



University of Strasbourg Insitut Terre Environnement Strasbourg Ecole et observatoire des sciences de la Terre

# Master's thesis

## in Earth Sciences

Master 2nd year Earth and Planetary Sciences, Environment: Excellence in Earth and Environmental Sciences

Clément Artigue

Geochemical record of anthropogenic activity in the Rhine paleochannels

Clément Artigue<sup>1</sup> supervised by Cassandra Euzen<sup>3</sup>, François Chabaux<sup>2</sup> and Laurent Schmitt<sup>3</sup>

<sup>1</sup>EOST, university of Strasbourg, France <sup>2</sup>EOST/ITES, university of Strasbourg, France

<sup>3</sup>LIVE, university of Strasbourg, France

June 10, 2022

### ABSTRACT (En)

his study is part of a research project of the Observatoire Homme Milieu de Fessenheim and the thesis of Cassandra EUZEN which aims to study the evolution of the chemical signature of sediments deposited along the Upper Rhine over the last 200 years. We observed variations in the chemical composition of the collected sediments, in particular enrichments in heavy metals and potassium in the sediments dating from the second half of the 20<sup>th</sup> century. A hypothesis tested in the framework of my master's degree is to know if these observations on floodplain and paleochannel sediments could be linked to past anthropogenic activity. This study shows that it is likely that the observed heavy metal and potassium enrichments are of anthropogenic origin. Nevertheless, the uncertainties in the data and the difficulty in defining the natural chemical composition of the sediments make it premature on the basis of the current data to conclude definitively on the origin (anthropogenic vs. natural) of the heavy metal and potassium enrichments observed in the sediments of the Rhine paleochannels.

## RÉSUMÉ (Fr)

ette étude fait partie d'un projet de recherche de l'Observatoire Homme Milieu de Fessenheim et de la thèse de Cassandra EUZEN qui vise à étudier l'évolution de la signature chimique des sédiments déposés le long du Rhin supérieur au cours des 200 dernières années. Nous avons observé des variations dans la composition chimique des sédiments collectés notamment des enrichissements en métaux lourds et en potassium dans les sédiments datant de la seconde moitié du 20ème siècle. Une hypothèse testée dans le cadre de mon master est de savoir si ces observations sur les sédiments de plaine d'inondation et de paléochenaux pourraient être liées à l'activité anthropique passée. Cette étude montre qu'il est probable que les enrichissements en métaux lourds et en potassium observés soient d'origine anthropique. Néanmoins les incertitudes sur les données et la difficulté à définir avec précision la composition chimique naturelle des sédiments font qu'il paraît prématuré sur la base des données actuelles à conclure définitivement quant à l'origine (anthropique vs. naturelle) des enrichissements en métaux lourds et en potassium observés dans les sédiments des paléochenaux du Rhin.

**keywords:** geochemistry, Rhine sediments, geochronology, anthropogenic pollution **mots-clefs:** géochimie, sédiments du Rhin, géochronologie, pollution anthropique

## Contents

1	Intro	oduction	4
2	Mate	erial and methods	5
	2.1	Sampling locations	5
	2.2	Sampling method	6
	2.3	Sample processing	6
		2.3.1 Rock crushing	6
		2.3.2 solution-tratment	7
		2.3.3 Mass spectrometry analysis	8
	2.4	Geochronology	9
		2.4.1 Infrared stimulated luminescence method (IRSL)	9
		2.4.2 Cs137 dating method	9
		2.4.3 Determination of the Depth/Time equations	9
	2.5	Display of geochemical data and uncertainties	10
3	Resu	lts and discussion	11
	3.1	Heavy metals in the Rhine sediment	11
		3.1.1 Zinc variations	11
		3.1.2 Tin variations	13
		3.1.3 Lead variations	15
		3.1.4 Copper variations	17
	3.2	Potassium variations	19
	3.3	Correlation between economic context and heavy metal enrichment in Rhine	
		sediments	23
4	Cone	clusion	23
5	Bibliography		24
6	Арр	endix	27

## List of Figures

1	Map showing the location of sediments samples (white dots) used for our analysis	5
2	Old maps focused on the Marckolsheim core site (red dots). This figure shows	_
_	the evolution deposit environment (figure realised by Cassandra Euzen <sup>3</sup> )	5
3	Mortar and sieve of 2mm mesh size used	6
4	A fixed channel sampler in inox	6
5	To the right : crushed sample at a fraction less than 2 mm and after quartering.	
	To the left : the same sample after being crushed to less than 100 $\mu m$	6
6	Electric rock crusher from Fisher bioblock scientific.	7
7	Sieve with a 100 $\mu m$ mesh size $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	7
8	Bandelin Sonorex RK 255 H Ultrasonic Cleaning Unit used to dissolve sample in	
	nitric acid	7
9	Interior of the ICP-AES from thermo-scientific used for this thesis. We see in the	
	center of the device the plasma torch and on the right the autosampler	8
10	ICP-MS from thermo-scientific used for this thesis.	8
11	"Time-depth equations" determined through linear regression of sediments age	
	versus sampling depth	10
12	Geochemical profil of potassium zinc by silicum versus time. The deposit ages	
	are indicated in the format A.D./B.C.	11
13	Geochemical profil of zinc normalized by silicum versus aluminium/silicium ratio	12
14	Geochemical profil of tin normalized by silicum versus time. The deposit ages	
	are indicated in the format A.D./B.C.	13
15	Tin normalized by silicum versus aluminium/silicium ratio	14
16	Geochemical profil of lead versus time. The deposit ages are indicated in the	
	format A.D./B.C.	15
17	Lead normalized by silicum versus aluminium/silicium ratio	16
18	Geochemical profil of copper normalized by silicium versus time. The deposit	
	ages are indicated in the format A.D./B.C.	17
19	Copper (ppm) versus Organic matter proportion (%)	18
20	Copper (ppm) normalized by silicon versus aluminium/silicon ratio	18
21	Geochemical profile of potassium normalized by silicum versus time. The deposit	
	ages are indicated in the format A.D./B.C.	20
22	Potassium normalized by silicum versus aluminium/silicium ratio	21
23	Montmorillonite in (%) versus aluminium/silicium ratio	21
20	Orthoclase in (%) versus aluminium/silicium ratio	22
25	Evolution of the number of employees by sector of professional activity in Alsace	
20	France	23
26	Ternary granulometric diagram realised for Marckolsheim Rhinau and Baltzen-	20
20	heim samples	27
27	Evolution of the environment around the Marcholcheim campling point using	<u>ل</u> ک
<i></i> /	aerial photos and OGIS software.	27
		- /

## 1 Introduction

The Rhine basin has experienced many antrhopogenic impacts, especially since the beginning of the industrial era in Alsace at the beginning of the 19<sup>th</sup> century through the boom of industrial activity after World War II until its slowdown in the 1970s and 1980s (economic crisis, implementation of the first environmental measures) and its decline during the 2000s (Stoskopf and Vonau, 2004; Insee-Alsace, "chiffres pour l'Alsace" No. 9 April 2010).

Because of their activity, several of the industrial companies located in Rhine plain have discharged non-recoverable waste into the Rhine. This is the case, for example, of the potash mines in Alsace, where rainwater that runs off the slag heaps, which are rich in NaCl and potassium, continues to be enriched in these chemical elements before being discharged into the Rhine, despite the closure of the mines in 2004 (Lucas et al., 2010). As numerous heavy metal industries have been identified in Alsace over the past two centuries (Stoskopf and Vonau, 2004), it is possible that they could have been the source of Rhine sediment pollution. Indeed, we know that heavy metals tend to be captured by clay sediments (O. Otunola et al. 2020) and have already been detected in the world's major floodplains (Berger and Schwarzbauer, 2015). In addition, heavy metal pollution has already been identified, especially in the Lower Rhine region (Middelkoop, 2000).

In our Upper Rhine study area, some Rhine palaeochannels have benefited from a lowenergy current for a sufficiently long period of time to allow the deposition of sediments over the last two centuries and thus make this sedimentary record possible. In this context, a recent sedimentary record was analyzed in the Rorshollen anastomosis where a geochronological method (optically stimulated luminescence, OSL) was used to characterize a 200 year old sedimentary deposit (Eschbach et al., 2018). The results of the study "highlight that periods of engineering works [19<sup>th</sup> and 20<sup>th</sup> century] were closely related to fine sediment deposition, which also presents concomitant heavy metal accumulation". However, David Eschbach's study only considers 10 samples collected in a single site of the upper Rhine : the Roroshollen Island. Furthermore, only the zinc enrichment was proposed as being caused by anthropogenic activity. We speculate that, as observed in the Lower Rhine region (Middelkoop, 2000), other heavy metal enrichments could be caused by antrhopogenic activity, including copper, lead, zinc and tin.

To test this hypothesis, the current study combines geochemical and geochronological methods to trace the chemical context of sedimentary deposits over the last two centuries and discuss the origin of the observed variations. To do so, we use data from different pits collected in paleochannels and floodplains along the Rhine in the Upper Rhine region between Basel (Switzerland) and Strasbourg (France).

In addition to shedding additional light on the industrial history of Alsace and more broadly to better understand the interactions between humans and their environment, this study is also part of a preventive approach in view of the restoration projects of paleochannels and anastomoses in the Rhine (Eschbach, 2018). Indeed, the construction of dams, the canalization of the Rhine, the construction of dikes have impacted the hydromorphology of the river and have harmed the biodiversity in the vicinity. Some of the consequences are the alteration of the river plains, the disconnection of minor beds and channels caused by a deepening of the profile due to the increase of the flow (Bravard, 1994) and the decrease of liquid exchanges between surface water and groundwater (Eschbach et al., 2018). Faced with these problems, many stream restoration projects are being implemented (Morandi et al., 2015), including re-streaming and channel restoration. Therefore it seems important to know the state of pollution, especially heavy metals in the paleochannels, to avoid remobilizing these elements during the rehabilitation of these channels.

## 2 Material and methods

#### 2.1 Sampling locations



Figure 1: Map showing the location of sediments samples (white dots) used for our analysis

For our study, we selected sediment samples along the Upper Rhine in flood-prone areas where sediment could have been deposited during the last 200 years (see figure 1, white dots). To select the locations of the different sampling sites (Rhinau, Marckolsheim, Baltzenheim and Kembs), we analyzed old maps of the Upper Rhine dating from 1778 to 2012 and georeferenced using QGIS software (see figure 2). On this figure, we see that the location chosen for the Marckolsheim core is located at the edge of a paleochannel, an area where it is likely that sediments were deposited in a regressive manner. We also observe on these maps the anthropogenic impact on the geomorphology of the Rhine. Indeed, we see between 1838 and 1872 this portion of the Rhine being canalized during the "Tulla correction" (Tulla, 1825; Herget et al., 2005) which resulted in the obstruction of the channels and the increase of energy and erosion of the Rhine. As with the Marskolsheim core, the same site selection process (regularly flooded low-energy environment) was applied to find the location of the other cores. Thus, three locations that were former flood zones and paleochannels were selected along the Upper Rhine for sampling. The first is from the island of Rhinau, the second from the island of Marckolsheim, and the third from Kembs (see figure 1). The Baltzenheim core is not located in an area of recent sedimentary deposition, sediments dating from before the industrial era. The chemical data from the Baltzenheim samples will therefore constitute our natural chemical signal and a reference core for more recent data from other cores that are potentially polluted. A flood that occurred in 2021 in the region also allowed us to recover sediments deposited along the Rhine that year. These data will allow us to evaluate the signatures of paleochannel sediments in relation to the current sediments that were deposited during floods.



Figure 2: Old maps focused on the Marckolsheim core site (red dots). This figure shows the evolution deposit environment (figure realised by Cassandra Euzen <sup>3</sup>)

Figure 2 also shows the decrease in the size of the floodplain with time and anthropogenic

developments (canalization of the Old Rhine, construction of the Grand Canal). We can thus see that the site of the Marckolsheim core sample, initially located on the edge of an active watercourse, is now in a dry zone after the canalization work, as shown on the 2012 map and as observed in the field.

#### 2.2 Sampling method

#### 2.3 Sample processing

#### 2.3.1 Rock crushing

After collection, the samples were oven dried at 40°C. We then ground the samples to a fraction less than 2mm using an agate mortar and pestle. A sieve with a mesh size of 2mm was used to select only grains smaller than or equal to this diameter (see figure 3). The purpose of this step is to have grains small enough to facilitate the work of the crusher and to eliminate the undesirable of anthropogenic or natural origin which are not representative of the whole sample (pieces of brick, plastics, pebbles).



Figure 3: Mortar and sieve of 2mm mesh size used

The next step was to perform a quartering using a fixed channel sampler (Figure 4). During this step, the objective is to collect a representative fraction of the original sample whose volume is adapted to the capacity of the shredder and nevertheless sufficient for laboratory analysis (solution treatment and spectrometric analysis) (Figure 5).



Figure 4: A fixed channel sampler in inox



Figure 5: To the right : crushed sample at a fraction less than 2 mm and after quartering. To the left : the same sample after being crushed to less than 100  $\mu m$ 

While the fraction of grains larger than 2mm was kept for the granulometric study of the whole sample, the fraction of grains smaller than 2 mm has been crushed with an electric rock crusher "Fisher bioblock scientific" (cf. figure 6) at a fraction of 100  $\mu m$ . As with the mortar, the grinding wheel and container are made of agate to prevent contamination of sediments.



Figure 6: Electric rock crusher from Fisher bioblock scientific.

A second sieve, this time with a mesh size of 100 micrometers, was used to verify that the sediments exiting the crusher did not exceed this diameter (figure 7).



Figure 7: Sieve with a 100  $\mu m$  mesh size

It should be noticed that all the steps presented above have been realised under a laminar flow hood. The laminar flow hood protect sediments from dust and other airborn contaminants by maintaining a constant, unidirectional flow of HEPA-filtered air over the work area.

#### 2.3.2 solution-tratment

Once the samples are reduced to a grain size less than 100  $\mu m$ , we put them a first time in a hoven at 375°C in melting pots to measure the loss of mass which represents the quantity of organic matter in the sample (values shown in the results chapter). A second passage in the oven at a higher temperature allows to reach the melting temperature of the sediments which then take the aspect of a glass ball. The whole is then dissolved in a chemical solution of nitric acid diluted to 50% with water. To accelerate the dilution. the carbon crucibles are placed in the ultrasound tank. This solution was chosen rather than the more traditional one of the magnetic stirrer (dissolution by mechanical stirring of the solution) to avoid that projections go from one crucible to another and thus contaminate our samples.



Figure 8: Bandelin Sonorex RK 255 H Ultrasonic Cleaning Unit used to dissolve sample in nitric acid

Before proceeding to the last step which consists in analyzing the chemical composition of the sediments using mass spectrometers. The solutions obtained following the ultrasound dissolution undergo a dilution of 1 in 10 with the solution of nitric acid diluted to 50% with water.

#### 2.3.3 Mass spectrometry analysis

To obtain major elements proportion in the sample (expressed as a percentage), we used an inductively coupled plasma atomic emission spectrometer (ICP-AES, Figure 9). The principle of this spectrometer is to use an inductively coupled plasma to excite the atoms and ions of a sample which in turn emit electromagnetic radiation with a characteristic wavelength for each chemical element. An autosampler was used on our solutions previously placed in test tubes.



Figure 9: Interior of the ICP-AES from thermoscientific used for this thesis. We see in the center of the device the plasma torch and on the right the autosampler.

To obtain minor elements proportion in the sample (expressed in ppm), we used an inductively coupled plasma mass spectrometer (ICP-MS, cf. Figure 10). The separation of elements is achieved by separating the ions generated by an argon plasma according to their mass/charge ratio. It allows the analysis of solids (after dissolution or alkaline fusion) and liquids (after dilution) with a high accuracy and is particularly reliable for measuring very low concentrations. The precision is of the order of the ppb for ICP -MS against the ten of ppb for ICP-AES. Therefore, in the following results, the major element data are from the ICP-AES and the minor element data, which require greater sensitivity, are from the ICP-MS.



Figure 10: ICP-MS from thermo-scientific used for this thesis.

#### 2.4 Geochronology

The dating of the samples to establish the time/depth equation for each core (Figure 11 was done by combining different geochronological methods.

# 2.4.1 Infrared stimulated luminescence method (IRSL)

The oldest sediments analyzed during this study and from the Baltzenheim core were dated with the IRSL (Infrared stimulated luminescence) applied on feldspar. IRSL was chosen instead of the more traditional method of OSL (Optical Stimulated Luminescence) because the latter only works on quartz, an element that was in too low a quantity in our samples to use this technique. However, the principle of operation of IRSL remains very close to that of OSL. The first step is to stimulate the feldspar minerals in the sample with infrared light which has the effect of releasing the electrons accumulated in the felspar. This accumulation of electrons occurs by radioactive decay of certain elements that surround the feldspar when it is buried. When the feldspar is then exposed to sunlight or infrared light, the electrons that have accumulated during the burial period are released, which is called "bleaching" (Mercier, 2008). This release of electrons creates a signal of luminescence which gives the total absorbed radiation dose (in Gy). Thus, by knowing the radiation dose rate (radioactive radiation rate in Gy/year), one can know when the mineral has "seen the sun" for the last time before being buried and accumulating electrons by radioactive radiation from the underground (see equation 1, Cordier, 2010).

$$Age \text{ (in a)} = \frac{P \text{ (in grays Gy or J/kg)}}{Dr \text{ (in Gy/a)}} \quad (1)$$

The IRSL results and equation 1 allowed us to obtain the time-depth conversion equation (Figure 11) for Baltzenheim core and thus to model the profiles of chemical elements as a function of time (see results section).

#### 2.4.2 Cs137 dating method

The cesium-137 dating method has already been used to date recent sediments (less than a century) and study heavy metal contamination (Rapin, 1981; Bonte et al., 2001) This radiodatation method is based on the atmospheric fallout of Cs-137 that occurred during the nuclear tests of the 1950s and the accident at the Chernobyl nuclear power plant on 26 April 1986. In the case of regular sedimentation such as at the edge of a channel, analysis of the distribution of 137Cs as a function of depth allows precise dating of the deposits with the recognition of a sudden enrichment of caesium in the sediments of 1986 and a more diffuse enrichment in the sediments of the 1950s.

The 137Cs results have allowed us to date certain sediments at a given depth in the Rhinau and Kembs cores and thus to contribute to the establishment of the time-depth equation for these two cores (Figure 11).

# 2.4.3 Determinaion of the Depth/Time equations

Once the age of some samples was obtained via the methods summarized above, a plot of sediment age versus depth was made for each of the four cores (Figure 11). Since the age of deposition of each sample is not known, a linear interpolation is performed to define a function linking depth and age of deposition. The choice of a linear interpolation was made because we noticed that the few dating data we had evolved linearly with age deposit (linear regressions with a correlation coefficient R2 > 0.9 whatever the core)

#### Geochemical record of anthropogenic activity in the Rhine paleochannels



Figure 11: "Time-depth equations" determined through linear regression of sediments age versus sampling depth

# 2.5 Display of geochemical data and uncertainties

Once the data provided by the spectrometers were placed in an Excel file, a python application, programmed specifically for this study in python, was used to allow the production of graphs showing the proportion of chemical species as a function of the depth sought, time or the proportion of another chemical species with their uncertainty and statistical information (linear regression, correlation coefficient). This application provided us with all the graphs presented in the Results section. Thus the graphs were made using the python library "matplotlib". The curves connecting the points of the geochemical profiles as a function of time are 2nd order interpolations calculated with the python function interp1d (scipy library). Each point is ploted with its error bar symbolized by an horizontal thin line.

The uncertainties are estimated based on the blank and of the deviations of the measured values of the standards whose values are known accepted

## 3 Results and discussion

All the sediments were analyzed for major and trace elements, their mineralogical composition and their grainsize. For this study, we focused on the concentrations of heavy metals (Zn-Sn-Pb-Cu) and Potassium following the preliminary results of Eschbach et al., 2018 and Euzen (thesis in progress). These results will be presented and discussed here.

# 3.1 Heavy metals in the Rhine sediment



#### 3.1.1 Zinc variations

Figure 12: Geochemical profil of potassium zinc by silicum versus time. The deposit ages are indicated in the format A.D./B.C.

#### **Results:**

The Figure 12 shows the evolution of the ratio  $Zn/SiO_2$  in samples from four different cores and pits named after the locality where they were collected (see exact localization on Figure 1). As Zn and SiO<sub>2</sub> are expressed in the same unit (ppm), the ratio is unitless. This chemical ratio is ploted versus year of deposit

obtained from sample depth and the "depthtime conversion equations" (Figure 11) .

We observe in the Figure 12 that the Zn/SiO<sub>2</sub> ratio in all samples still approximately constant until 1940 whatever the core  $(0.4e-4 < Zn/SiO_2 < 1.6e-4)$ , except for two samples from Baltzenheim (blue dots). It should be noted that the loss of Zn/SiO<sub>2</sub> observed about the year 1880 in Rhinau samples is due to a sandy level enriched in quartz and hence characterized by a high SiO<sub>2</sub> concentration in sample. The data point out that from 1940 to 1973, the Zn/SiO<sub>2</sub> ratio in Rhinau samples increases from 1.44e-4 to 3.5e-4. It then stablilizes around 3.5 before decreasing from 1999 (Zn/SiO<sub>2</sub>=3.73e-4) to 2021  $(Zn/SiO_2=2.44e-4)$ . Similar variations, although with smaller amplitude are observed in Kembs core from 1960, age of the oldest sediment recovered from this site.

In surface environments heavy metal are often complexed with clay (e.g. O. Otunola et al. 2020). In river sediments, the aluminum/ silicon ratio  $(Al_2O_3/SiO_2)$  can be considered as a good proxy of the ratio between clay minerals and the so-called primary silicate minerals.It is why the Zn/SiO<sub>2</sub> ratio are compared with the  $Al_2O_3/SiO_2$  ratio (Figure 13). For Rhinau samples Figure 12 show that the higher the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio, the higher the Zn/SiO<sub>2</sub> ratio. In the Figure 13 the blue line represents the linear regression of Baltzenheim data for which sediments are older than the other sites and therefore supposedly free of any anthropogenic contamination in depth. For all the following results, the Baltzenheim data, will therefore be considered as the natural signal. However, note that for some chemical species, it could be more complex in the upper part of the core as the site is located in an agricultural area. The results of Figure 13 show that most of the point follow a positive linear trend. We observe that the linear trend of Rhinau samples (green triangle) is a bit under the Baltzenheim linear regression. It should be noticed that of the three samples of sediments deposited during the 2021 Rhinau flood, two are aligned with the Rhinau core data (see the



Figure 13: Geochemical profil of zinc normalized by silicum versus aluminium/silicium ratio

two black diamonds at  $Al_2O_3/SiO_2 = 0.188$ and  $Al_2O_3/SiO_2 = 0.164$ ). From Figure 12 it thus appears that the high Zn/SiO<sub>2</sub> ratios observed in Rhinau time profile (Figure 13) can be explained by a higher proportion of clay fraction in these sediment deposits, and do not necessary represent a contamination of these samples by Zn. For Kembs data which presented also a zinc enrichment at the same decade of the deposited sediments of Rhinau (Figure 12). However, on Figure 13, unlike Rhinau where the values ranges within the natural signal, in Kembs, the Zn/SiO<sub>2</sub> ratio is higher than the natural signal.

This is confirmed by two of the three 2021-flood samples deposited in the area of Kembs which appear to be in the same graphic area that the other Kembs sample with a  $Zn/SiO_2$  ratio above Baltzenheim regression (see the two black diamonds at  $Al_2O_3/SiO_2 = 0.097$  and  $Al_2O_3/SiO_2 = 0.134$ ).

#### Interpretation:

Although, at first glance, there is a zinc enrichment observed on the time profile (Figure 12), the results from the geochemical profile of zinc normalized by silicum versus  $Al_2O_3/SiO_2$  (Figure 13) seem to challenge this idea. Indeed, in Rhinau sample the zinc normalized by silicium evolves linearly with the proportion of clay (R2 of Rhinau data = 0,70) and this at the same level or below the natural signal.

It is interesting to see however that Kembs data (purple dots) in addition to not respect this linear trend depending from clay proportion (R2=0.05), are above the natural signal. We could then think that an anthropogenic pollution would be responsible of the zinc enrichment. However, because zinc enrichment can also be observed in 2021 flood sediments in Kembs is strange since no zinc pollution was reported at that time to our knowledge.

It is then possible that these sediments deposited in 2021 are in fact old zinc-polluted sediments remobilized during the flood or that the new sediments deposited in Kembs in 2021 still contain zinc pollution (caused by its use in the agricultural field for example).

It is also possible that the natural signal, which is assumed to be the linear regression of the Baltzenheim data, is not the correct one given the possible mobility of zinc within the sediment core and the relatively low correlation coefficient of this linear regression (R2=0.49, see Figure 13).

Thus, the results, in my opinion, do not allow to know with certainty the origin of the zinc anomaly observed in the temporal profile.



#### 3.1.2 Tin variations

Figure 14: Geochemical profil of tin normalized by silicum versus time. The deposit ages are indicated in the format A.D./B.C.

#### **Results:**

Figure 14 shows the fraction of tin (ppm) normalized by the fraction of silicon dioxyde (ppm) versus time. We see in this figure two horizontal lines at 1836 and 1930 indicating respectively the date of the opening of a tin

factory in Brustatt (company name: CLAUDE (Antoine)) and the date of the opening of a metallurgical factory in Huningue which used tin and zinc (company name: PROMENS. ANISA Société, ex ANILINE SA, closed in 2010). Concerning the variations of tin, one initially observes a Sn/SiO2 ratio of about 0.3e-5 in the Baltzenheim core (blue crosses on the graph). We see that between 1860 and 1900 the sediments of Marckolsheim have Sn/SiO<sub>2</sub> ratios systematically higher than the values of Baltzenheim (between 1.2e-5 and 2e-5, red squares, see Figure 14). During this same period, the sediments of Rhinau are located in the sandy past and thus have a particularly low clay content which is translated between 1860 and 1900 by a particularly low Sn/SiO<sub>2</sub> ratio. Furthermore, a clear increase of this ratio is observed in Rhinau from 1939 and to a lesser extent in Marckolsheim and Kembs during the same period. In Rhinau  $Sn/SiO_2 = 1.2e-5$  in 1905 and 4.6e-5 in 1948, in Marckolsheim  $Sn/SiO_2 = 0.8e-5$  in 1906 and 1.4e-5 in 1960 and in Kembs  $Sn/SiO_2 =$ 1.1e-5 in 1963 and 0.5e-5 in 2014. We thus note that the two peaks of tin observed in Rhinau and to a lesser extent in Marckolsheim and Kembs takes place at approximately the same ages of deposition (maximum observed around 1950 for Rhinau and around 1960 for Kembs and Marckolsheim).

As seen with zinc (section 3.1.1), tin complexation is correlated to clay proportion (O. Otunola et al. 2020). Clay proportion increases with that of the ratio aluminium/silicon (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>), we looked then Sn/SiO<sub>2</sub> ratio values versus Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio values (Figure 15) to see if the two assumed tin enrichments observed in the 20<sup>th</sup> century and in the second half of the 19<sup>th</sup> century(Figure 14) is explained by a higher clay poportion in these samples.

In the Figure 15 we see that all  $Sn/SiO_2$  values are above the natural signal defined by the linear regression of Baltzenheim (blue line). However, a part of the values of the three cores that cover the period of the tin enrichment (Marckolsheim, Kembs and Rhinau)



Figure 15: Tin normalized by silicum versus aluminium/silicium ratio

seem to be aligned with floods data (black diamonds on Figure 15). This new alignment is, relative to the order of magnitude of the observed variations, very close to Baltzenheim linear regression. We see that some of the samples from Rhinau, Marckolsheim and Kembs have Sn/SiO<sub>2</sub> values that deviate from the observed linear trend. Moreover, it is interesting to note that the samples with values furthest from the line, and thus with zinc content least correlated with the proportion of clay, are the same samples that correspond to the tin peak observed in the 50s/60s. See the sets of samples noted Sn R, Sn M and Sn K (see Figure 15 and Figure 14). It should be noticed that the four samples of Marckolsheim (ref square, Figure 15 between  $0.11 < Al_2O_3/SiO_2 < 0.12$ which are also far from the naturel signal corresponds to the deposit age between 1860 -1887. This first enrichment is not visible in the Rhinau data because of the sandy pass characterized by a low proportion of clay in the sediments that this induces.

#### Interpretation:

A Tin enrichment is clearly visible throughout the  $20^{th}$  century, with a maximum during the 50s/60s in Rhinau samples and also, to a lesser extent, in Marckolsheim and kembs samples. We think that the difference of scale in the Tin enrichment between on one side Rhinau sediments and the other side Marckolsheim followed by kembs samples, is due to a difference of clay proportion which is more important in Rhinau sediments while it still appoximately the same in kembs and Marckolsheim sediments. However it is important to underline that this enrichment begin at the same time (around 1920) and the Tin rate begin to decrease also at the same moment (around 1960). Results of Figure 15 suggest that clay proportion doesn't explain Tin enrichment observed simultaneously in Rhinau, Marckolsheim and Kembs sediments because their Tin fraction does'nt increase linearly with the aluminum/silicon ratio.

Therefore, we suspect anthropogenic activities in upstream of the sampling locations to be responsible of this Tin enrichment, which is consistent in view of Tin factories activity during the  $20^{th}$  century . Indeed numerous heavy metal industries have been identified in Alsace over the past two centuries (Stoskopf et al. 2015). This is the case of the Huningue metal factory which started its activity shortly before the peak of tin pollution observed in the sediments (see Figure 14). Moreover during this century boats were treated with tin which for a part could have been deposited at the bottom of the Rhine.

The enrichment observed in Marckolsheim between 1860 and 1890 could be caused by the opening of the tin factory in Brunstatt. It is interesting to see that this rate decreases at the beginning of the  $20^{th}$  century, perhaps due to the temporary stop of the activity of the Brunstatt factory or to a disruption of the metallurgical activity during the first world war.

Concerning the natural signal of tin as a function of clay proportion, although the recent flood deposits have a chemical behavior much closer to that of the Baltzenheim sediments (cf. Figure 15) these sediments seem to align along a new line thus defining a new linear trend characterized by a different linear function between clay and Sn proportion. We believe that these higher Sn levels in the 2021 flood sediments compared to the Baltzenheim sediments are due to diffuse discharges upstream and in the floodplain and/or diffuse remobilization of Sn during floods.

The fact that the tin enrichments observed in the 20<sup>th</sup> and 19<sup>th</sup> centuries are consistently higher than those observed in the 2021 data suggests that tin pollution in the Rhine is currently declining. However, tin concentrations in the Rhine have still not returned to their initial levels measured in sediments deposited between -900 and -4055 BC.

#### 3.1.3 Lead variations



Figure 16: Geochemical profil of lead versus time. The deposit ages are indicated in the format A.D./B.C.

#### **Results:**

We see in the figure 16 the lead fraction (in ppm) normalized by silicium (in ppm) versus the age of deposits of sediments determined thanks to the depth-time equations (see method 2.4.3). The figue shows that until 1950, Pb/SiO<sub>2</sub> values oscillate between 0.15e-5 and 0.4e-5 for Baltzenheim (reference) and Marckolsheim. These values oscilate between 0.4e-5 and 0.6e-5 in Rhinau if we neglect the loss observed in the 1880s, which corresponds to the sandy layer observed in a field trench and characterized by a very high proportion of silica in samples. Since 1950 we observe an enrichment in lead, the values of the ratio Pb/SiO<sub>2</sub> passing in Rhinelander from 0.5e-5 to 0.95e-5 from 1948 to 1982 and then falling back to 0.55e-5 in 2016. We see that the same trends occur at the same ages of deposition in Marckolsheim and Kembs (Pb/Si = 0.2e-5 in 1948 in Marckolsheim, 0.6e-5 in 1977 and 0.2e-5 in 2010). It should be noted that there

#### Geochemical record of anthropogenic activity in the Rhine paleochannels



Figure 17: Lead normalized by silicum versus aluminium/silicium ratio

are large uncertainties in these results which make it difficult to analyze the variation of this ratio before 1950.

Still on the figure, the two horizontal lines correspond in 1940 to the democratization of leaded gasoline which is known to have had during the second half of the 20<sup>th</sup> century visible effects in the environment in France (pollution of watercourses, contamination of living organisms etc.). The second horizontal line on the figure, which corresponds to the year 1986, refers to the year when the sale of engines using leaded gasoline was prohibited in France. This moment marked the decline of leaded gasoline. We can see on the graph that these two moments coincide respectively with the beginning of lead enrichment and its peak. On the Figure 17, which is interesting to see if the proportion of clay could explain the lead enrichment observed previously, we see that most of the samples have a Pb/SiO<sub>2</sub> ratio aligned according to the Baltzenheim linear regression which here has a correlation coefficient R2 = 0.71. It is interesting to note that the samples that constituted the peak observed in Figure 16 and grouped under the names Pb\_K and Pb\_R (samples circled in black, see Figure 17 and 16) correspond here to the samples that are furthest from the natural signal (the "linear regression of Blatzenheim data").

#### Interpretation:

Results of Lead suggest that a lead enrichment, not caused by a higher clay rate is present in the sediments at the depth corresponding to the 1950s to 1980s.We think that after 1940, the massive use of leaded gasoline in France (called "super") could be responsible of this lead enrichment. Moreover, we know that in 1984 the sell of cars with leaded gasoline motors was forbidden which corresponds with the begin of the Pb decrease in sediments.

Thus, the hypothesis of a direct impact of anthropogenic activity in Pb composition of

sediments is highly probable and would be in line with numerous studies that demonstrated the presence of lead in living and non-living organisms caused by anthropic activity (Perdrial et al., 2008).

However it is intriguing to see the current sediments in Rhinau have not recovered their original lead level despite the end of leaded gasoline. Even if the particularly high uncertainties on lead should make us take some distance from these results, they suggest that the pre-industrial level of lead has probably not been recovered due to the possible presence of other sources of pollution or remobilization phenomena of this element.

Nevertheless, the data on the proportions of tin in the 2021 sediments suggest that the level of pollution is decreasing from the end of the  $20^{th}$  century to the present, decrease attributed to the end of the use of lead in gasoline.

#### 3.1.4 Copper variations

#### **Results:**

We see in the copper profile (cf. Figure 18) that until about 1960 the proportion of copper still approximately the same in Rhine sediments oscillating in Baltzenheim and Marckolsheim sediments between 0.1e-5 and 0.45e-5 (blue crosses and red squares in the graph). In the same way Rhinau sediments have a  $Cu/SiO_2$  ratio almost constant until 1948 with values oscilating between 0.4e-5 and 0.6e-5 if we neglect, as seen before, the loss observed in the 1880s which corresponds to the sandy layer (cf. 3.1.2).

After 1960, copper proportion increases strongly until reach a maximum in Kembs and Rhinau sediments (respectively 0.75e-5 in 1970 and 1.25e-5 in 1973). These maximum are surrounded in black and called Cu\_K for Kembs maximum and Cu\_R for the Rhinau maximum in the Figure 18.



Figure 18: Geochemical profil of copper normalized by silicium versus time. The deposit ages are indicated in the format A.D./B.C.

It should be noted that a phase of continuous decrease of the copper content occurs at the same time for the samples from Kembs and Rhinau from 1970s until today with values ranging from 0.75e-4 in 1970 to 0.05e-4 in 2014 for the Kembs core and values ranging from 1.25e-4 in 1973 to 0.72e-4 in 2016 for Rhinau.

As we know that copper is correlated with organic matter (Lenoir, 2006), we observed the results of coppers vs organic matter (cf. Figure 19) to verify if the copper enrichment in the 70's sediments would be due to an enrichment in organic matter. These results show that as expected the copper proportion of samples increases with organic matter proportion. We see on the graph that linear regression of Baltzenheim has a low correlated coefficient (R2 = 0.40). The linear regression of floods sediments has also been drawn (R2 = 0.79).

We observe that Cu\_K values, which constitutes the enrichment observed in time profil

#### Geochemical record of anthropogenic activity in the Rhine paleochannels



Figure 19: Copper (ppm) versus Organic matter proportion (%)



Figure 20: Copper (ppm) normalized by silicon versus aluminium/silicon ratio

from the Kembs core, are not aligned on the Baltzenheim of floods regressions. Concerning the copper-enriched samples from Rhinau (Cu\_R), three of these five samples seem to be in line with the natural signal while the two samples with the highest proportion of Cu seem to deviate from this natural trend. The origin of the enrichment can also be caused by a higher clay fraction (Lenoir, 2006). Thus we ploted, as for the other heavy metals, the copper normalized by silicium (Cu/Si) versus Al/Si (Figure 20).

The results show a well alignment of samples along the Baltzenheim linear regression or floods data linear regression (dark line, 20). We see that Cu\_K values does not follow the linear trend defined by the other samples. However, the copper-enriched samples from Rhinau seem to be aligned with the Cu/SiO<sub>2</sub> values of the floods sediments.

#### Interpretation:

Regarding copper, the main difficulty is that the natural reference signal is complicated to establish here. Indeed, as observed in the figure, two linear trends seem to coexist: the one from Baltzenheim whose R2 (correlation coefficient of the linear regression) is particularly low compared to what has been seen for the other heavy metals, and the one from the flood data. Moreover, it is necessary to consider that the proportion of copper evolves in theory linearly with the proportion of organic matter and clay.

Thus, the Kembs sediments, which contribute to the copper enrichment observed on the profile showing the proportion of copper as a function of age of deposition (Cu\_K, Figure 18), by evolving distinctly from the linear trends defined by the Baltazenheim or flood data, make the hypothesis of anthropogenic contamination plausible. However, the Rhinau sediments that contribute to the copper enrichment observed on the profile (Cu\_R) challenge this hypothesis. Indeed, most of these samples seem to be aligned with floods data. Furthermore, it should be noted that the sediments from the 2021 floods collected in Rhinau have a chemical signature very close to the Rhinau sediments of the Cu\_R group, whether on the graph of copper versus organic matter or on the graph representing the evolution of the proportion of copper versus clay.

Thus it is complicated at present to conclude on the origin of this copper enrichment in the sediments, perhaps it is caused by a greater proportion of organic matter and clay at this depth or perhaps it is caused by anthropogenic activity which includes this copper pollution that still exists as suggested by the 2021 sediments and which may be caused by agriculture (copper being used as a natural fungicide treatment in agriculture).

#### 3.2 Potassium variations

#### **Results:**

Although Potassium is not a heavy metal, unlike the other elements we studied, it seemed relevant to us to look at the variations in the proportions of potassium in view of the mining activity linked to the exploitation of potash which was active in Alsace until 2004. Moreover, we know from the study of (Yann et al. 2010) that pollution linked to the slag heaps (see introduction) has been detected in the water of the Rhine until recently.

Figure 21 shows the evolution of the potassium along our four sedimentary cores. First, we observe a slight increase in the potassium content of the Baltzenheim core with a K<sub>2</sub>O/SiO<sub>2</sub> ratio equal to 2 .1e-2 in 1560 against 2.7e-2 in 1800. From 1850 to 1940 we see in Marckolsheim and Rhinau K<sub>2</sub>O/SiO<sub>2</sub> values remain approximately constant between 2.5e-2 and 3.1e-2 for the first core and between 3.0e-2 and 3.4e-2 for the second core (if we neglect the Rhinau data between 1870 and 1890 largely influenced by the sandy past). We see that while the potassium fraction increases in the Rhinau sediments from 1940 ( $K_2O/SiO_2 = 3.25e-2$ ) to 1990 ( $K_2O/SiO_2 = 4.5e-2$ ) for the same deposition period, the Kembs sediments show constant or even decreasing K<sub>2</sub>O values (2.25e-2  $< K_2O/SiO_2 < 2.75e-2).$ 

Thus this figure shows a potassium enrichment "K2O R" circled in balck in the figure (enrichment relative to the Baltzenheim data). The brown horizontal line, in the same figure, represents the year the brine pipeline was put into service in 1936, which allowed polluted water from the potash mine slag heaps in Alsace to be discharged into the Rhine so that it would not seep into the water table. The brine pipeline is still active today. Knowing that, We see in the figure 21 an augmentation in  $K_2O$ concentration in Rhinau sediments after the commissioning of the brine pipeline. Note that he brine pipeline is located upstream of the Rhinau core and downstream of the Kembs core. (cf. Figure 1).



Figure 21: Geochemical profile of potassium normalized by silicum versus time. The deposit ages are indicated in the format A.D./B.C.

Clay has captation properties and for many chemical species grows linearly with the porportion of the minor element. We looked then if  $K_2O/SiO_2$  ratio values versus  $Al_2O_3/SiO_2$  ratio values (Figure 22) to see if the potassium enrichment observed in Figure 21 (K2O\_R scatter plot) is explained by a higher clay proportion in these samples.

We can see on the results showing the evolution of the K<sub>2</sub>O/SiO<sub>2</sub> ratio as a function of the clay content that most of the data are aligned with the Baltzenheim linear regression (supposed as the geochemical background free of any pollution) except for two scatter plots of points that we will note K2O\_M and K2O\_R (see Figure 22). The first one corresponds to the samples of Marckolsheim located between 1900 and 1960 while the second scatter plot corresponds to the samples of Rhinau between 1960 and 2021. The samples of the K2O\_R scatter plot are the same as those which constitute the potassium enrichment identified on the Figure 21.

Some minerals, namely orthoclase and montmorillonite, contain potassium. The next results aim to verify whether or not the enrichments observed on the time profile can be explained by a higher proportion of these minerals in the sediments concerned (K2O M and K2O R). We observe, in the figure 23 that K2O R The scatter plot of samples have varying percentages of montmorillonite ranging from 1.4% to 2.7% (green triangles circled in black). This order of magnitude seems similar for the flood samples (blue crosses) have a montmorillonite percentage ranging from 1.1% to 2.4%. It should be noted, however, that most of the samples from Marckolsheim and Baltzenheim (red squares and purple dots) contain less than 1.5% Montmorillonite.

Concerning the percentage of orthoclase observed in the figure 24. We can see that the sediments of the K2O\_R scatter plot (which are enriched in potassium) have a percentage of orthoclase similar to that observed in Baltzenheim and in the flood deposits (percentage of orthoclase between 2.4 % and 4.5 %).

#### Interpretation:

Regarding potassium in Rhine sediments, results of temporal profile (see Figure 21) suggest that a potassium enrichment exists in Rhinau sediments between 1960 until 2021

#### Geochemical record of anthropogenic activity in the Rhine paleochannels



Figure 22: Potassium normalized by silicum versus aluminium/silicium ratio



Figure 23: Montmorillonite in (%) versus aluminium/silicium ratio

#### Geochemical record of anthropogenic activity in the Rhine paleochannels



Figure 24: Orthoclase in (%) versus aluminium/silicium ratio

(scatter plot named K2O\_R in the figure 21) while Kembs no shows any enrichment in potassium in the same period. As we know that Kembs sediments are in upstream of the brine pipeline (which, discharge NaCl and potassium into the river), while Rhinau sediments are in downstream, our first hypothesis is that this potassium anomaly is directly caused by the activity of Alsacian potassium mining.

To verify this hypothesis, it is interesting to talk about the other results. Indeed, the figure 22 suggest in first view that the sediments of the scatter plot K2O\_R don't seem to be aligned on the line governed by the law of proportionality between  $K_2O$  and clay content and on which the other sediments are aligned except for the K2O\_M. However, the uncertainty in the  $K_2O/SiO_2$  values of the Rhinauenriched sediments is such that it is possible that these sediments follow the observed linear trend (Figure 22). It is therefore difficult, in view of the results, to completely rule

out the hypothesis that a greater proportion of clay is responsible for the enrichment observed in the time profile. Note that in this same figure the sediments with the highest potassium anomaly are those with the highest clay content. Here again the reason may be related to the brine pipeline. Indeed, we know that in addition to NaCl and potassium, the pipeline also discharged clays (fine fraction) while the mines were still in operation before 2004. This explanation is also consistent with the fact that the data of the sediments deposited during the floods in Rhinau (black diamond) have a lower clay content than those deposited during the second half of the 20<sup>th</sup> century. Moreover, it is to be noted that within the K2O R point cloud the sample with the lowest clay content is the one at the surface of the core (between 0 and 5cm depth) which was therefore deposited in the years following the end of the clay release into the Rhine via the brine pipeline. The mineralogical results (Figure 23 and Figure 24) suggest that the montmorillonite and orthoclase content, not being higher than that observed for flood deposits, are not responsible for the potassium enrichment observed at Rhinau.

All of these arguments make it likely that potassium enrichment observed is caused by anthropogenic activity, and more specifically by potash mines in Alsace.

It would be interesting to make other samples in other recent deposit locations and directly on the slag heap of the Alsacian potassium mining to conclude on the origin of the potassium enrichment.

#### 3.3 Correlation between economic context and heavy metal enrichment in Rhine sediments.



Figure 25: Evolution of the number of employees by sector of professional activity in Alsace, France.

It is interesting to observe a certain correlation between the dynamics of the observed enrichments in heavy metals and the industrial activity in France. Indeed, as presented in the introduction, the figures of the Insee (National Institute of Statistics and Economic Studies) and the study of Stoskopf and Vonau, 2004 show that the industrial activity is booming until a slowdown in the 70s and 80s in Alsace before a decline in the 2000s. In parallel we see that the time interval 1960-2000 includes all of the heavy metal enrichments observed not only at the Rhinau site but also at Kembs and Marckolsheim even though the enrichment amplitudes were smaller. In addition, a systematic decrease in the heavy metal content can be observed from the year 2000 onwards. Thus, the observations of heavy metal levels in Rhine sediments are consistent with industrial and economic changes in Alsace. Note that the study of the evolution of heavy metal levels, in particular lead, over the ages to characterize the hazards of economic development of a society has already been carried out to study the periods of prosperity and decline of the Roman Republic/Empire (McConnell et al., 2018).

### 4 Conclusion

The results of this study show it is likely that the recent sediments of the Rhine found in paleochannels and old flood plains recorded anthropogenic activity during the second half of the  $20^{th}$  century.

We see however a clear decrease of these pollutions which is well correlated with the period of deindustrialization of Rhine basin (late 20<sup>th</sup> century early 21st century). Indeed, we have seen that systematically the heavy metal pollution is lower today (sedimentary deposits of 2021) than during the industrial era of the second half of the 19<sup>th</sup> century and the 20<sup>th</sup> century. This recent decrease in the rate of metals could be the conjuncture of the deindustrialization of the region in the 21st century and the implementation of environmental policies which could be conducted for example by the ICPR (International Commission for the Protection of the Rhine).

I think it would be interesting in the future to compare these results with geochemical data upstream Basel to see the impact of past factories of the city on heavy metal concentration that we detected downstream as we did for the potash mines of Alsace studying a sediment core downstream and upstream of the brine pipeline. Other data along Rhine in recent deposit systems would be interesting to confirm our observations. Moreover, it would be interesting to improve our estimation of the natural signal that serves as a reference by taking more samples like those obtained in Baltzenheim. In addition, it would be interesting to carry out an ecotoxicological study to know if, at such concentrations, the observed enrichments in heavy metals and potassium could represent a danger for the human beings and the biodiversity if these paleochannels and other formerly floodable environments were to be drained again in particular following projects of restoration of these old hydraulic connections.

## 5 Bibliography

## References

- Berger, M. and J. Schwarzbauer (Dec. 2015).
  "Historical Deposition of Riverine Contamination on Terrestrial Floodplains as Revealed by Organic Indicators from an Industrial Point Source". In: *Water, Air, & amp Soil Pollution* 227.1. DOI: 10.1007/s11270-015-2708-8. URL: https://doi.org/10.1007/s11270-015-2708-8.
- Bonte, Philippe et al. (2001). "Datations au 137Cs, 134Cs et 210PB de dépôts de crues du XXe siècle". In: *Datation*. Ed. by J.-N. Barrandon, P. Guibert, and V. Michel. Datation XXIe rencontres internationales d'archéologie et d'histoire d'Antibes. Antibes, France: Editions APDCA, pp. 141–157. URL: https://hal-amu.archives-ouvertes.fr/hal-01569357.
- Bravard, Jean-Paul (1994). "L'incision des lits fluviaux : du phénomène morphodynamique naturel et réversible aux impacts irréversibles / The incision of river beds : from a natural and reversible morphodynamic phenomenon to irreversible impacts".
  In: *Revue de géographie de Lyon* 69.1, pp. 5–10. DOI: 10.3406/geoca.1994.4231. URL: https://doi.org/10.3406/geoca.1994.4231.
- Cordier, Stéphane (Apr. 2010). "Optically stimulated luminescence dating: procedures and applications to geomorphological research in France". In: *Géomorpholo*-

gie : relief, processus, environnement 16.1, pp. 21-40. DOI: 10.4000/geomorphologie. 7785. URL: https://doi.org/10.4000/ geomorphologie.7785.

- Eschbach, David et al. (May 2018). "Long-term temporal trajectories to enhance restoration efficiency and sustainability on large rivers: an interdisciplinary study". In: *Hydrology and Earth System Sciences* 22.5, pp. 2717–2737. DOI: 10.5194/hess-22-2717-2018. URL: https://doi.org/10.5194/hess-22-2717-2018.
- Lenoir Thomas, et al. (Mar. 2006). "Mécanismes de rétention du cuivre dans les sols : évaluation statistique des approches macroscopiques et spectroscopiques". In: *Geochemistry, Geophysics, Geosystems* 7.2, pp. 4477–4479. URL: https://doi.org/ 10.4000/vertigo.2171..
- Lucas, Y. et al. (Nov. 2010). "Geochemical tracing and hydrogeochemical modelling of water-rock interactions during salinization of alluvial groundwater (Upper Rhine Valley, France)". In: Applied Geochemistry 25.11, pp. 1644–1663. DOI: 10.1016/j. apgeochem.2010.08.013. URL: https:// doi.org/10.1016/j.apgeochem.2010.08. 013.
- McConnell, Joseph R. et al. (May 2018). "Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity". In: *Proceedings of the National Academy of Sciences* 115.22, pp. 5726–5731.
  DOI: 10.1073 / pnas.1721818115. URL: https://doi.org/10.1073 / pnas.1721818115.
- Mercier, Norbert (Sept. 2008). "Datation des sédiments quaternaires par luminescence stimulée optiquement : un état de la question". In: *Quaternaire* vol. 19/3. DOI: 10. 4000/quaternaire.3932. URL: https:// doi.org/10.4000/quaternaire.3932.
- Middelkoop, H. (2000). "Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands". In: *Netherlands Journal of Geosciences - Geologie en Mi*-

*jnbouw* 79.4, 411–427. doi: 10 . 1017 / S0016774600021910.

- Morandi, Garrett D. et al. (Sept. 2015). "Effects-Directed Analysis of Dissolved Organic Compounds in Oil Sands Process-Affected Water". In: *Environmental Science* & amp Technology 49.20, pp. 12395–12404. DOI: 10.1021/acs.est.5b02586.URL: https://doi.org/10.1021/acs.est. 5b02586.
- Perdrial, Nicolas et al. (Aug. 2008). "TEM evidence for intracellular accumulation of lead by bacteria in subsurface environments". In: *Chemical Geology* 253.3-4, pp. 196–204. DOI: 10.1016/j.chemgeo.2008.05.008. URL: https://doi.org/10.1016/j. chemgeo.2008.05.008.
- Rapin, F. (June 1981). "Chronologie et evolution de la contamination par les metaux lourds des sediments de la baie des anges (Mediterranee, France)". In: *Environmental Technology Letters* 2.6, pp. 253–262. DOI: 10.1080/0959338109384048. URL: https://doi.org/10.1080/0959338109384048.
- Stoskopf, Nicolas and Pierre Vonau (2004). "L'Alsace du second XXe siècle : la grande mutation industrielle". In: *Revue d'Alsace* 130, pp. 159–192. URL: https://hal. archives-ouvertes.fr/hal-01164228.

## Acknowledgements

I would like to express my sincere thanks to those who contributed to the development of my Master's thesis.

I would particularly like to thank Cassandra Euzen, doctoral student at LIVE (image city environment laboratory) for her precious daily help on this project, her availability and her kindness. It was a real pleasure to work with Cassandra on this motivating project.

I also want to thank my internship supervisor, François Chabaux, teacher researcher at ITES (Institut Terre Environnement Strasbourg) for guiding me in my work, for encouraging me throughout this internship and for trusting me for the realization of this scientific study.

Of course I would like to thank the other interns and now friends who shared my office during these last four months. Thanks to Romane Bazzano, Salomé Berthier, Margaux Claudepierre, Léon Dupré, Coraline Fuchs, Mathilde Mauger-Vauglin, Maxime Pujeaut, Jorge Sanchez and Séverin with whom I shared very good moments, and who participated to make this internship, more than a professional experience, a beautiful human experience.

Thanks to my colleagues and friends from EOST (Ecole et Observatoire des Sciences de la Terre) who supported me during this internship. Thanks to Emile Serra for having helped me for the formatting of the thesis in Latex, the calculation of uncertainties, and more generally for having been an exceptional friend during these last 3 years. Thanks to Solen Chanony and Emma Vairé for all those exciting discussions over a meal or a tea.

Finally, I would like to thank my family who supported me throughout my studies and this internship.

## 6 Appendix



Figure 26: Ternary granulometric diagram realised for Marckolsheim, Rhinau and Baltzenheim samples



Figure 27: Evolution of the environment around the Marckolsheim sampling point using aerial photos and QGIS software.