Interreg North-West Europe
NWE-REGENERATIS
European Regional Development Fund

D. I2.4.3. Lessons learnt on the Pompey pilote site (FR)

P. Kessouri[1], C. Ryckebusch[1], I. Isunza-Manrique[2], B. Mignon[3], A. Janus[4], C. Waterlot[5]

[1]BRGM ; [2]U. Liège ; [3]CTP ; [4]IXANE ; [5]JUNIA

SUMMARY

1 LIST OF FIGURES

2 LIST OF TABLES

3 INTRODUCTION

Pompey is one of the three pilot sites of the NWE-REGENERATIS project. It is a former tailing pond owned by the EPFGE (Etablissement Public Foncier de Grand Est, Public Real-Estate Company of Grand Est region). The site was chosen for two main reasons: (1) it hosted various activities for iron based alloys production; (2) it was just rehabilitated on surface, and historic documentation and investigations were done with respect of the French legislation and threshold values. One of the interest of this site is that it allows testing the NWE-REGENERATIS methodologies developed within WPT1 and WPT2 on a site that has already been remediated.

Site works provided access to material to perform lab trials and also allowed on-site geophysical measurements. Laboratory tests including XRF (X-ray fluorescence) analysis and mineral processing; along with greenhouse tests for ecocatalists production were also run on Pompey's samples.

This report contains a description of the main results obtained on-site and at the lab scale. They will be used to feed up the guidelines for replication of the NWE-REGENERATIS tools on other PMSD sites.

4 PRESENTATION OF THE POMPEY SITE

The Pompey site is a former tailing pond from the iron and steel complex of Pompey-Frouard-Custines, located 10 km North from Nancy. The steel complex was active from 1870 to 1986. It is renowned for producing cast iron and special steels, such as ferromanganese (ferro-alloy rich in manganese). The last blast furnace of the Pompey-Frouard-Custines iron and steel complex was stopped in 1986. Over time, a forest ecosystem developed on the former tailing pond. The dike delimiting the site was planted with a curtain of black locust trees in 1997. The rest of the pond gradually got covered with diversified deciduous vegetation, more or less dense depending on the area.

The geological substratum of the former tailing pond consists of the Lias marl formations (at 181 m NGF), which are covered by alluvium from the two rivers, composed of coarse siliceous materials (sands, gravel and pebbles) at the base over 3 to 6 m surmounted by finer materials (sands, silts and clays) on 1 to 3 m. These alluvial formations were locally exploited and backfilled with waste rock and iron and steel by-products.

The depth of the deposits in the basin is estimated at around 10 m. The surface of the former pound is estimated to 26 000 m^2, for a total estimated volume of wastes equal to 260 000 m^3.

The waters of the alluvial table would circulate from the channeled Moselle towards the Meurthe, whose level is lower. The piezometric levels measured in 2002 are 187.5 m NGF upstream (South-West of the island) and 184 m NGF downstream (East of the island). The basin surface varies between 199 and 194.5 m NGF, with a mean altitude at 195 m (ANTEA, 2002).

On-site work included a two-stages geophysical campaign (see deliverable DI2.2.1) and two sampling campaigns (see deliverable DI2.2.2).

The following data from Pompey's site was used to further develop the project results: 2 geophysical campaigns, chemical analysis tests, XRF analysis, production of ecocatalyst, mineral processing (the summary of the lab tests can be consulted in the document – *"5.02_T3.1.1_Main output description").*

5 Main results

5.1 Geochemical laboratory analysis

5.1.1 Geochemical results

Detailed results on the geochemical laboratory analysis can be found in deliverable DI2.2.2.

Two conventional sampling campaigns were run at the Pompey pilot site (see investigation plan - deliverable DI2.1.2). The first one, prior to the geophysical investigations, took place in the fall 2020. A pit is already digged since 2010 on site for the first 2 meters of soils (see “fosse” in Figure 1). pXRF and XRF analysis were run on 19 samples extracted from the trench to characterize their chemical composition (see fosse_pXRF and fosse_CTP in Figure 1). The second campaign, posterior to the geophysical investigations, took place in the summer 2021. Six soundings were led at locations determined using the interpreted geophysical measurements (see FP1, FP2, FP3, FP4, I1 and I2 in Figure 1). 45 samples were taken from 0 to 9 m deep. pXRF analysis, as well as physical characterization (for 2 locations) were run on samples extracted to characterize their chemical composition (see Figure 1.b to .d).

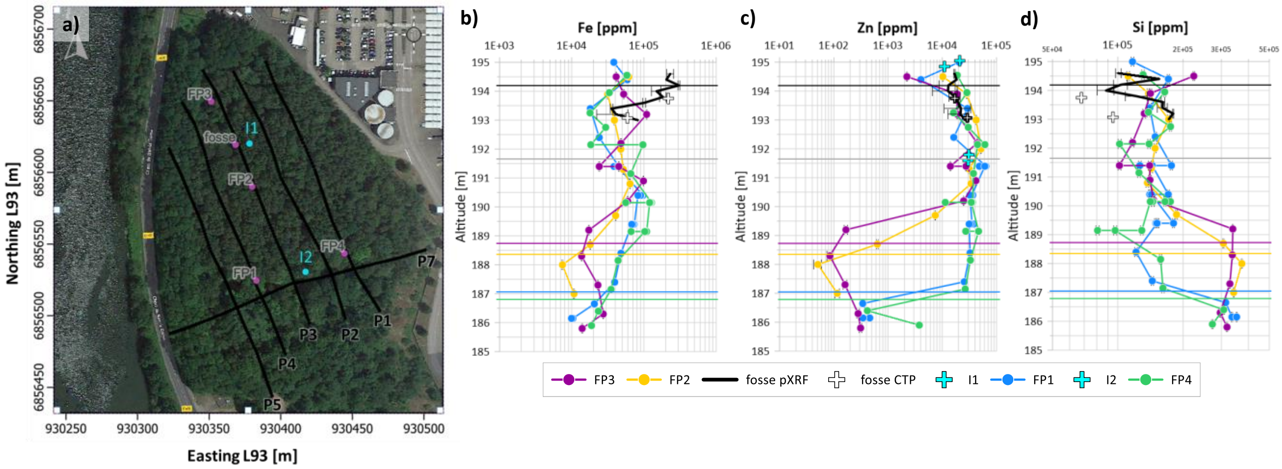

Figure 1: a) Map of the different sampling locations on the Pompey site. The fosse location was used prior to the geophysical investigations. FP1 to FP4, along with I1 and I2 were used posterior to the geophysical measurements. The black lines indicate the ERT/IP geophysical profiles measured on site (P1 to P7); b), c) and d) Variation of concentrations of different selected chemical elements (Fe, Zn, Pb and Si) versus altitude for all soundings (FP1 to FP4, I1 and I2) (see deliverable DI2.2.2). These results are compared to samples extracted from the pit (fosse): (1) pXRF analysis on two profils down to 1.8 m depth (fosse pXRF); and (2) XRF results on two samples S1 and S2 analyzed at CTP (fosse CTP). The horizontal lines correspond to interpreted limits of layers. The deepest limit is variable depending on the borehole observed: they are represented with the respective color of the boreholes to differentiate them.

The chemical analysis carried by various laboratories (CTP, IXANE and BRGM) are indicating consistent metallic element concentrations, indicating the reliability of the data obtained.

Three main layers can be distinguished for all the metallic chemical elements discussed here:

- **From the altitude ~195 m to ~194 m (thickess ~1m):** The heavy metal concentrations are mostly lower than in the layer bellow, but not as low as within the bottom layer. This first layer of techno-soil is the one the most subject to anthropic shuffle (uncontrolled dumping…). As the site is covered by vegetation, it is also remodeled by roots and other life forms that can potentially mobilize some of the metallic elements.

  An exception can be made for sounding FP1, where the concentration of Mn, Zn, Pb and Cu is higher at the surface, and then drops at 194.5m. This observation can linked to the presence of anthropic wastes posterior to the closure of the settling pond that form a mound where metal bars and concrete block have been observed.

- **From the altitude 194 m to a variable altitude ranging from 188.6 to 186.7 m (5.4 m < thickness < 7.3 m):** The concentration of each of the metallic elements is the highest. This layer is interpreted as the main deposits from the former tailing pound.

  It can be noted that the thickness of the deposits is higher in the South of the field site (FP1 and FP4) than in the north (FP2 and FP3).

  It can also be noted that this main deposit layer can be divided into 2: <u>around 191.5 m</u>, a drop in the concentrations of the different metallic elements can be observed. This can be indicative of a change in the nature of deposit, linked with the history of the plant (change in composition of the metals processed…)

- **Bellow a variable altitude ranging from 188.6 to 186.7 m:** the concentration of all the metallic elements drops drastically from several order of magnitude. This trend might be indicative of the bottom of the deposit. The lower concentration in heavy metals and higher concentration in silicon might indicate the transition with a layer of natural alluvial deposits.

  The drop is observed at a depth ranging between 6.4 and 8.3 m, which is lower than the expected depth of the deposits, previously estimated to around 10 m. The total recoverable material is thus lower than expected.

Furthermore, although these samples contained various metals, their grades are still too low to justify any economic interest in recovering them.

Regarding the agronomical analysis obtained, this type of deposits seemed to be more suitable for recovery by eco-catalysis.

5.1.2 Correlation study: Principal Component analysis (PCA)

Detailed results on the correlation study can be found in deliverable DI2.2.3.

A principal components analysis (PCA) was run on the geochemical dataset to identify the most relevant chemical elements in our results. A cluster interpretation was made on the principal components identified during the PCA step.

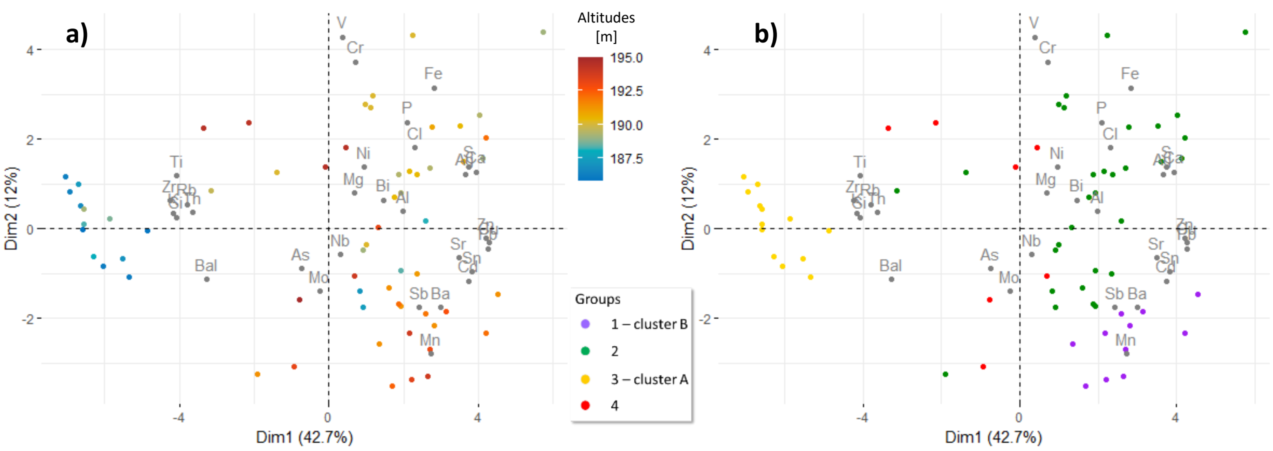

Figure 2: a) Bi-plot representing on one graph the chemical PCA analysis on PC1 vs PC2 for both variables (points in grey) and individuals (points colored by selected clusters); b) Same bi-plot represented using the chose 4 groups, 2 of which are identified clusters (A and B) (see deliverable DI2.2.3).

We chose to separate the dataset into 4 groups (see Figure 2). We use 2 clusters extracted from the PCA analysis of the chemical elements (cluster A and cluster B), and that also corresponds to 2 different altitude ranges. We add two other groups (group n°2 and n°4) with altitudes in between group n°1 and group n°3. These results were compared to geophysical measurements close to the borehole for the different alitutdes.

The results of this analysis are summarized in Table 1. They correspond well to the geochemical (see section 5.1.1) and geophysical (see section 5.2.1) qualitative analysis made beforehand. These analyses will be used to build the RAPIDM model for Pompey (see section 5.2.2).

Table 1: Summary of the observations made for each layers of materials, based on the cluster selection

Altitudes [m]	Group n°	Chemical composition	Geophysical parameter variations	Interpretation
195 – 193.3	4	scattered	– High rho – Average M – Low MF	Anthropic wastes placed after the closure of the settling pond Present mostly for FP1 and FP4
193.9 – 191.4	1 (cluster B)	Main contributions: Zn, Cu and Pb, Mn	Transition zone: – Decrease of rho – Scattered M – Increase of MF	Settling pond layer n°1
193.2 – 187.4	2	Main contribution: Fe	– Low rho – Scattered M – High MF	Settling pond layer n°2
Very variable limit: ~186.5 for FP1 and FP4 ~189 for FP2 and FP3	3 (cluster A)	Main contributions: Si and K	– Low rho (slightly increasing) – Scattered M (decreasing) – High MF (slightly decreasing)	Natural alluvia with high ionic strength electrolyte?

5.2 GEOPHYSICAL FIELD CHARACTERIZATION

5.2.1 Geophysical results

Detailed results on the geochemical laboratory analysis can be found in deliverable DI2.2.1.

> <u>Warning:</u>
>
> During the preparation of this report, we noted that the elevations used for the report DI2.2.1 are not accurate. They are estimated approximately 3 m higher than the real altitudes measured on site. The corrections on the dataset are ongoing. The interpretations added bellow are taing into account a correction on all altitudes of -3 m. They are not yet reported on the figures.

The geophysical results highlight the following succession of horizons (see Figure 3 for an example of electrical results for profile P7):

- **From altitude ~195 to ~192 m (maximum thickness of ~3 m):** A layer R4, that is more resistive, with lower phase shift signature and low Vs. This layer could correspond to a layer of anthropogenic deposits, part of the former settling pond deposits. As they are more resistive than the layer bellow, the nature of the deposits might be different. They could potentially contain less metallic elements (maybe linked with the vegetation cover and its root network)
- **At the surface of the ground,** the layer R4 is edged laterally by resistive layers: R1 in the S-SE corner, R5 and R6 in the N-NW corner, R2 in the E-NE corner. These layers are probably of anthropic origin, but not part of the former settling pond deposits. For R1, R5 and R6, they are interpreted as all comers household and construction wastes, including metal bars, concrete blocks explaining the presence of magnetic dipoles in these areas.
- **From altitude ~192 to a variable altitude ranging from 189 to 177 m (4 m < thickness < 10 m):** A layer C3 that is conductive, with a higher phase shift and lower Vs. Its thickness is ranging from 4 m (in the Northern part of the site) to 10 m (in the southern part of the site). This layer could correspond to a layer of anthropogenic deposits, part of the former settling pond deposits. The layer is limited laterally for several profiles, indicating the lateral limits of the former settling pond. Because of its electrical properties, it might be the most interesting layer in terms of metal content.
- **Bellow a variable altitude ranging from 189 to 177 m:** A layer R3 of medium resistivity, low chargeability and high shear wave velocity Vs, with a top limit varying from 189 to 177 m of altitude. This layer could correspond to the natural formations in which the waste was deposited: Quaternary alluvium from the Meurthe and the Moselle surrounding the site.

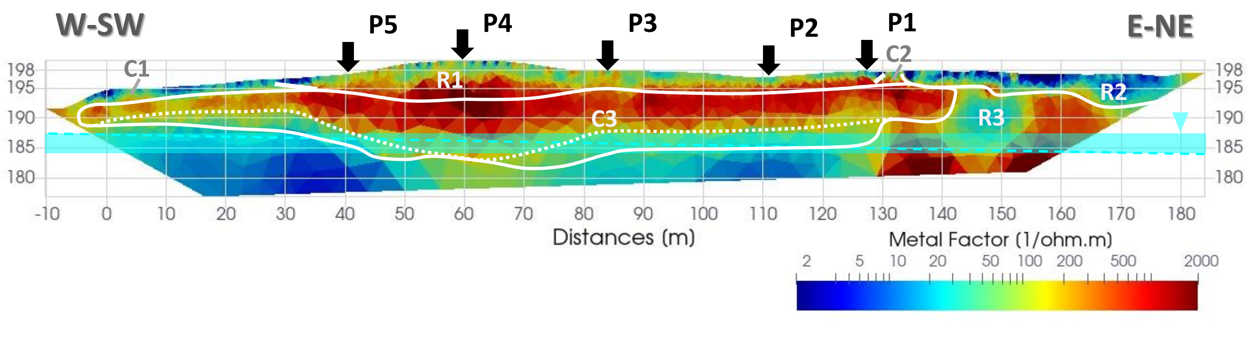

Figure 3: Tomography results in terms of metal factor for profile P7 (see Figure 1.a). The black arrow and line represent the position of the perpendicular profiles (P1 to P5). The turquoise rectangle and associated dotted line corresponds to the known range of the water level that is higher in the W-SW side (profile P5, close the Moselle river) and lower in the E-NE side (profile P1, close to the Meurthe river). White lines corresponds to interpreted limits of electrical resistivity layers named Cn or Rn, depending on their resistive or conductive relative nature (see Figure 5). Dotted white lines correspond to the limits interpreted from the metal factor variations.

These results are in good agreement with the geochemical observations (see 5.1). Indeed layer R4 could correspond to the shallow deposit layer of the geochemical datasets and layer C3 to the deep deposit layer. We note that the geophysical dataset also show a thickening of the deposit in the south part of the field site.

To go further in the interpretation, the electrical results (electrical resistivity tomography (ERT) and induced polarization tomography (IP)) are chosen.

Geophysical methods, and in particular electrical methods are integrative, and the results are outcomes of non-unique inversion processes. We propose to use the geochemical ground truth dataset to refine the vertical limits estimated qualitatively with the electrical datasets.

5.2.2 Raw distribution model (RAPIDM) generation

Detailed results on the raw material distribution model generation (RAPIDM) can be found in deliverable DT3.1.1.

Based on the defined groups using PCA analysis (see section 5.1.2) at the borehole locations, we carried out a novel probabilistic classification of the geophysical field data (inverted models of resistivity and chargeability). Details on the probabilistic approach used can be found in deliverable DT3.1.1 (part 4.2) and in Isunza-Manrique *et al.* (2023).

The results of the field scale probabilistic classification are shown in Figure 4, where the probabilistic classification and the associated probability of occurrence for each group are presented. A high probability of occurrence is represented in red and a low probability in blue. For each cells of each profile, we then attribute a group number, corresponding to the maximum probability of occurrence.

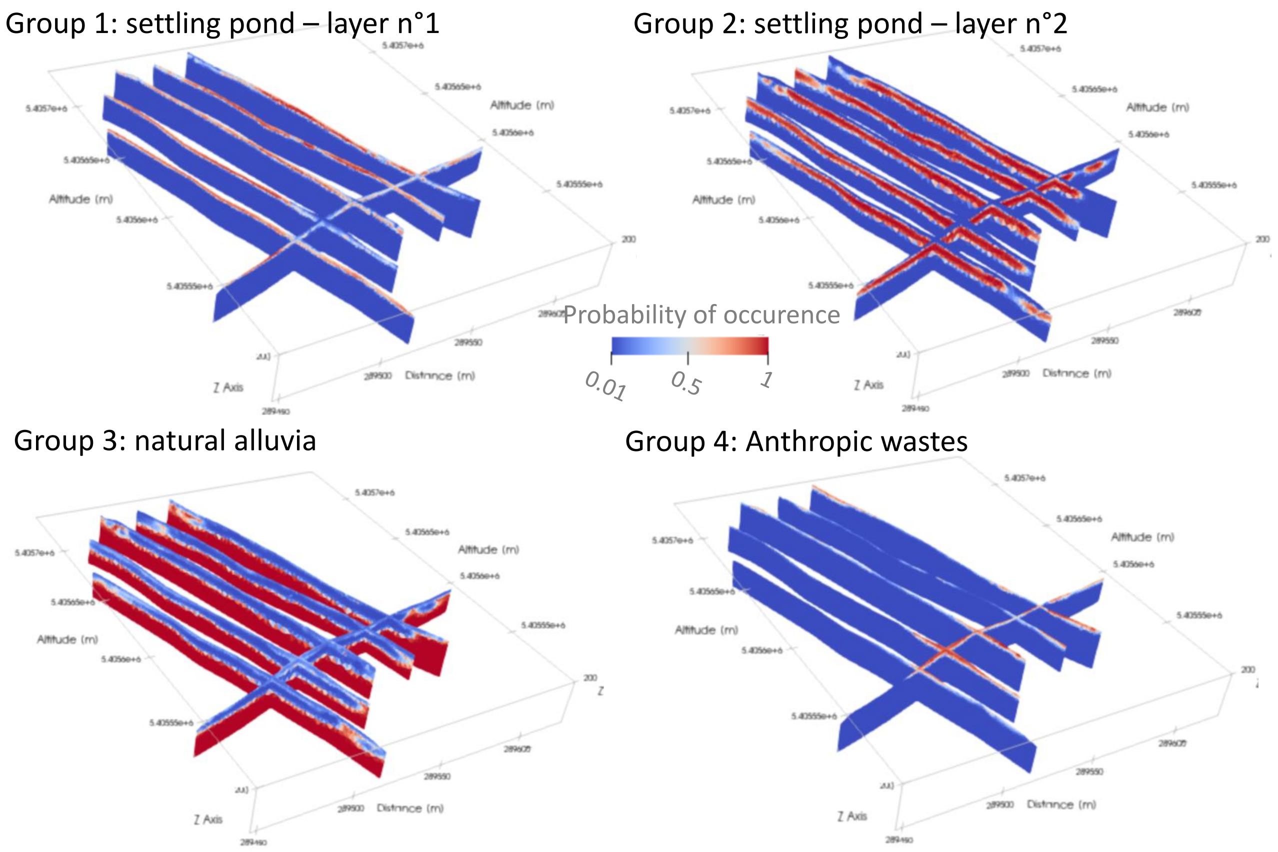

Figure 4: Probability of occurrence of the 4 groups estimated using the PCA analysis on geochemical results.

Figure 5 defines the raw materials distribution model for the Pompey site. Most of the material correspond to group 3, which is identified as the natural alluvia in which the settling pond was installed. Two layers corresponding to the settling pond material were identified (groups n°1 and 2). The lateral north and south boundaries of these layers could be determined qualitatively with the electrical resistivity results. They are not as well defined with the geostatistical analysis. However, their vertical limit can be very well identified in Figure 5. Group n°4 corresponds to a layer of anthropic wastes. Their localization in Figure 5 corresponds to topographic heights, which is very realistic.

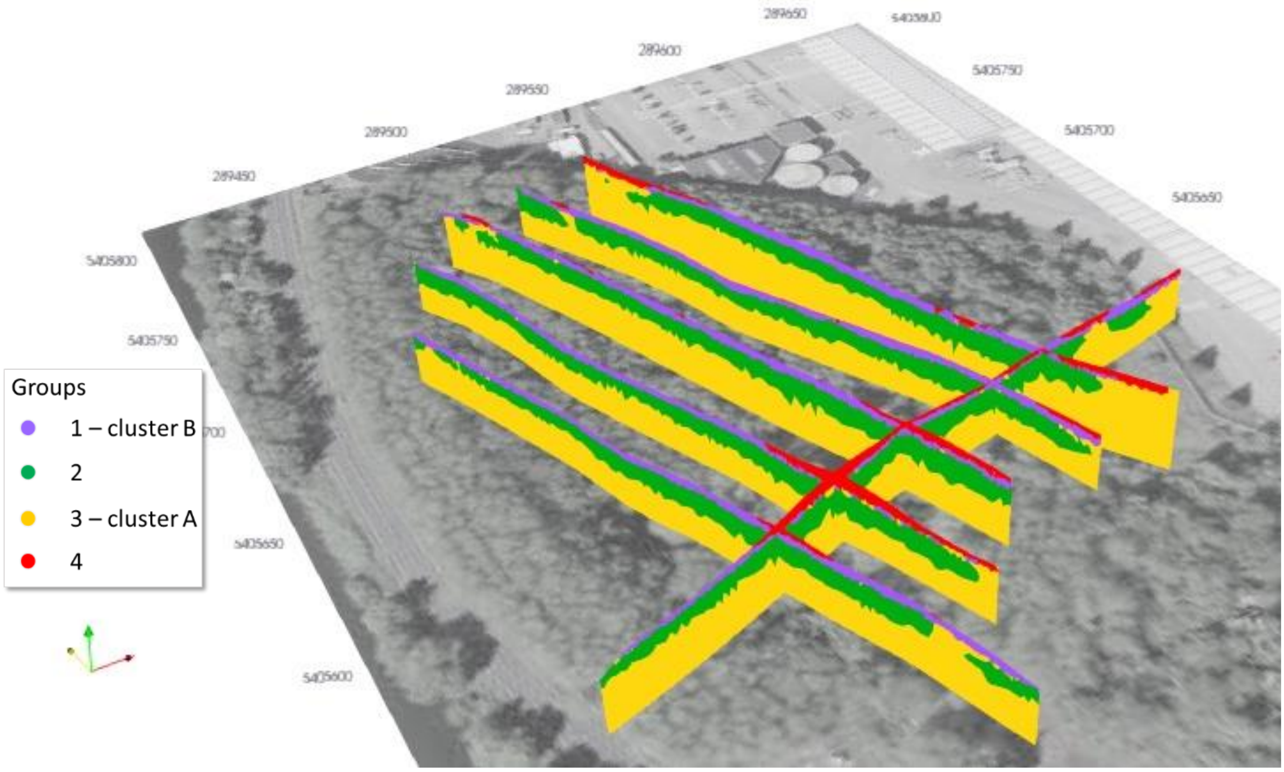

Figure 5 : Maximum of probability for each of the 4 groups.

Because the geophysical measurements are only 2D, an estimation of the volumes for each cluster would need to interpolate the layers over the entire studied area. This result couldn't be achieved during this study, but would be interesting to go further in the quantitative approach. Laboratory geophysical dataset as well as mineralogical analysis would also be a good addition to go further in the recovery potential of the Pompey site

5.3 MINERAL PROCESSING

Mineral processing, also known as ore dressing, mineral beneficiation, or mineral engineering, is defined as the science and art of separating valuable metallic and nonmetallic minerals from unusable gangues (Mineral Exploration (Second Edition), 2018).

Mineral processing, at the lab scale, were performed by CTP on two samples taken at different depths (1m depth and 1.8m depth at the pit (fosse) location, see DI2.2.2). The mineral processing was implemented in two steps (see Figure 6). First, a screening stage was carried on both samples (106µm, 600µm, 1.18mm, 2.36mm and 10mm). Secondly, granulometric fractions larger than 106µm were separated magnetically using magnetic bars (2000 and 6000 gauss).

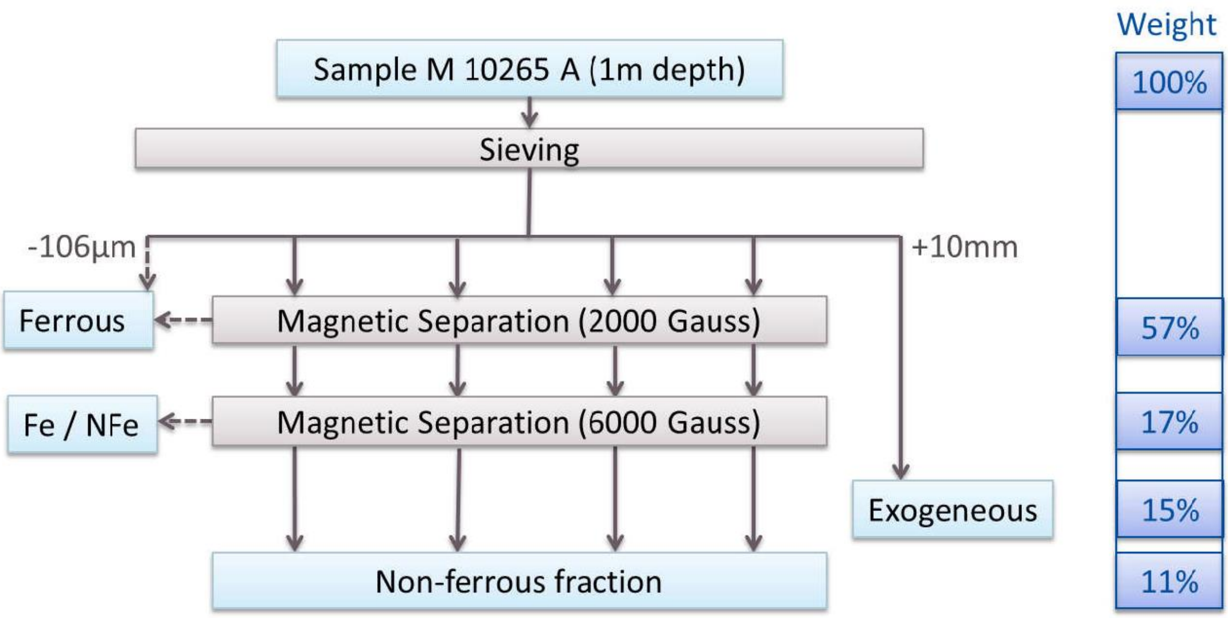

Figure 6: Example of mineral processing steps applied by CTP on sample from Pompey(1m depth) (from DT2.1.1)

Several findings were made (see DT2.1.1 and main output 5.02-T3.1.1) :

- Particles smaller than 600 µm are more concentrated in iron.
- Except for iron, the sieving of the material did not seem to have impact on its chemical composition.
- The magnetic fractions are mainly composed of iron (28-30%) with various concentrations of other non-ferrous metals. Iron-enriched fractions can be melted for iron recovery.
- Manganese is more concentrated in the low-magnetic and non-magnetic fractions (between 1 and 12 % w/w). Its grade remains low compared to that observed in an ore (about 40%).
- The composition of fractions less than 106 µm change with depth. A sample taken at 1 m depth could be valued for its iron content whereas at 1.8 m, manganese is the predominant metal.

Although these samples contained various metals, their grades were still too low to justify any economic interest in recovering them using these mineral processing techniques.

5.4 ECOCATALYSTS PRODUCTION

The concept of ecocatalysis combines phytotechnologies with green chemistry, using hyperaccumulators (Grison et al. 2016). In ecocatalysis, the harvested accumulator plants, rich in pollutants, are considered as a bio-ore. The metallic elements in plants are recovered and transformed into eco-friendly plant-based catalysts called ecocatalysts. These ecocatalystscan be used in organic chemistry as catalysts. A catalyst is considered as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. The first results obtained by Grison et al. (2016) showed that ecocatalysts are more efficient and selective than traditional homogeneous and heterogeneous catalysts.

Sample collection

During the NWE-REGENERATIS project, four samples were collected on the Pompey site to conduct greenhouse tests for ecocatalyst production (see DI2.2.2 and DT2.3.1). Two at the surface (0-0.5 m): I1-A and I2-A, and two at the center of the former settling pond (3-4 m): I1-B and I2-B.

Sample characterization

The Four samples were analyzed in terms of metallic contamination, and fertility. The four samples present very high contamination by zinc (Zn), with higher concentrations for deep samples than at the surface. However, the deep samples present a lower fertility than the surface samples. In a practical point of view, the deeper layers will be harder to access to plant ryegrass on site in the future. The two shallow samples (I1-A and I1-B) were thus selected for the greenhouse experiments.

Sample amendments

Two amendments were tested in the greenhouse experiment: (1) bone ashes; (2) hydroxyapatites. The objectives of these amendments is to fix metals considered as undesirable for ecocatalyst production in the soil (e.g. Cd, Pb), while allowing the transfer of desirable elements from the soil (Zn) to the aerial biomass of the plant.

Ryegrass development

The greenhouse experiment revealed a very high ryegrass development on all tested samples (see Figure 7.a).

The tested soil amendments by bone ash or hydroxyapatites have no effect on metal concentrations in ryegrass, and a low effect on the samples fertility. Only small differences can be observed on the ryegrass development between samples I1-A and I2-A. It is also the same for metal concentrations in ryegrass, even if some metallic elements are slightly higher in ryegrass cultivated on the soil I2-A.

The measured Zn concentration in ryegrass was higher than for samples from other NWE-REGENERATIS experimental sites. Based on these results, the production of a Zn-enriched ecocatalyst was tested.

Ecocatalyst production

On collected Pompey's samples, two ecocatalysts have been produced, both highly enriched with Zn (see Figure 7.b and c). Results from February 2023 indicated:

- From ryegrass grown on I1-A: 5.15 g of ecocatalyst was obtained from 6 g of ash from ryegrass
- From ryegrass grown on I2-A: 4.25 g of ecocatalyst was obtained from 6 g of ash from ryegrass

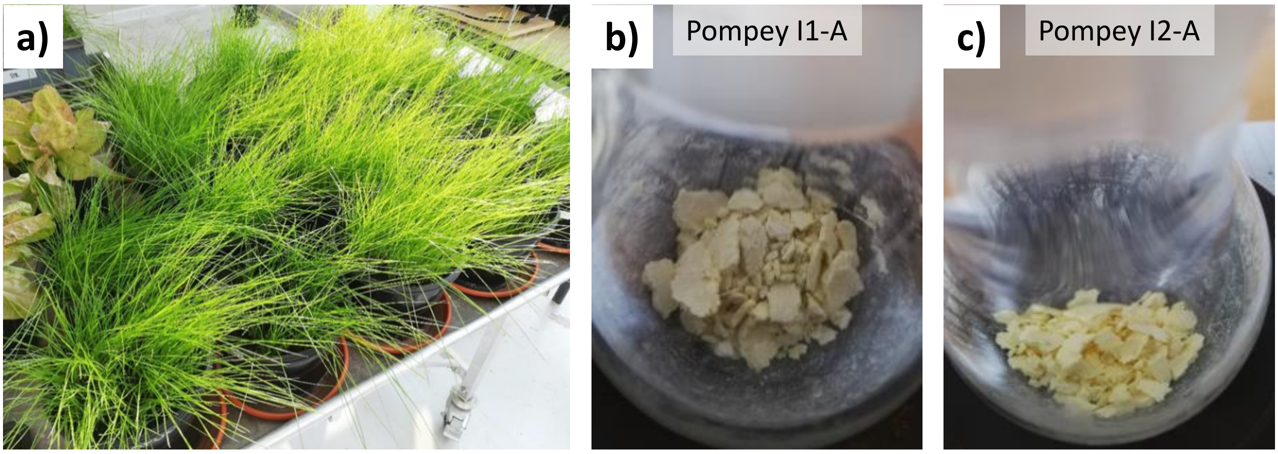

Figure 7: a) Ryegrass development on samples from Pompey; b) eco-catalyst produced for sample I1-A; c) eco-catalyst produced from sample I2-A.

6 RECOMMENDATIONS

The main results have been summarized in the sections above. The geochemical and geophysical datasets are consistant in terms of layers observed and their associated thicknesses. A raw material distribution model was developed using a geostatistical approach combining both the geophysical field datasets and the geochemical laboratory datasets. It allows characterizing the pilot site in terms of layers' extension and thickness, as well as associated chemical composition.

Only pXRF geochemical analysis were led during the project, allowing detection of chemical element concentration variations. To go further in the identification of the nature of the metallic particles, it would be interesting to run other geochemical analysis such as X-ray diffraction (XRD) and inductively coupled plasma (ICP), to understand their mineralogy.

Moreover, only 4 boreholes could be drilled on site, and the electrical profiles were inverted in 2D. Additional boreholes for geochemical analysis and 3D acquisition of electrical data would be recommended to go even deeper in the understanding of the metallurgical deposits.

Laboratory mineral processing was conducted on two samples from the Pompey pilote site. Although these samples contained high concentration of several metals (e.g. Fe, Mn, Zn, Pb), their grades are too low, to this day, to justify any economic interest in recovering them using these mineral processing techniques. Based on these results and the site characteristics (dense vegetation, water level…), we developed a site specific report on excavation activities and civil engineering that could be applied on Pompey site in the future, if any higher interest arise for revalorization of the material on site (see DI2.3.1).

Greenhouse experiments on the production of eco-catalysts were also led on 4 samples of the pilot site. The four samples present high zinc concentrations, and good fertility parameters. The samples allow a very high development rate of the planted ryegrass. The tested amendments did not improve this rate. Two ecocatalysts were produced from the ryegrass harvest, both highly enriched with Zn. Thus, the material on site seems to be more suitable for recovery by eco-catalysis than mineral processing.

A pilot test on site was not developed for several reasons:

- The pilot test could not provide the required useful additional information to characterize the pilot site efficiently. Additional geophysical and lab tests were run instead,
- The site is already rehabilitated, and a dense vegetation naturally developed on site. This rare ecosystem is studied by several research groups,
- Lab trials revealed a variety of heavy metals present on site at various concentrations and very fine materials, that are, to this date, not recommended for mineral processing or extraction processes.

However, the data from the field geophysical prospections and laboratory trials provided very good quality and quantity of information about the Pompey pilot site, which was used for the development of the project results.

7 REFERENCES

Deliverables of NWE-REGENERATIS

DI2.1.1: Kessouri and Gourry, 2020, Site specific report summarizing available historical data on Pompey site (FR), 42 p.

DI2.2.1: Kessouri *et al.*, 2022, Site specific report on geophysical survey on Pompey site (FR), 35 p.

DI2.2.2: Kessouri et al., 2022, Site specific report on traditional sampling investigations on Pompey site (FR), 29 p.

DI2.3.1: Lommel *et al.*, 2023, Site specific report on excavation activities and civil engineering methods to be applied on Pompey site, 24 p.

DI2.4.2: Kessouri and Ardito, 2023, As-built document on Pompey site (FR), 10 p.

DT2.3.1: Janus *et al.,* 2022, Technical report on lab test undertaken for remaining metallic contamination management in soil, 22 p.

DT2.1.1: Mignon, B. 2020. Report on Mineral Processing lab-scale tests on samples from Pompey site (2020). 10 p.

Main output 5.02: Number of innovative uses of waste processes/products/services from waste materials (T3.2.1), T.DEBUIGNE, C.WATERLOT, A.GHINET, A.JANUS, 2023, 6p.

Main output 5.02: Amount of increased material recovery, re-use, and recycling (T3.1.1), T.SEBASTIAN, S.HIGSON, I. Tezyapar Kara, V. Huntington, F.COULON, S.WAGLAND, S.ACQUAVIVA, A.MASSE, 2023, 27 p.

Papers, books and reports

ANTEA, 2001a. Site du Ban-la-Dame à Frouard: Etude technique pour la mise en place d'une couverture étanche et pour l'aménagement paysager, octobre 2001 – A24803/A

ANTEA, 2001b. Site du Ban-la-Dame à Custines-Frouard : Diagnostic du bassin de décantation Sud, novembre 2001 – A25070/A

ISUNZA MANRIQUE I., CATERINA D., NGUYEN F., HERMANS T., 2023 – Quantitative interpretation of geoelectric inverted data with a robust probabilistic approach. p. 93.

Swapan Kumar Haldar, Chapter 13 - Mineral Processing, Editor(s): Swapan Kumar Haldar, Mineral Exploration (Second Edition), Elsevier, 2018, Pages 259-290, ISBN 9780128140222, https://doi.org/10.1016/B978-0-12-814022-2.00013-7.