The starting point of our work was the question of whether copper concentrations along the Ahr River are still elevated. Furthermore, We aimed to determine to what extent copper is absorbed from the soil by typical garden plants and what impact the potential accumulation has on plant growth. After testing the soils near the river, we then asked ourselves to what extent a “normal” application of these fungicides could lead to copper contamination, and whether gardens near vineyards could also be exposed to high levels of contamination. Additionally, we aimed to contextualize the copper concentrations measured in the study, thereby assessing the potential risk posed by copper contamination.

3 Theoretical Foundation — Spectrophotometry

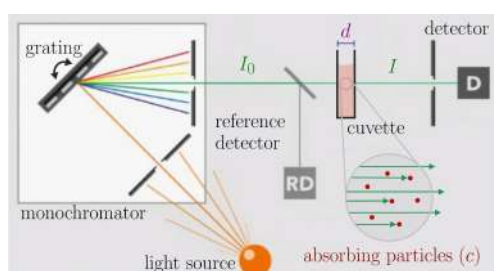
To determine the copper concentrations in various samples, this study employs spectrophotometric analysis as the method of investigation.

A spectrophotometric analysis is carried out with a spectrophotometer (cf. fig. 1a), a device in which monochromatic light with a selectable wavelength λ and the intensity I_0 is shone through an aqueous solution contained in a cuvette, a small glass vial with minimal light absorption characteristics and the width $d = 1\text{cm}$. The intensity I of the light, which has passed through the cuvette, is measured. Assuming the solution contains a substance with the molar concentration c , the logarithmic ratio of the light intensities I_0 and I , i.e. the absorbance A_λ , can be described by the Lambert-Beer law [1]

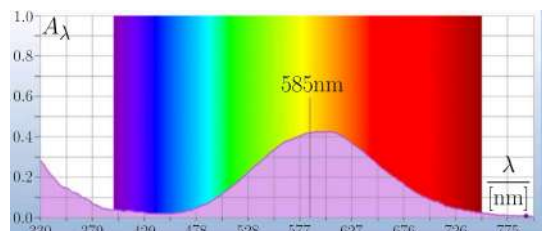
$$A_\lambda := \log_{10} \left(\frac{I_0}{I} \right) = \varepsilon_\lambda d c \quad (1)$$

where ε_λ is the molar attenuation coefficient. $b := \varepsilon_\lambda d$ can be considered to be the proportionality constant of the relation $A_\lambda \propto c$ for a unique substance and wavelength. Therefore, if b is known, it is possible to calculate the concentration c from absorption values A_λ measured with the spectrophotometer.

To exclude influences of scattering and reflection caused by the cuvette and solvent, a measurement of a so-called blank solution is performed before the actual examination of the sample, where only the pure solvent is present in the cuvette.



(a) Schematic diagram of a single beam spectrophotometer [4]



(b) Exemplary absorption spectrum of a $[\text{Cu}(\text{BCO})_2]^{2+}$ -solution (cf. 4.1.2) [9]

Figure 1

4 Procedure

4.1 Spectrophotometric Analysis

The following describes the experiment used in this study for the quantitative determination of copper concentrations in aqueous solutions. The procedure is a slightly modified version of the one presented in [17].

4.1.1 Materials

Equipment volumetric flasks (100ml and 250ml), scale, watch glass, spatula, pH meter, pipettes with bulbs of different sizes, funnel, buret, hotplate, spectrophotometer with analytical software, cuvettes

Chemicals di-ammonium hydrogen citrate, ammonia solution ($w = 0.25$), oxalic acid bis(cyclohexylidenehydrazide), methanol, copper(II) sulfate pentahydrate, distilled water, sample (aqueous solution with known mass fraction of dry matter containing copper ions (Cu^{2+}) of unknown concentration)

4.1.2 Preparation of Solutions

Copper Stock Solution (CSS) The copper stock solution is intended to be a solution with a known copper ion content $w_{\text{CSS}}(\text{Cu}^{2+}) = 200\text{mg/kg}$. A total volume of $V(\text{CSS}) = 100\text{ml}$ of CSS is to be prepared, with copper ions added in the form of copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Given $M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 249.69\text{g/mol}$ and $M(\text{Cu}^{2+}) = 63.55\text{g/mol}$, the mass fraction of copper ions in the salt is $w_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}(\text{Cu}^{2+}) = M(\text{Cu}^{2+})/M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 0.255$. Since $m_{\text{CSS}}(\text{Cu}^{2+}) = 20\text{mg}$ of copper ions are to be dissolved in 100ml of water, $m_{\text{CSS}}(\text{Cu}^{2+})/w_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}(\text{Cu}^{2+}) = 78.59\text{mg}$ of copper(II) sulfate pentahydrate needs to be added to 100ml of distilled water in a volumetric flask. Thus, the copper concentration amounts to $c_{\text{CSS}}(\text{Cu}^{2+}) = m_{\text{CSS}}(\text{Cu}^{2+})/V(\text{CSS})M(\text{Cu}^{2+}) = 3.14 \cdot 10^{-3}\text{mol/l}$.

Citrate Buffer Solution (CBS) Here, 10g of di-ammonium hydrogen citrate is dissolved in 200ml of deionized water in a 250ml volumetric flask. Using ammonia solution and a pH meter, the pH is adjusted to 9, and then the flask is filled up to the graduation mark with water.

BCO Solution 0.5g of oxalic acid bis(cyclohexylidenehydrazide) (abbreviated as BCO) is dissolved in a solution of 140ml of methanol and 110ml of deionized water with gentle heating.

Photometer Solution (PS) The photometer solutions are solutions whose copper concentration is to be determined using a spectrophotometer. Initially, a volume $V(\text{Dilution})$ of a copper-containing sample solution is pipetted into a 100ml volumetric flask. 20ml of water, 10ml of CBS, and 10ml of BCO solution are added, and after 30min reaction time, the flask is filled up to the mark with distilled water. Thus, the sample was diluted to $V(\text{PS}) = 100\text{ml}$.

During the reaction time, the copper ions react with BCO to form a copper complex

$(\text{Cu}_{(\text{aq})}^{2+} + 2 \text{BCO}_{(\text{aq})} \longrightarrow [\text{Cu}(\text{BCO})_2]_{(\text{aq})}^{2+})$ with an intensely dark blue color. This color can be measured in the spectrophotometer by high absorption values around the complementary color at $\lambda = 585\text{nm}$ (cf. fig. 1b).

Photometer Stock Solution (PSS) Five photometer stock solutions are prepared. These solutions are photometer solutions with CSS as the sample solution and $V(\text{Dilution}) = 200\mu\text{l}, 400\mu\text{l}, 600\mu\text{l}, 800\mu\text{l}$ and $1000\mu\text{l}$ and are used to establish the calibration curve (cf. 4.1.4).

4.1.3 Spectrophotometric Analysis of Solutions

First, the spectrophotometer is calibrated. For this purpose, a photometer solution with water as the sample is filled into the cuvette and analyzed at the wavelength $\lambda = 585\text{nm}$ in calibration mode. The measured extinction value is then set as the new zero value. All subsequent photometer (stock) solutions are then sequentially filled into the cuvette, and the absorption values for $\lambda = 585\text{nm}$ are determined.

4.1.4 The Calibration Curve

For each PSS with a known copper concentration of $c_{\text{PSS}}(\text{Cu}^{2+}) = c_{\text{CSS}}(\text{Cu}^{2+})V(\text{Dilution})/V(\text{PS})$, an absorption value $A_{585\text{nm}}$ has been measured. According to the Lambert-Beer law (cf. equation 1), $A_{585\text{nm}} \propto c_{\text{PSS}}(\text{Cu}^{2+})$ holds for all solutions with proportionality constant $b = \varepsilon_{\lambda}d$. A straight line through the origin, also called the calibration curve, can now be drawn through the data points $(c_{\text{PSS}}(\text{Cu}^{2+}), A_{585\text{nm}})$ using linear regression. The slope \bar{b} of this line can now be considered the average proportionality constant in the given context. Thus, the relationship $A_{585\text{nm}} = \bar{b}c_{\text{PS}}(\text{Cu}^{2+})$ holds for all subsequent PS, implying

$$c_{\text{PS}}(\text{Cu}^{2+}) = \frac{A_{585\text{nm}}}{\bar{b}}. \quad (2)$$

This relationship can now be used to calculate the copper concentration in the photometer solutions and, consequently, in the dissolved sample.

4.2 Soil Samples from the Riverbank

At the beginning of this project, as part of the school project week at the Peter Joerres Grammar School, samples were taken from the locations, where elevated copper levels have been detected by the SGDN [19], specifically in the two villages Walporzheim and Dernau. Samples of sediment at the edge of the river and soil approximately 3m up the embankment were taken and then dried. Solutions were prepared with a mass fraction of $w_{\text{Prep}}(\text{DM}) = 200\text{g}/\text{kg}$ of dried soil. Stepwise filtration ensured that the solutions were nearly clear and

free of suspended particles, minimizing potential distortion of the absorption spectrum. For the dilution, the value $V(\text{Dilution}) = 10\text{ml}$ was chosen. In this project week experiment, a different calibration curve was created and used to directly associate the absorption value with a copper concentration $w_{\text{PS}}(\text{Cu}^{2+})$ measured in mg/kg. This calibration curve is represented by the equation $w_{\text{PS}}(\text{Cu}^{2+}) = (A_{585\text{nm}} - 0.0057)/(0.2693\text{kg/mg})$. This value must be multiplied by a factor of 50, since the soil was initially diluted to five times and then to ten times its volume. [8]

4.3 Experiments with Plants

To determine the effects of copper contamination on plant growth and to measure whether copper accumulates in typical crops, a planting experiment was conducted. Radishes were planted in soil with varying copper concentrations. The growth was documented, and at the end, the copper concentrations in the radishes were measured.

4.3.1 Growth Phase

First, five planting boxes were filled with 4kg of soil bought at a hardware store, which had been dried in the summer sun for about a week at low humidity. The soil was then amended with copper ion concentrations of $w_{\text{add}}(\text{Cu}^{2+}) = 0, 116, 189, 1000$ and 2000mg/kg dry matter (DM) in the form of copper(II) sulfate pentahydrate. The amount of copper salt to be added and mixed in can be calculated with $m_{\text{add}}(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 4\text{kg} \cdot w_{\text{add}}(\text{Cu}^{2+})/w_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}(\text{Cu}^{2+})$. The boxes are referred to sequentially as K_1 to K_5 . The planting boxes with no and high copper addition serve as control boxes. Boxes K_2 and K_3 are based on the concentrations measured in the aforementioned study [19], which found copper ion concentrations of 189mg/kg DM at the Walporzheim riverbank and 116mg/kg DM in Dernau. 40 radishes were planted in each box, watered, and placed in a weather-protected location. Until day 25 of the experiment, germination rates were counted, height measurements were taken, and growth was qualitatively assessed. The experiment concluded after 47 days of growth. The radishes were harvested, and the leaves and bulbs were separately weighed and dried. (For more details, refer to the experiment protocols [10, 11])

4.3.2 Examination of Bulbs and Leaves

The dried bulbs and leaves were each finely ground in a mortar to prepare aqueous solutions with a mass fraction of $w_{\text{Prep}}(\text{DM}) = 50\text{g/kg}$. These solutions were then treated similarly to the soil sample solutions (cf. 4.2), meaning they were left for several days allowing the copper ions to diffuse into the solution. Afterward, the solutions were filtered to remove

the organic material and other particles, yielding nearly clear solutions. These solutions were then used as sample solutions in the described spectrophotometric method (cf. 4.1) to determine absorption values. $V(\text{Dilution})$ of the sample solution was topped up with various solutions to $V(\text{PS}) = 100\text{ml}$. Using equation 2, the copper concentration in the photometer solution can now be calculated. This can then be converted back to the copper concentration in the radish leaves and bulbs using the relationship

$$\begin{aligned} w_{\text{DM}}(\text{Cu}^{2+}) &= \frac{c_{\text{Prep}}(\text{Cu}^{2+})M(\text{Cu}^{2+})}{w_{\text{Prep}}(\text{DM})\rho(\text{H}_2\text{O})} = \frac{c_{\text{PS}}(\text{Cu}^{2+})V(\text{PS})M(\text{Cu}^{2+})}{V(\text{Dilution})w_{\text{Prep}}(\text{DM})\rho(\text{H}_2\text{O})} \\ &= \frac{c_{\text{PS}}(\text{Cu}^{2+})}{V(\text{Dilution})} \cdot \frac{0.11 \cdot 63.546 \frac{\text{g}}{\text{mol}}}{50 \frac{\text{g}}{\text{kg}} \cdot 1 \frac{\text{kg}}{\text{l}}} = \frac{c_{\text{PS}}(\text{Cu}^{2+})}{V(\text{Dilution})} \cdot 0.127 \frac{\text{l}^2}{\text{mol}} \quad (3) \\ &= \frac{A_{585\text{nm}}}{bV(\text{Dilution})} \cdot 0.127 \frac{\text{l}^2}{\text{mol}} \end{aligned}$$

to find the copper concentration in the radish leaves and bulbs. [12]

4.4 Soil Samples from Vineyards

4.4.1 Procurement of Samples

Originally, we intended to conduct measurements in vineyards along the Ahr River; however, we found no local winemaker willing to participate in these investigations. Therefore, we had to relocate our experiments to a wine-growing region along the Moselle River.

There, we had the opportunity to collect soil samples from two different fields, that were treated weekly with copper-containing fungicides. Samples were taken before and after the application of fungicides, as well as after the next rainfall. All samples were collected from the center of the fields at a depth of 0 to 30cm. Field 1 has been managed as an organic field for two years, with rows spaced 2.20m apart. In contrast, Field 2 is situated on a slope with rows spaced 1.80m apart and has been an organic field for 30 years. [6]

4.4.2 Examination of Soil Samples

The vineyard soil samples, along with a control sample of store-bought soil used in the planting experiment (cf. 4.3), were treated similarly to the method described for the bulbs and leaves (cf. 4.3.2). After drying the samples, a solution with $w_{\text{Prep}}(\text{DM}) = 250\text{g/kg}$ was prepared and filtered after a waiting time of several days. $V(\text{Dilution}) = 10\text{ml}$ were used in the preparation of $V(\text{PS}) = 100\text{ml}$ of photometer solution, which was analysed.

The relationship between $w_{\text{DM}}(\text{Cu}^{2+})$ and $A_{585\text{nm}}$ for these samples is given by

$$\begin{aligned} w_{\text{DM}}(\text{Cu}^{2+}) &= \frac{A_{585\text{nm}}}{\bar{b}} \cdot \frac{V(\text{PS})M(\text{Cu}^{2+})}{V(\text{Dilution})w_{\text{Prep}}(\text{DM})\rho(\text{H}_2\text{O})} = \frac{A_{585\text{nm}}}{\bar{b}} \cdot \frac{0.11 \cdot 63.546 \frac{\text{g}}{\text{mol}}}{0.011 \cdot 250 \frac{\text{g}}{\text{kg}} \cdot 1 \frac{\text{kg}}{\text{l}}} \\ &= \frac{A_{585\text{nm}}}{\bar{b}} \cdot 2.542 \frac{1}{\text{mol}}. \end{aligned} \quad (4)$$

5 Results

5.1 Computation of the Calibration Curve

As described in 4.1.4 the absorption values $A_{585\text{nm}}$ of the PSS were determined and intermediate values for $c_{\text{PSS}}(\text{Cu}^{2+})$ were calculated (cf. tab. 1). The slope of the calibration curve (cf. fig. 2) was calculated to be $\bar{b} = 17359.6\text{l/mol}$ using linear regression [12]. The literature value for $\varepsilon_{595\text{nm}}$ of $[\text{Cu}(\text{BCO})_2]^{2+}$ is 16900l/mol cm . The differences between \bar{b} and $d\varepsilon_{595\text{nm}}$ of about 2.6% and of $A_{585\text{nm}}$ and $A_{595\text{nm}}$ of about 1% are acceptable [18].

quantity	values regarding CSS and PSS				
$c_{\text{CSS}}(\text{Cu}^{2+})$	— $3.14 \cdot 10^{-3}\text{mol/l}$ —				
$V(\text{PSS})$	— 100ml —				
$V(\text{Dilution})/[\mu\text{l}]$	200	400	600	800	1000
$c_{\text{PSS}}(\text{Cu}^{2+})/[10^{-6}\text{mol/l}]$	6.29	12.59	18.88	25.18	31.47
measured $A_{585\text{nm}}$	0.12	0.23	0.32	0.43	0.55

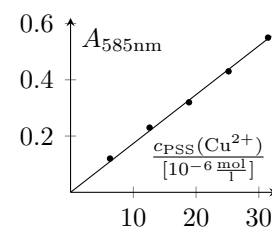


Table 1: Measured absorption of PSS for calibration and intermediate values [12]

Figure 2: calibration curve [12]

5.2 Soil Samples from the Riverbank

quantity	village of Walporzheim		village of Dernau	
	river's edge	3m away	river's edge	3m away
$A_{585\text{nm}}$	0.04	0.01	0.04	0.02
$w_{\text{PS}}(\text{Cu}^{2+})/[\frac{\text{mg}}{\text{kg}}]$	0.165	0.0160	0.165	0.053
$w_{\text{DM}}(\text{Cu}^{2+})/[\frac{\text{mg}}{\text{kg}} \text{DM}]$	8.225	0.798	8.225	2.655

Table 2: Mass fractions of copper in soil samples from the Ahr River [8]

With the calibration curve described in 4.2 and the absorption values measured during the project week, the copper concentrations in the soil samples were determined (cf. tab. 2). The two samples from the edge of the river have the highest copper concentration amounting to over 8mg/kg DM. The samples taken from the embankments have lower copper mass fractions in the range of approximately 0.8mg/kg DM to 2.7mg/kg DM.

5.3 Experiments with Plants

5.3.1 Impacts on Plant Growth

Using the methods described in 4.3.1 data on the radishes in the planting experiment was collected. All quantitative data is presented in table 3 and figure 3. Qualitatively, it is noted that the leaves in the boxes with higher concentrations appeared significantly more “unhealthy”, i.e., they had yellow spots and lacked a rich green color. Towards the end, many leaves, especially in K_5 , appeared very shriveled and partially dead (cf. fig. 4).

K_2 is an outlier and will only be partially included in the following considerations (cf. Error Analysis 6.1). It can be observed that the boxes with lower copper concentrations achieve relatively stable maximum germination rates $n(25)$ (32 out of 40 seeds). In K_5 , noticeably fewer radishes germinate. The mortality rate indicates that in the boxes with high copper concentrations, a relatively high number of radishes, some of which had already matured, die off again. The average height of the plants on day 21 of the experiment, i.e., in the middle of the growth phase, decreases with increasing copper levels. The weight $m(47)$ of the total biomass and the weight of an average radish at the end of the experiment is maximal in K_3 and decreases with both increasing and decreasing concentration.

measured quantity	K_1	K_2	K_3	K_4	K_5	error
$w_{\text{add}}(\text{Cu}^{2+})/[\frac{\text{mg}}{\text{kg}} \text{DM}]$	0	116	189	1000	2000	
$n(25)$	32	25	32	32	15	± 1
$n(47)$	29	24	31	27	9	0
$n(25) - n(47)$	3	1	1	5	6	
$h(21)/[\text{cm}]$	9.7	4.9	6.0	6.3	3.9	$\bar{\sigma} = 2.7$
$m(47)/[\text{g}]$	170	180	353	219	51	± 5.0
$m(47)/n(47) /[\text{g}]$	5.9	7.4	11.4	8.1	5.7	

Table 3: Measurements of germination rate $n(t[\text{d}])$, average plant height $h(t[\text{d}])$ and total bulb mass $m(t[\text{d}])$ depending on time in days [13–15]

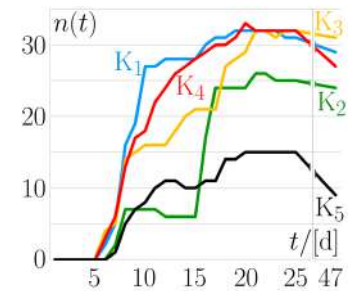


Figure 3: Germination rates from day 1 to 25 and at day 47 [15]



(a) K_1 on day 21



(b) K_5 on day 21



(c) K_5 on day 47

Figure 4: Pictures taken in the growth phase

5.3.2 Concentrations in Bulbs and Leaves

As described in 4.3.2, absorption values were measured and the mass fraction of copper ions in bulbs and leaves was calculated with equation 3 (cf. tab. 4).

quantity	values for bulbs					values for leaves				
$w_{\text{add}}(\text{Cu}^{2+})/[\frac{\text{mg}}{\text{kg}} \text{ Ts}]$	0	116	189	1000	2000	0	116	189	1000	2000
$A_{585\text{nm}}$	0.12	0.275	0.109	0.458	0.305	0.161	0.149	0.133	0.131	0.067
$V(\text{Dilution})/[\text{ml}]$	10	10	10	10	6	10	10	10	10	10
$w_{\text{DM}}(\text{Cu}^{2+})/[\frac{\text{mg}}{\text{kg}} \text{ DM}]$	87.9	201.3	79.8	335.3	372.2	117.9	109.1	97.4	95.9	49.1

Table 4: Mass fraction of copper in bulbs and leaves of radishes [12]

For the concentrations in the bulbs, K_3 is an outlier and will not be further considered here (cf. Error Analysis 6.4). It is evident that the copper concentration in the bulbs increases with rising concentration in the soil. For K_1 and K_2 , the concentration in the bulbs even significantly exceeds the concentration in the soil. However, the increase in concentration does not rise linearly but rather can be modelled with a limited growth function that gradually levels off. Despite a doubling of the soil contamination between K_4 and K_5 , $w_{\text{DM}}(\text{Cu}^{2+})$ changes only minimally.

The concentration in the leaves, however, has its maximum in K_1 and decreases almost linearly with increasing concentration in the soil. It is noticeable that $w_{\text{DM}}(\text{Cu}^{2+})$ in K_1 is significantly higher than $w_{\text{add}}(\text{Cu}^{2+})$ and in K_4 and K_5 this relationship reverses.

5.4 Soil Samples from Vineyards

5.4.1 Background Knowledge on Copper-based Fungicides

The vintner who allowed us to collect soil samples from two of his fields also provided us with some background information on the use of copper in viticulture.

As an organic winemaker, he spreads fungicides containing about 100 to 150g of copper per hectare once a week. Additionally, potassium bicarbonate is used as a fungicide at a rate of 10kg per hectare per year. These two substances are mixed in a solution and applied from early/mid-April to early/mid-August. In a difficult year, 1.8kg of copper per hectare is needed to combat downy mildew, fungal diseases, and black rot. Additionally, 40kg of sulfur-based fungicides per hectare per year are used against powdery mildew.

According to the vintner, there is no harm to insects important for the ecosystem from copper, but sulfur particularly damages wild bees. Therefore harming and rewarding factors have to be evaluated on a case-by-case basis. Since vineyards are a monoculture, compensation (e.g., through field margins) is necessary for both animals and soil. In general, copper acts as a contact agent on the undersides of leaves and on the berries.

To monitor copper usage, each vintner has a so-called “copper balance”, where the purchase of copper products is documented. Additionally, he analyses his own soil samples every five years, and once a year the Society for Resource Protection performs a control according to guidelines of organic agriculture: a maximum of 3kg of copper per hectare per year is allowed, and 3.5kg/ha every three years in difficult years.

There are no real alternatives for copper-based fungicides in organic viticulture. Although “Fytosave” has been available for purchase since 2022, it is both untested and expensive. Phosphorous acid has been banned since 2014 because, unlike copper, it is absorbed through the leaves into the plants.

Moreover, because copper has been used in large quantities as a fungicide for over 200 years, there is a large legacy contamination present in vineyard soils. [6]

5.4.2 Concentrations in Vineyard Soil

As described in 4.4.2, absorption values were measured and the mass fractions of copper ions in the soil samples were calculated with equation 4 (cf. tab. 5).

quantity	vineyard soil						soil bought in hardware store
	field 1			field 2			
	(i)	(ii)	(iii)	(i)	(ii)	(iii)	
A_{585nm}	0.014	0.007	0.012	0.003	0.040	0.019	0.025
$w_{DM}(Cu^{2+})/[\frac{mg}{kg} DM]$	2.05	1.02	1.76	0.44	5.86	2.78	3.66

Table 5: Mass fractions of copper in soil samples before (i) and after (ii) application of fungicides and after the next rainfall (iii) [12]

The soil samples taken from field 1 show copper concentrations in the range from 1 to 2mg/kg DM. The copper concentration before the application of the fungicide in Field 2 is the lowest overall at about 0.5mg/kg DM. After the application, the highest measured concentration of just under 6mg/kg DM occurs in the soil. After the first rain, the concentration drops by about 50%.

6 Error Analysis

6.1 Growth Phase of the Planting Experiment

Start of Experiment At the beginning of the plant experiment, there could have been minimal discrepancies such as too much or too little soil being added to the plant boxes, one too many or too few seeds being planted, some inferior seeds being randomly planted in one box, or slightly too much or too little copper(II) sulfate

pentahydrate being added.

However, a significant systematic, non-stochastic error occurred unfortunately, which invalidates the entire result of the growth phase for box K₂ with $w_{\text{add}}(\text{Cu}^{2+}) = 116\text{mg/kg DM}$. When watering the seeds, too much water was added, causing the box to become waterlogged. No water leaked out of the box, and the water evaporated over a few days, leaving the copper concentration unchanged. However, it appears that the seeds were either permanently damaged or pressed deeper into the soil, resulting in only a few seeds sprouting initially, followed by a “growth spurt” after 15 days. Additionally, the maximum germination rate of the other boxes was not reached (cf. fig. 3) [11]. However, the copper concentration values in the radishes from this box are consistent with the other results and seem plausible.

Growth Phase During the growth phase (June to July), the weather was initially very sunny and dry. Therefore, the radishes were placed in a shady to partially shady, wind-protected area in Benedikt Lamberty’s garden. The radishes were monitored daily and watered as needed. However, while no one was present, the weather changed unexpectedly, producing a heavy thunderstorm. As a result, all boxes were more or less waterlogged but did not overflow. This occurred after the end of the daily germination rate recordings on day 30. To remove the standing water, it was siphoned off, stored in bottles, and gradually reintroduced through watering. Although this temporarily affected the copper concentration in the boxes, it did not have a long-term impact. [10]

During the rainy days, which increased in frequency during the second half of the growth phase, the plants were kept in a carport. This carport is closed on the sunny side. Nevertheless, the plants received enough sunlight. However, the duration of sunlight exposure for each box in the carport may vary slightly. The boxes with higher concentrations received more sunlight than the others. This could explain the relatively small biomass of the radishes in the box without any addition (cf. tab. 3).

6.2 Propagation of Error in Calibration Curve Data

There are many variables used for the computation of the calibration curve, some of which are interdependent and prone to error, that will be examined in more detail below.

Copper Concentration $c_{\text{CSS}}(\text{Cu}^{2+})$ The copper concentration of the copper stock solution is an error-prone variable, which in turn depends on the error-prone variables $m_{\text{CSS}}(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O})$, $V(\text{Dilution})$, $V(\text{PSS})$, and $V(\text{CSS})$. $m_{\text{CSS}}(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O})$ was weighed using a laboratory scale with a measurement uncertainty of $\pm 0.0004\text{g}$. $V(\text{Dilution})$ was pipetted with an uncertainty of $\pm 0.01\text{ml}$, and $V(\text{PSS})$ and $V(\text{CSS})$

were measured in $100 \pm 0.08\text{ml}$ volumetric flasks. Using Gaussian error propagation, for the maximum value 1ml of the only non-constant variable $V(\text{Dilution})$, the value $c_{\text{PSS}}(\text{Cu}^{2+}) = (31.47 \pm 0.52) \cdot 10^{-6}\text{mol/l}$ with uncertainty is obtained. For the minimum value 0.2ml , $(6.29 \pm 0.36) \cdot 10^{-6}\text{mol/l}$ is calculated. The average value $\pm 0.44 \cdot 10^{-6}\text{mol/l}$ of the uncertainties of these two values is taken as the average error of this variable and measurement range.

Absorption A_λ The absorption is determined using the school’s spectrophotometer with the “AK-Analytik” laboratory program resulting in an error of ± 0.05 .

Proportionality Constant \bar{b} The proportionality constant \bar{b} depends on the quantities $c_{\text{PSS}}(\text{Cu}^{2+})$ and A_λ . If the largest negative error for $c_{\text{PSS}}(\text{Cu}^{2+})$ and the largest positive error for A_λ are assumed, and these errors are added to the measurements (cf. tab. 1), a maximum value for the proportionality constant is obtained through regression, differing from the original \bar{b} by $216.71/\text{mol}$. Therefore, the error of \bar{b} is $\pm 216.71/\text{mol}$.

6.3 Propagation of Error in Copper Concentration Data

The mass fraction $w_{\text{DM}}(\text{Cu}^{2+})$ of copper in soil samples and plant material is also subject to errors. According to equation 3, this quantity depends on A_λ with an error of ± 0.005 , $V(\text{PS})$ with an uncertainty of $\pm 0.08\text{ml}$, \bar{b} with an error of $\pm 216.71/\text{mol}$ and $w_{\text{Prep}}(\text{Cu}^{2+})$. The latter has an error of $\pm 0.01\text{g/kg}$ for the analysis of bulbs and leaves. Unfortunately, errors occurred in the soil samples, leading to inaccuracies of up to $\pm 50\text{g/kg}$ for few individual samples. This value is assumed as a worst-case scenario for all soil samples. Using Gaussian error propagation, errors can now be calculated for all $w_{\text{DM}}(\text{Cu}^{2+})$ values (cf. tab. 6).

	$w_{\text{PS}}(\text{Cu}^{2+}) / [\frac{\text{mg}}{\text{kg}} \text{DM}]$	
$\frac{w_{\text{add}}(\text{Cu}^{2+})}{[\frac{\text{mg}}{\text{kg}} \text{DM}]}$	bulbs	leaves
0	87.9 ±4.9	117.9 ±5.4
116	201.3 ±6.6	109.1 ±5.2
189	79.8 ±4.8	97.4 ±5.1
1000	335.3 ±8.5	95.9 ±5.0
2000	372.2 ±12.0	49.1 ±4.4
numbers like in tab. 5	field 1	field 2
(i)	2.05 ±1.2	0.44 ±0.83
(ii)	1.02 ±0.95	5.86 ±2.0
(iii)	1.76 ±1.1	2.78 ±1.3
store-bought soil	3.7 ±2.5	

Table 6: Mass fractions of copper with errors

For the soil samples from the Ahr River, error propagation cannot be calculated because the errors of the underlying quantities are unknown, as the measurements were conducted

during the project week (cf. 4.2).

From the calculated errors, it can be concluded that the data collected in the plant experiment is very precise. The errors range from approximately 3% to 5%, which are relatively insignificant compared to other sources of error.

However, the errors for the soil samples are very high. Here, errors range much higher, between 34% and 189%, sometimes exceeding the actual value. Therefore, this data is much less precise. Nonetheless, some conclusions can still be drawn.

6.4 Apparent Errors without Explanation

The value for the copper mass fraction in the bulbs in box K₃ with a copper concentration of 189mg/kg dry substance is an outlier that does not fit into the series of measurement results (cf. tab. 6). In the other boxes, the concentration in the bulbs increases with increasing copper level in the soil. However, in this case, this concentration is even smaller than that from the box without any contamination. We were neither able to find a plausible explanation in biological or chemical terms, nor a possible source of error that could lead to such a significant outlier.

6.5 Possibly Incorrect Assumptions

In this project, it is assumed that the differences in plant growth primarily arise from the increased copper concentrations. However, copper was added to the soil in the form of copper(II) sulfate pentahydrate salt. Consequently, the changes in growth could also be caused by increased ion concentrations and the resulting osmotic pressure. To clarify the cause of these effects, further experiments with various other metal sulfates are currently being conducted (cf. 9).

6.6 Discarded or Repeated Experiments

Another planting experiment with cress was conducted analogously and in parallel to the one with radishes. However, due to the low mass of the cress plants and consequently extremely low absorption values, no meaningful results could be obtained.

The computation of the calibration curve had to be repeated once because the copper concentration chosen was too high. The faulty calibration curve resembled the graph of a logarithmic function since the Lambert-Beer law is only valid up to approximately $A_\lambda = 1$.

7 Conclusions

7.1 Contextualization of Copper Concentration in Radishes

At first glance, the copper concentration in the radishes from box K_1 appears quite high. However, considering that radishes lose almost 94% of their mass during drying [14, 16], it can be concluded that, for example, the copper mass fractions in the undried radishes from box K_1 are only 5.27mg/kg, which is much closer to the copper concentration in the soil of approximately 3.7mg/kg.

$\frac{w_{\text{add}}(\text{Cu}^{2+})}{[\text{mg/kg DM}]}$	$\frac{m(\text{Cu}^{2+})}{[\text{g}]} / \text{radish}$	AI	UL
0	0.038	32	106
116	0.087	14	46
1000	0.145	9	28
2000	0.160	8	25

Table 7: Number of radishes to be eaten to exceed maximum doses

To understand exactly what the calculated copper mass fractions mean, it is helpful to calculate how many contaminated radishes one can consume without exceeding certain maximum intake doses. The adequate intake (AI) of copper per day for adolescents is approximately 1.2mg/d, and the tolerable upper intake level (UL) of copper for adolescents is approximately 4.0mg/d [3]. One can now calculate how many radishes, with an average weight of 7.2g [14], from the various planting boxes would need to be consumed to reach the AI or UL. These results are shown in Table 7 in the columns “AI” and “UL” respectively. It can be seen that exceeding the limits with radishes from K_1 is unrealistic. With radishes from K_2 , exceeding the AI value is possible with 14 radishes. With radishes from K_4 and K_5 , exceeding the AI value is even likely. The UL value could theoretically be reached with approximately 25 radishes. In summary, daily consumption of radishes grown in lightly contaminated soil, as found in the study [19] conducted at the Ahr River, could easily result in surpassing of the AI value. However, exceeding the UL value is unrealistic, making the consumption of such radishes relatively safe. However, it should be noted that other plants in areas effected by the flood may also absorb copper, thus increasing daily copper intake. For instance owners of private vegetable gardens could potentially surpass the UL value.

7.2 Interpretations and Unresolved Phenomena

7.2.1 Copper Uptake by Radishes

In K_1 , the copper concentration in undried radishes is 5.27mg/kg, which is higher than the concentration in hardware store soil of approximately 3.7mg/kg. Therefore, copper

seems to accumulate in radishes when present in low doses in the environment. While the concentration in the bulbs increases with increasing concentration in the soil, the rate of increase slows down. It appears that the concentration approaches a maximum saturation. The positive correlation between concentrations inside and outside the bulbs can be explained by the diffusion of copper ions. However, it would be interesting to further investigate the transition from hypertonic to hypotonic conditions. Interestingly, the concentration in the leaves decreases with increasing concentration in the environment. We currently lack an explanation for this phenomenon. Finding an explanation would require further research and delving into higher topics of biology and chemistry.

7.2.2 Radish Growth

With increasing copper concentration in the soil, radishes appear to have difficulty germinating and progressing quickly through early growth stages. Additionally, mortality rates are higher. This is not surprising, as copper can be harmful to plants in excessive doses. However, to better understand these relationships, further research into the effects of copper contamination on plants would be necessary.

Interestingly, the largest mass of plant material overall and the heaviest radishes occurred in box K_3 . This raises the question of whether low copper contamination may assist germinated plants in their subsequent growth. Since copper is also used as a fertilizer and for combating fungal infections during leaf development, this could indeed be the case [21]. However, it is not certain whether external factors may be responsible for this observation in this case. Additional planting experiments could provide clarity on this matter as well.

7.2.3 Concentrations in Vineyard Soil

In field 1, which is flat, the copper concentration in the soil appears to increase slightly after the first rain. This could be related to the rain washing the copper film off the leaves, with the copper remaining in the soil as the water drains. However, as mentioned earlier, the values here are not particularly conclusive.

In field 2, which is on a slope, the copper concentration in the soil seems to increase significantly after the application of the fungicide and decrease after the next rain. This could be because rainwater runoff carries the copper away more than it infiltrates into the soil. Despite the high error, at least the increase after the application is clearly noticeable.

7.2.4 Concentrations at the Ahr River Bank

It appears that copper contamination along the Ahr River bank has largely been washed out since the study [19], which was conducted immediately after the flood in 2021. Particularly

along the slopes, copper concentrations are of no concern.

8 Summary

In conclusion, it can be stated that in the years following the flood, the copper concentrations in the soil of the Ahr River basin have fallen to safe levels, allowing food cultivation to continue without concern in this regard. Furthermore, no elevated levels have been detected in viticulture. These conclusions align with the views of the city of Bad Neuenahr-Ahrweiler and expert groups [2].

Immediately after the flood, during the time in which the aforementioned study [19] was conducted, copper concentrations were significantly higher. Therefore, in our opinion, it was rightly advised against food cultivation for larger personal consumption and commercial use during that time.

9 Outlook

Currently, some research efforts of this project are still ongoing as a part of Benedikt Lamberty's term paper. More precisely, planting boxes of radishes were contaminated with different concentrations of other metal sulfates (Na_2SO_4 and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$) to clarify if there are effects unique to copper(II) sulfate pentahydrate. The concentrations of the added metal sulfates were chosen in such a way that the osmotic pressure is equal among boxes with different salts. This time, more care was taken to ensure the accuracy of the collected data by setting up multiple boxes per concentration and salt and by not grouping similar boxes together. Solutions to even out the water supply have also been found. Unfortunately, the radishes have not yet matured, such that concrete data and results cannot be included in this paper. However, qualitative observations so far seem to reinforce the hypothesis that some effects intensify or only arise in soils contaminated with copper. The final results will be available by the time of the Stockholm Junior Water Prize in August 2024.

The reproducibility of the collected data could be tested through the repetition of already conducted experiments, and effects on other plants that grow edible roots, like carrots, could also be examined. Moreover, the research could be expanded to include the analysis of water samples and the impact of copper contamination on aquatic organisms, because copper is especially toxic for those species.

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All important sources, some of which are unpublished elsewhere, as well as the original German version of this paper are available for download at [benediktlamberty.github.io](https://github.com/benediktlamberty). Furthermore, it was decided not to include all measurement data in an appendix. The original data and calculations, however, can be found in the online sources [12–16] and the experiment protocols [8, 10, 11]. All figures and tables were created by us, unless otherwise noted in the sources. A collection of additional pictures related to the work can be found in source [5]. Note that many sources are written in German and may not be understood by non-German speakers. The date format used is yyyy–mm–dd.

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