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Sustainable approach towards extractive waste management: two case studies from Italy

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1. Introduction

The present paper deals with the different approaches to follow to evaluate the problems (eg. environmental impacts) and potentialities (eg. chance to recover valuable materials from waste - landfill mining approach) connected to mining waste management. Very few research investigated the chance to recover raw materials (RM), critical raw materials (CRM) and secondary raw materials (SRM) from mining waste, on the contrary, several studies investigated the environmental problems associated to mining waste management (transport, landfilling, temporary waste facilities, etc.): these two perspectives have been presented and developed in section 2 (Resource efficiency and environmental protection (REEP) approach).

Mining industry represents the most important productive activity (at global level) to exploit RM fundamental for society development. Indeed, resource security is a priority for governments of developed countries. This priority is partly due to considerable concern over the security of the supply of CRM. Their supply is essential to the maintenance and development of the EU economy, as its industries rely on a steady supply of raw materials (RM). Over the centuries, the need for RM continued to expand, as did the number of RM utilised in industry, involving also metals and elements not known or used in the past (Bellenfant et al. 2013). Most of CRM are exploited from countries outside of the EU, causing high economic dependence on non-EU countries (China above all). RM and CRM can be exploited from ore deposits (primary mining), but are also present in landfills and waste streams.

The consequence of mining industry is not only the volume of mineral products obtained but also generation of mining waste (also referred to as extractive waste - EW). Extractive wastes (including waste rock - WR, operating residues – OR, and tailings) represent, on the one hand, a problem due to environmental impacts associated to their production and management and, on the other hand, a potential source to recover SRM and CRM. The need of minimizing the negative impacts

on the environment has led to an increasingly high interest in recovery and recycling. The principles of minimizing waste production and reusing/recycling waste materials (waste recycling EU pillar), and contemporary reducing the use of non-renewable natural resources (natural resource preservation EU pillar) are in line with the EU policy expressed in the Europe 2020 strategy to reduce-efficient Europe and EU Strategy for Sustainable Development (as reported in the document: *EUROPE 2020 A European strategy for smart, sustainable and inclusive growth*).

In this context, EW facilities, together with the advanced treatment of EW flow streams, can represent untapped resources to be exploited (in line with landfill mining and circular economy approaches). Indeed, extractive industry, in 2014, represented the second most important sector in terms of waste quantities produced in the European Union (EU) across 27 different countries (28.1% of total waste or 703 million tons. Eurostat 2017). The total amount of EW which is stored in the entire EU exceeds 5.9 billion tones (BRGM 2001). At a wider scale, about 25 billion of EW are produced world wide each year (Lottermoser, 2010). A part from the yet presented data, very scarce official info about specific waste volume in landfills, about EW flow streams, and about their characteristics are accessible, and without secure data it is very difficult to plan and project the (potential) exploitation of resources from waste.

It has to be highlighted that EW facilities, mostly containing homogeneous materials, are often rich of RM, not exploited in the past, because the yield of mineral was too low to be exploitable without modern technologies, and of CRM, not known (or not used) at the time of mining activities (eg. REE). Thus, EW exploitation is one of the possibility to exploit RM and CRM from integrative sources (EW facilities).

In recent years two projects, Smartground (Dino et al. 2016, 2017.a) and Remediate, have been funded by the EU, with the aim of improving awareness and knowledge about RM sustainable supply, including issues as resource efficiency, risk assessment and site remediation, also using new techniques connected to RM recovery from waste.

The present paper describes the workflow of RM recovery from EW in an environmentally sustainable way: two pilot sites (Campello Monti Ni-mining site and Gorno Zn-Pb- mining district) were used to test the resource efficiency and environmental protection approach, object of the present research.

These studies are needed to enrich the data present on possible recovery of raw materials (mainly metals and CRM) from different abandoned mine sites. In turn this can lead to better availability of information to aid decision making process for the management of sites.

2. Resource efficiency and environmental protection (REEP) approach

Extractive waste as said, can be indicated as potential sources for CRM/SRM exploitation, but, to evaluate if an EW facility can be considered as a potential new ore-body for CRM/SRM exploitation, we need to define the object to exploit and the environmental context. In general, it is not possible to identify a common methodology for CRM/SRM recovery, because it is closely connected to specific characteristics of the ore-bodies, to the RM exploitation techniques (mining and dressing activities) and to the efficiency of exploitation. Thus, as in the landfill mining approach, the EW facilities exploitation procedure is not unique at EU and National level and requires the investigation of the specific sites, starting from general information and focusing, step by step, on the characterisation of the waste to exploit. It is possible, however, to identify a common methodology to estimate, thanks to a site and waste characterisation, the quantity, quality and value of SRM and CRM present in the EW facilities (Dino et al. 2018).

The recovery and reprocessing potential of EW has already been studied in recent years. At least the existence of metal sinks greater in EW than other waste streams had been pointed out by publications from Hatayama et al., 2015 for recovering base metals and Gordon, 2002 for copper.

Several researchers have investigated the chance to recover CRM/SRM from EW, both from quarry waste from dimension stones (to be used as aggregate, artificial stones, industrial minerals. See André et al. 2014; Bozzola et al., 2010, Dino and Marian, 2015; Dino et al., 2017.b; Gencel et al., 2012; Hebhouh et al. 2011; Luodes et al. 2012; Rincón and Romero 2010) and from mining waste and tailings facilities (Bellenfant et al. 2013; Careddu and Dino, 2016; Díaz and Torrecillas, 2007; Dino et al., 2015; Pacheco-Torgal et al. 2009, Sivrikaya et al., 2014). Such research investigated the chance to recover CRM/SRM from EW facilities, at the laboratory or pilot scale.

On the other side, it is important to focus on the environmental risks connected to EW and, in general, to the risk analysis for different scenarios: (1) the environmental and human health risks related to EW facilities as such, (2) the environmental and human health risks related to EW facilities, in case it is decided to exploit them, (3) the environmental and human health risks if it is decided to move the EW to another place. Numerous studies have investigated the environmental impacts connected to EW facilities and EW management in general (Azam et al. 2007; Fields 2003; González-Corrochano et al. 2014; Helios Rybicka 1996; Lim et al. 2009; Schaidler et al. 2007; Talavera Mendoza et al. 2016; Tiruta-Barna et al. 2007; Wong 2003; WHO 2015). Tailings, which are conventionally stored in tailing dams, have often caused damage to nearby soils, agricultural land, natural reserves and aquatic life due to dam failure in places like China, Bolivia and Spain (Grimalt et al. 1999; Hudson-Edwards et al. 2001; Liu et al. 2005). It should be noted that the contamination of environmental matrices near the EW facilities depends largely on the type of ore extracted and of the host rocks, the exploitation methods (mining and processing), the efficiency of exploitation, the pollution control efforts, the presence of alkaline or acidic environments, and the hydrogeological and hydrochemical characteristics of site. (Banks et al.

1997; Bèjaoui et al. 2016 ; Gray 1997; Plante et al., 2015)

To appreciate if the recovery of CRM and SRM from EW facilities is sustainable or not, it is fundamental to consider the “recovery scenario” calculating the potential CRM/SRM supply and evaluating the potential risks associated to EW exploitation. **Figure 1** shows the steps to follow, both for the resource efficiency and environmental protection, to evaluate if the CRM/SRM exploitation from a specific EW facility is sustainable/needed or not. Each step to follow for the two approaches is presented in the Materials and Methods section.

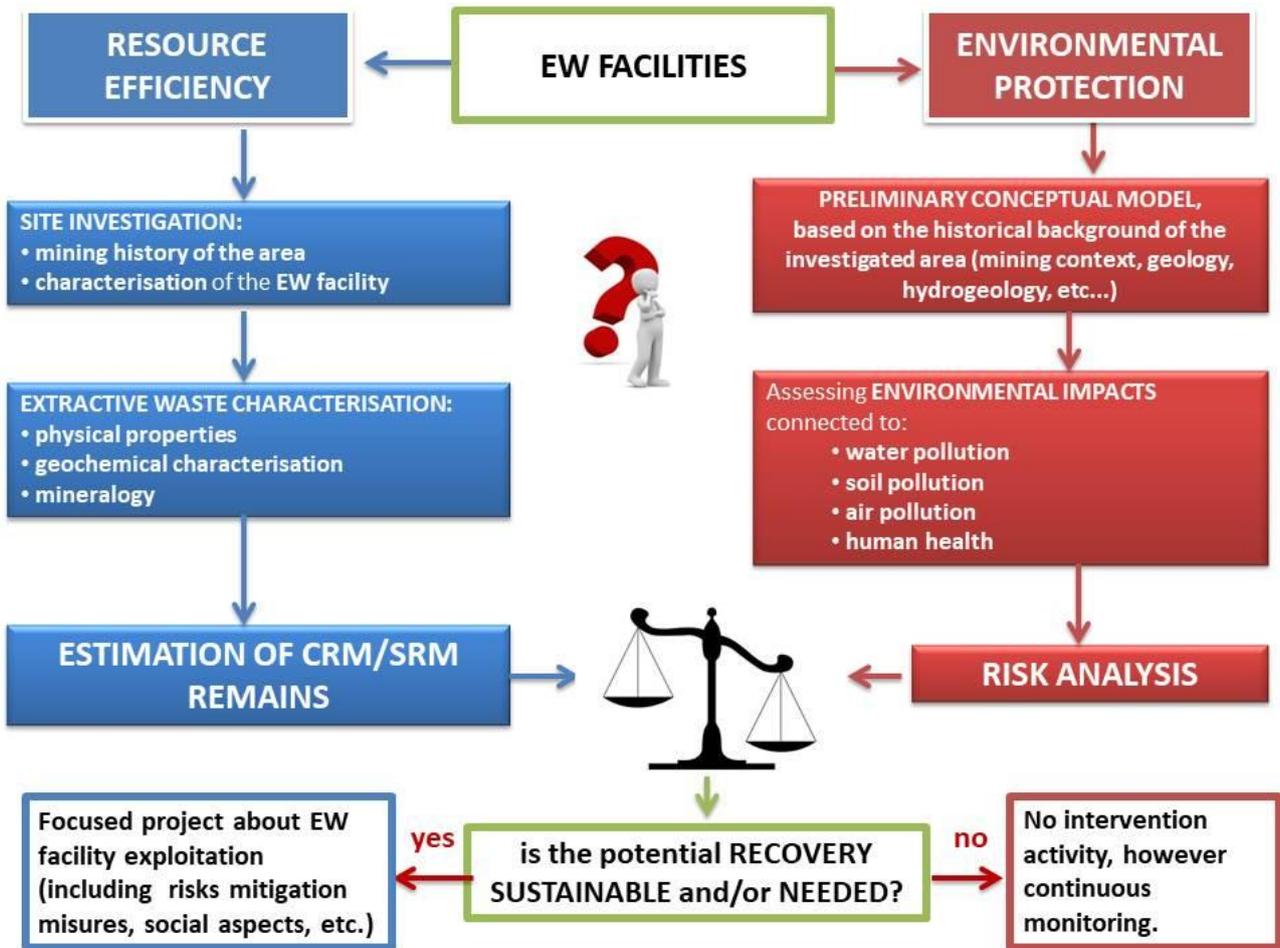


Figure 1 - scheme of factors to consider if the EW facilities are to be exploited.

On the basis of the CRM/SRM estimation and of the risk analysis for the investigated area, it is possible to have a first idea about the sustainability and profitability of EW landfill mining. A positive evaluation does not always correspond to the real exploitation of the “EW ore-body”: indeed, if the preliminary technical investigation is positive a more detailed CRM/SRM estimation has to be carried out (based on focused drilling activities, ore body “real” volume calculation, wider and more detailed geochemical investigation) together with the evaluation of mitigation actions required to avoid/reduce impacts of the exploitation and dressing activities. Thus, after the preliminary CRM/SRM and risk analysis evaluation (object of the present paper), a more focused Cost Benefits

Analysis (CBA) and specific risk analysis are required, considering all the single technology steps present in the future mining and dressing activities.

3. Materials and methods

3.1. Case Studies

3.1.a The Campello Monti mining site

The mine in Campello Monti was exploited mainly for its Fe-Ni-Cu-(Co) sulphide deposits, occurring as lens-shaped, sulphide-rich, subvertical bodies, in ultramafic layers/dykes of the Mafic Complex, in the Ivrea Verbano Zone, a tectonic unit which extends, from NE to SW for about 120 km from Locarno to Ivrea (**Fig. 2**). It consists of three main Formations: Mantle Tectonites, Mafic Complex and Kinzigite Formation (Garuti et al., 1980; Rivalenti et al., 1984; Sinigoi et al., 1994). The dominant primary ore assemblage is composed by pyrrhotite (Fe_{1-x}S), pentlandite ($(\text{Ni,Fe})_9\text{S}_8$), chalcopyrite (CuFeS_2), mackinawite ($(\text{Fe,Ni})\text{S}_{0.9}$) and cubanite (CuFe_2S_3); accessory metallic phases include ilmenite (FeTiO_3), magnetite (Fe_3O_4), chromite (FeCr_2O_4), hematite (Fe_2O_3), sphalerite (ZnS), pyrite (FeS_2), marcasite (FeS_2) and graphite. Some Platinum Group Elements (PGE) enrichments have been locally reported. The primary sulphides occur as interstitial aggregates around the silicates, passing to massive concentrations that usually include roundish silicates. Secondary sulphides also occur, as microscopic vein networks, very fine fissure fillings or, alternatively, sulphide cementing microgranular silicate breccia.

The mine operated intermittently between 1850 and 1945; the average grade of the ore was ca. 1-2 wt. % Ni (0.5 wt. % in the last years of activity). Nickel was extracted from pentlandite, occurring as both coarse-grained intergrowths and very fine-grained exsolutions in pyrrhotite. Exploitation was organized into (sub-) levels connected by shafts and excavation was performed with drilling and blasting method. The ore was transported by Decauville railway to the surface, where it underwent a first (manual) sorting process before being stockpiled and then taken by ropeway to the processing plant downhill: a concentrate of 5-6 wt. % Ni was recovered by enrichment through a flotation process (Rossetti et al. 2017).

3.1.b The Gorno mining district

The Gorno mining district is located in the Seriana, Riso and Brembana valleys (Lombardy, Northern Italy) (**Fig. 3**). It belongs to the Alpine Type zinc-lead-silver stratabound ore deposits, associated with the middle Triassic carbonatic series. The mineralization ($\text{Zn-Pb} \pm \text{Ag} \pm \text{baryte} \pm \text{fluorite}$) mostly occurs within the “Metallifero” (i.e., “ore-bearing”) Formation of upper Ladinic – lower Carnian age. The dominant distribution trend of the orebodies is approximately N-S, as

tabular “columns” up to over 2 kilometers long, with a width ranging from 50 to 400 meters and thickness between 3 and 20 metres (Assereto et al. 1977; Omenetto and Vailati 1977; Rodeghiero and Vailati, 1978). The primary mineralisation is mainly composed of sphalerite (ZnS) and galena (PbS) (average Zn/Pb ratio= 5:1), with minor pyrite (FeS₂), marcasite (FeS₂), chalcopyrite (CuFeS₂) and argentite (Ag₂S). A secondary mineralisation, which historically has been preferred, is composed of oxidation products of sphalerite, i.e., Zn-rich carbonate and silicate. The dominant gangue minerals are calcite, dolomite and quartz (± ankerite).

The history of Gorno mining district started in Roman Age, but the beginning of the industrial exploitation started in 1837 and continued until 1982, carried out by several mining companies (Italian, Belgian and English). The last mining company was the Italian public company A.M.M.I (ENI Group) which from 1940 to 1982 led the exploration, exploitation and processing of the deposits. The mining activity in the whole district closed definitively in 1982.

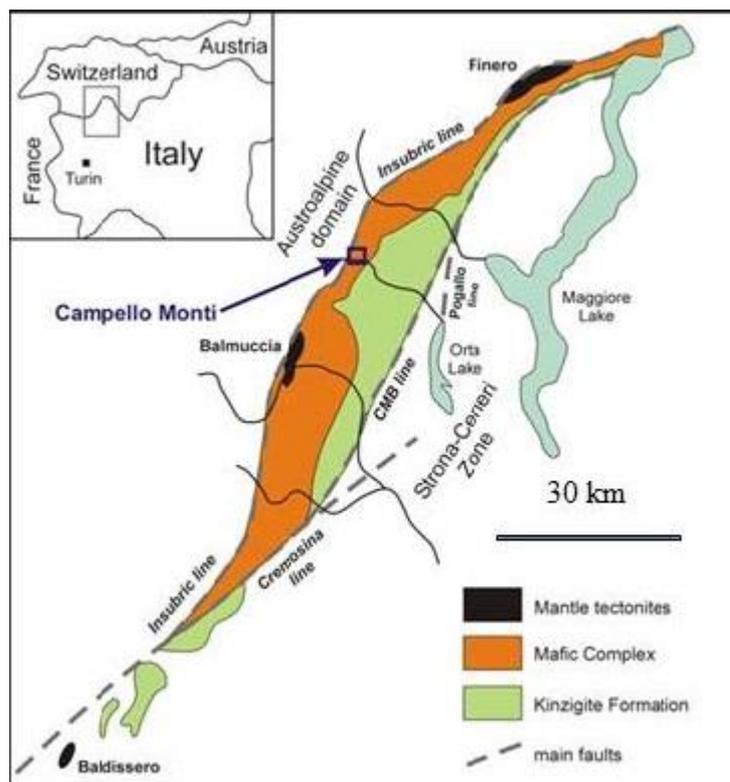


Figure 2- Geological sketch map of the Ivrea-Verbania Zone, showing the location of the Campello Monti area (modified from Fiorentini & Beresford, 2008).

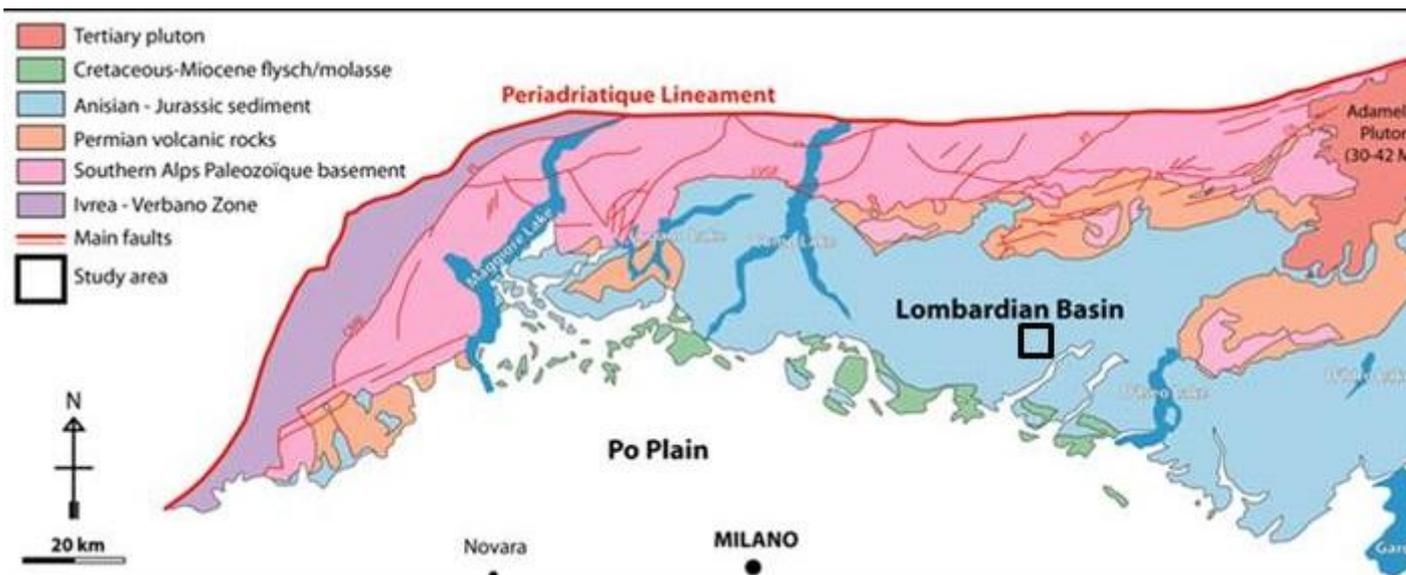


Figure 3- Geological sketch map of Southern Alps showing Gorno location in black square (modified from Beltrando et al., 2015).

3.2. Resource efficiency: estimation of CRM/SRM remains

To estimate the CRM/SRM remains in the EW facility, several investigation steps have to be followed (as shown in Fig. 4): Site investigation, Extractive waste characterisation and Estimation of the recoverable commodities at the site.

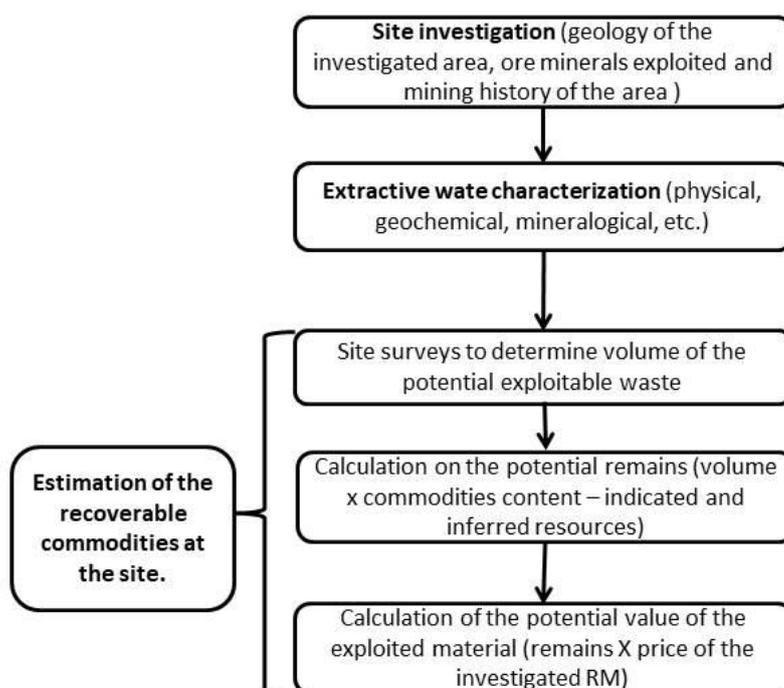


Figure 4 - Flow chart to summarise the protocol adopted to estimate RM/CRM remains.

Site investigation includes the collection of information on geology, ore minerals exploited and mining history of the area (mining and dressing activity), together with the characterisation of the EW facility.

Most of the time, the information about localization of EW facilities, volume of EW in old dumps, and volume of EW from still operating mining activities are scarce or not easily accessible. The data connected to waste quantity are often estimated, together with the localization of old dumps, and this is a big concern, because the reliability of the data is low. Thus, to determine the characteristics of the investigated area, such as morphology, extension, thickness, characteristics of the original rocks, evaluation of the volume to exploit, evaluation of the yield of CRM/SRM present in the EW facilities, it is fundamental to apply a correct protocol for site investigation, to use photogrammetry, laser scanner, geophysics techniques to evaluate the volume to exploit, and to have info about geochemistry and mineralogy to calculate the potential yield of CRM/SRM to exploit (Dino et al, 2018).

Extractive waste characterisation (WR, OR and tailings). The main properties to be checked are linked to physical, geochemical and mineralogical characterisation. Particle size in WR is highly variable (from metric boulders to very fine material). In particular, WR is conventionally subdivided in two fractions: fine and coarse material. The size distribution influences the chance to recovery RM/SRM; indeed it influences the planning of excavation and dressing activities. The geochemical characterisation determines the total metal content of the waste which may provide information on whether the waste can be used for economic recovery of minerals from waste. The geochemical properties depend on the ratio of fine to coarse fractions and on the particle size distribution among fine fractions (Amos et al. 2015).

For the geochemical characterisation, the analytical method must be chosen based on the type of investigated waste material, taking into account the potential SRM to exploit:

- For EW related to Ni sulphide ore mining (Campello Monti), the potential SRM are mainly represented by metals as Ni, Cu, Co and possibly PGE.
- For EW related to Zn-Pb sulphide ore mining (Gorno), the potential SRM are mainly represented by Zn, Pb, In, Cd, Ge, Ga, Fluorite, Baryte.

Accordingly, the following geochemical methods were adopted (**Tab. 1**); analyses were performed by an external laboratory (ACTLABS, Canada).

Table 1- Geochemical methods adopted for Campello Monti and Gorno characterisation.

CAMPELLO MONTI	GORNO
Multi-elements analysis of all samples by ICP-MS method, for a general geochemical	Multi-elements analysis of all samples, carried out by total digestion followed by

screening. A “near total” digestion method was chosen, i.e., the most vigorous digestion used in geochemistry, employing hydrochloric, nitric, perchloric and hydrofluoric acids.	ICPMS/ICP-AES analysis to obtain a general geochemical screening.
Analysis by ICP-OES using 4-acid digestion for samples with a content of some metals (Ni and/or Cu) exceeding the upper limit for the previous analytical package (5.000 and 10.000 mg/kg, respectively).	ICP-AES was used for the samples with a content of Zn and/or Cd exceeding the upper limit for ICP-MS instrument (10.000 mg/kg and 1.000 mg/kg, respectively)
Fire Assay - ICP-MS analysis of Au, Pt and Pd of samples strongly enriched in Ni and Cu.	Fusion Specific Ion Electrode (FSIE) method was used to determine the concentration of fluorine.
NiS Fire Assay – INAA analysis of Pt, Pd, Os, Ir, Ru, Rh, Au and Re of selected samples among those strongly enriched in Ni and Cu.	Samples with a content of S exceeding the upper limit for ICP-AES (20 wt.%) were analyzed using IR.
	Samples with a content of Hg exceeding the upper limit for ICP-AES (10,000 µg/kg) were analyzed by cold vapor Flow Injection Mercury System (FIMS).

Furthermore, the mineral content in the waste is fundamental to understand if and how to recover CRM/SRM: not all the minerals can be profitably exploited and treated to exploit RM. The mineralogical characterisation of coarse grained waste materials was performed by optical (transmitted and reflected light) microscopy on thin-polished sections of representative samples. On the same sections, after carbon coating, the chemical composition of the ore minerals was obtained by electron microscopy (SEM-EDS) technique. The operating residues (Campello Monti) and the tailings samples (Gorno), which are very finely grained, required a different approach: representative samples were incorporated in epoxy resin and, after polishing and carbon coating, observed and analyzed with electron microscopy (SEM-EDS) technique.

Mineralogical characterisation is fundamental for samples from EW facilities, because:

- the CRM/SRM recovery is strongly dependent on mineralogy: eg. Ni can be easily recovered from sulphides, and Zn can be easily recovered from calamina and sphalerite, while if contained in silicates their recovery is virtually impossible;
- ore processing is strongly influenced by rock microstructure. Eg. in nickel sulphide ores, pentlandite can be easily separated when it occurs as coarse to fine aggregates, while it is

difficult to separate the ore-minerals from the gangue when occurring as very fine grained exsolutions within pyrrhotite.

Estimation of the recoverable commodities at the site. It is based on the evaluation of the volume and value of the CRM/SRM to exploit. A market analysis of the commodities to exploit is fundamental. Another fundamental info to estimate the recoverable commodities is the yield of RM/SRM present in the EW facilities.

3.3. Environmental Protection: Risk Analysis

The environmental protection approach involves three different operative steps:

- The **definition of a preliminary conceptual model** based on the historical background of the investigated area.
- The **assessment of the environmental impacts associated to the EW facility**: presence of EW at sites, has detrimental effect on nearby matrices (such as soil and water). Size distribution, geochemical characterisation and mineralogy are associated to environmental risks. Particle size affects the specific surface area of the waste. The finer the particle the wider the specific surface area. Specific surface area in turn plays a role in determining the rate of chemical reactions such as sulphide oxidation rates (Hollings et al. 2001). Past research on correlation of hydraulic properties of the WR and fine fraction revealed that, if the fraction less than 5 mm is up to 30-35 % in the deposit, then it has impact on hydraulic properties (causing the reduction of hydraulic conductivity) (Azam et al. 2007). Moreover, the fine fraction can lead to variation in the Soil-Water Characteristic Curve (SWCC), air entry pressure and the matric suction at which residual saturation is achieved. Total metal content shows the potential level of contamination and the need of appropriate treatments to prevent secondary contamination (Lim et al. 2009). Furthermore, mineralogy may lead to variation in rate of oxidation of sulphide minerals, formation of secondary minerals and acid neutralization reactions and in turn also acid mine drainage (AMD) formation. The rate of AMD may determine the variation in water contamination potential of the waste (Jamieson et al. 2015).
- The **risk analysis**: risk analysis studies can provide quantitative measurement to the impacts caused by presence of EW in the mining site. This can eventually lead to decisional approach to management of EW and how to approach contamination present at site. Technical obstacles as well as potentially large costs mean that it is often neither feasible nor realistic to think in terms of total clean-up of contaminants. Instead, the goal is to find solutions that identify and deal with risks from contamination in a sustainable way. The process of risk assessment involves

constructing a site specific conceptual model containing pollutant linkages. These pollutant linkages in general for any site consist of:

- Source: EW forms source of contamination. As it is a substance that has the potential to cause harm or to cause pollution of soil, water, air. Source of contamination can also pose negative health impacts to exposed human beings.
- Receptor: in general terms, something that could be adversely affected by a contaminant, such as people and / or ecological system.
- Pathway: route or means by which a receptor can be exposed to, or affected by, a contaminant. Dispersion rate, volatilization, solubility, type of rocks, climate, precipitation, exposure frequency of human beings can lead to changes in final potential risks to environment and human health.

4. Results and discussion

This chapter presents the interdisciplinary approach reported in chapters 2 and 3, applied at two Italian case studies: the EW facilities present in Campello Monti mining site, and the ones present in Gorno mining basin (introduced in section 3.1). These pilot sites have been selected to test and validate the methodology proposed for the REEP approach.

4.1 Estimation of CRM/SRM remains (quantity and value)

4.1.a Site investigation

There were no previous data available on the SRM potential for both the investigated areas. Consequently, a preliminary survey was conducted to investigate the mining history, waste typologies and geological information of both the sites. After that, sampling campaigns were carried out to collect representative samples (May - October 2016). The types of waste sampled in the two sites were as follows:

- WR and OR in the **Campello Monti mining site**: each facility was sampled following a grid method. Each sample was collected in an area of 1.5 square meters: after cleaning the sampling point from organic residues, samples of 8-10 kg were collected. For each sample point all relevant information (operator, date, UTM WGS84 coordinates, type of material, photos etc.) were registered. 41 WR samples and 12 OR samples were collected (**Fig. 5.a**).
- WR (Arera area) and tailings (Gorno tailings deposits) in the **Gorno mining basin**. The EW sampling activity in the Arera area was focused on 6 WR dumps, in an area of approximately 0.5 km² at the exit of main mine adits. In total 30 WR samples were collected

(**Fig. 5.b**). Gorno tailings sampling was focused on the tailings deposit close to the Riso river (not present on the map, **Fig. 5.b**). Four sampling points have been identified within the deposit and sampled at different depth for a total of 18 samples.

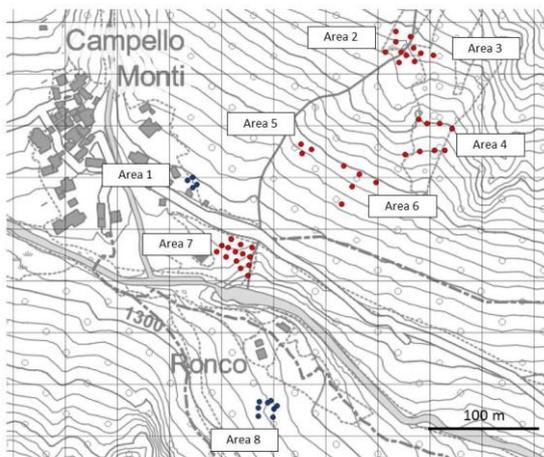


Figure 5.a - Location of the investigated areas in CM, including sampling point (waste rock in red and operating residues in blue). (Rossetti et al. 2017)



Figure 5.b - Location of the waste rock sampling points (yellow) in areas 2 to 7 (Arera Area) of the Gorno site.

4.1.b Extractive waste characterisation

All the samples were processed at the Mineral Dressing and Samples Laboratory (Earth Sciences Dept. – University of Torino) and analysed at ACTLABS (Canada). The results arising from the characterization phase are reported in following.

The samples collected in **Campello Monti** area show relatively high to very high Ni, Cu and Co content (Ni>Cu>Co); however, the extent of the metals enrichment can be strongly different, depending on the waste materials. In particular 4 groups can be recognized (Rossetti et al. 2017):

- “Group I” (area 1): very high Ni (>10000 mg/kg), Cu (≥5000 mg/kg) and Co (>600 mg/kg) values. Furthermore, the OR present in area 1 show very high PGE enrichments: Pd (404 to 556), Pt (282 to 362 µg/kg), Ru (106-133 µg/kg), Os (61-73 µg/kg), Ir (46-84 µg/kg) and Rh (38-66 µg/kg). Also the Au content is relatively high (170-241 µg/kg). The total PGE concentration (PGE_{tot}) was 1213 µg/kg.
- “Group II” (areas 3, 4, 8): high Ni (2000-10000 mg/kg), Cu (600-1500 mg/kg) and Co (100-300 mg/kg) values. Furthermore, the WR present in area 3 shows moderate PGE enrichments: Pd+Pt concentration range between 50 and 164 µg/kg. The Au content is highly variable (3 to 190 µg/kg).

- “Group III” (areas 2, 6): moderate Ni (700-1600 mg/kg), Cu (200-600 mg/kg) and Co (100-200 mg/kg) values.
- “Group IV” (areas 5, 7): relatively low Ni (100-700 mg/kg), Cu (50-200 mg/kg) and Co (50-100 mg/kg) values.

The mineralogical characterisation of samples from Campello Monti shows that Ni occurs as pentlandite, $(\text{Fe,Ni})_9\text{S}_8$ (32.5-33.6 wt.% Ni, up to 1.4 wt.% Co), Cu as chalcopyrite, CuFeS_2 (ca. 34.5 wt.% Cu) and cubanite, CuFe_2S_3 (ca. 23.4 wt. % Cu). These ore minerals generally are relatively coarse-grained, suitable for mineral dressing. The OR of area 1 (**Fig. 4**) are very fine-grained (particle size: <1–100 μm across) and consist of partially oxidized enriched ore material.

In **Gorno**, a strong difference is observed between the WR samples (areas 2 to 7) and tailings (area 1), especially for some metals. The WR is characterized by a high to very high Zn concentration (8.07 to 29.4 wt.% Zn), a relatively high Cd content (69.2 - 830 mg/kg), low to moderate Ga values (6.0 – 88.6 mg/kg), a very low Ge and In content (mostly <1 mg/kg) and a low Pb and Ag content. On the other hand, the tailing samples show much lower Zn (190 – 8950 mg/kg), Cd (1.1 – 39.1 mg/kg) and Ga (<0.1 – 7.0 mg/kg) contents, and a Pb content much higher than the waste rocks, but rather low as absolute values (38.7 – 2170 mg/kg) (Dino et al. 2018). The mineralogical characterisation of the collected WR samples shows that two types of mineralisation occur in the Gorno district: primary (i.e., sulphide) ore, and secondary (i.e., oxide) ore. The primary zinc mineralisation is mainly given by sphalerite, as coarse-grained crystals (up to 1 cm across) occurring along hydrothermal veins crosscutting the carbonate rocks. Sphalerite is generally the only sulfide, locally associated with very minor pyrite and/or galena. Scant grains of fluorite and baryte may also occur. The geochemical analysis of a sphalerite separate shows that sphalerite is almost devoid of iron, but shows a significant Cd content (1970 mg/kg). The secondary ore (calamine) is typically composed of very fine-grained intergrowths of Zn-carbonate (smithsonite, ZnCO_3 , and/or hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) and hemimorphite, $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2\cdot\text{H}_2\text{O}$.

For the tailings, the electron microscopy study shows that the material is composed of chemically very different minerals. The in situ chemical analyses recognised the following minerals: calcite, dolomite, micaceous/clay material, quartz, baryte, Fe sulphate, Zn-silicate (hemimorphite), Zn-carbonate (smithsonite and/or hydrozincite) and rare Cu-As-Sb±Pb sulphosalt(s) (these latter too fine grained for an even semi-quantitative analysis). In general, metallic phases are quite rare. Zn mostly occurs as very fine-grained “oxide” minerals, both as silicate (hemimorphite, containing ca. 67 wt.% ZnO) and carbonate (smithsonite and/or hydrozincite, containing ca. 65 and 74 wt.% ZnO, respectively). Furthermore, extremely fine grained baryte (BaSO_4) has often been detected.

4.1.c Estimation of the recoverable commodities at the site

No data were available before the SMART GROUND and REMEDIATE projects started and, also due to the topographic and morphologic setting, only manual sampling on the surface was possible: for these reasons, the results must be taken with caution and the estimated mineral resources must be considered as indicated and inferred¹. To evaluate the commodities quantity the data present in **table 2** have been used.

Table 2 - data used to evaluate the commodities quantity for Campello Monti (Rossetti et al. 2017) and Gorno (Dino et al. 2018).

Waste typology	Campello Monti		Gorno	
	Waste Rocks	Operating Residues	Waste Rocks	Tailings
Commodity average content arising from geochemical analysis	Ni, Cu, Co for areas 2-7	Ni, Cu, Co for for areas 1 and 8	Zn, Cd, Ga for areas 2-7	Baryte and Pb for area 1
Bulk density	2,235 kg/m ³	1,783 kg/m ³	1,334 kg/m ³	1,810 kg/m ³
Total estimated volume for indicated resources	31.484 m ³		33.914 m ³	249.477 m ³
Total estimated volume for indicated resources	52.512 m ³		23.400 m ³	53.460 m ³

¹ "Indicated resources" were calculated based on waste deposits which were sampled in detail during the characterisation phase. "Inferred resources" were calculated including also waste deposits whose characters were observed in the field, but that were not sampled and analysed. For them, resource estimates (always conservative) were made based on metals content of the nearest sampled dump and geological considerations.

For Campello Monti it has to be highlighted that the PGE content of the waste deposits has not be reported because the available geochemical analyses show that PGE are (relatively) abundant only within the small area n.1, and therefore their overall abundance across the Campello Monti pilot site is likely to be very low.

The content and value of commodities from each pilot site is reported in **Table 3**.

Table 3 - Content of commodities from Campello Monti EW (WR and OR) and from Gorno EW (WR and tailings).

Resource Type		Commodity	Commodity mass [kg]	Commodity in-situ value [€]*
Indicated resources	<i>Campello Monti (WR and OR)</i>	Ni	161.576	1.502.344
		Cu	40.498	218.485
		Co	8.817	460.954
	<i>Gorno (WR)</i>	Zn	5.271.000	13.388.757
		Cd	15.416	18.654
		Ga	1.125	132.754
	<i>Gorno (tailings)</i>	Baryte	24.904	≥1.992
		Pb	59.931	127.773
	Inferred resources	<i>Campello Monti (WR and OR)</i>	Ni	281.478
Cu			69.407	374.443
Co			14.924	780.244
<i>Gorno (WR)</i>		Zn	24.766.000	62.912.767
		Cd	73.043	88.382
		Ga	4.479	528.572
<i>Gorno (tailings)</i>		Baryte	56.896	≥4.552
		Pb	136.919	291.911

Footnotes - * based on values published on 18th October 2016 from www.snI.com (Campello Monti) and on www.snI.com and <https://minerals.usgs.gov/minerals/pubs/> for Zn, Cd, Ga and from www.snI.com and www.indmin.com for Pb and Baryte (Gorno).

4.2. Risk analysis

To measure the environmental impacts and determine future courses of action for the sustainable management of EW, a risk analysis approach was used. In simple terms, risk analysis can be defined as the process of estimating both the probability that an event will occur and the probable magnitude of its adverse effects, whether health/safety-related or ecological, over a specified time period (Gerba,2009). The human health risks due to the presence of contaminants in EW was evaluated using provisions of Risk Based Corrective Action (RBCA) (ASTM, 1995; ASTM, 2015). This method refers to an approach towards managing contaminated sites that examines the risks posed to human health due to contaminants. The amount of environmental management required to ensure the protection of human health is based on a scientific assessment of risks posed by contaminants. It indicates that sites should be managed to have low and acceptable risk levels rather than bringing them to pristine levels. The permissible limits for the chemical elements for the risk calculations were taken from the Italian Legislative Decree 152/06 and risk analysis guidelines (Ministero dell'ambiente e della tutela del territorio, 2006; APAT, 2008). Risk calculation and characterization for different categories was done following the below procedure:

The non-carcinogen health risk to the local habitants through waste rock (that forms the superficial layer) was measured on the basis of hazard quotient (HQ). HQ is the ratio of the estimated daily exposure of a contaminant through different pathway to the reference dose. It is based on the Eq. (1) for the inhalation, ingestion and dermal contact of a particular contaminant (U.S. EPA, 1989-risk assessment guidance for superfund sites; ASTM, 1995; ASTM, 2015).

$$(1) HQ = HQ_{\text{ingestion}} + HQ_{\text{inhalation}} + HQ_{\text{dermal contact}}$$

Hazard Index (HI) is equal to the sum of HQ for all the contaminants Eq. (2) and is used to assess the overall potential for noncarcinogenic effects posed by more than one contaminant at a site.

$$(2) HI = \sum_{m=1}^n HQ_m$$

where, n = no. of contaminants

An $HI < 1$ indicates that there is no significant risk of noncarcinogenic effects. Conversely, if the ratio is > 1 , the exposed population is likely to experience obvious non-carcinogenic effects with a probability that tends to increase as the value of HI increases.

Carcinogenic risk was defined as the incremental probability of getting cancer over a lifetime and calculated as the lifetime intake multiplied by a slope factor for individual chemical carcinogens. The potential risks for human receptors were calculated in terms of the Risk Index (RI) for cancer-causing elements due to exposure to EW. Carcinogenic risk to human beings is calculated by

adding carcinogenic risk due to ingestion, inhalation and dermal contact for a particular contaminant in the source, on the basis of slope factors as shown in Eq. (3).

$$(3) RI = RI_{\text{ingestion}} + RI_{\text{inhalation}} + RI_{\text{dermal contact}}$$

If the RI for a single contaminant exceeds 1×10^{-6} , that element poses carcinogenic risk to exposed inhabitants, the probability of the carcinogenic effects increases with increase in RI.

Total carcinogenic risk is calculated for all the contaminants and is used to assess the carcinogenic risk for more than one chemical element at the site. It is defined as given in Eq. (4)

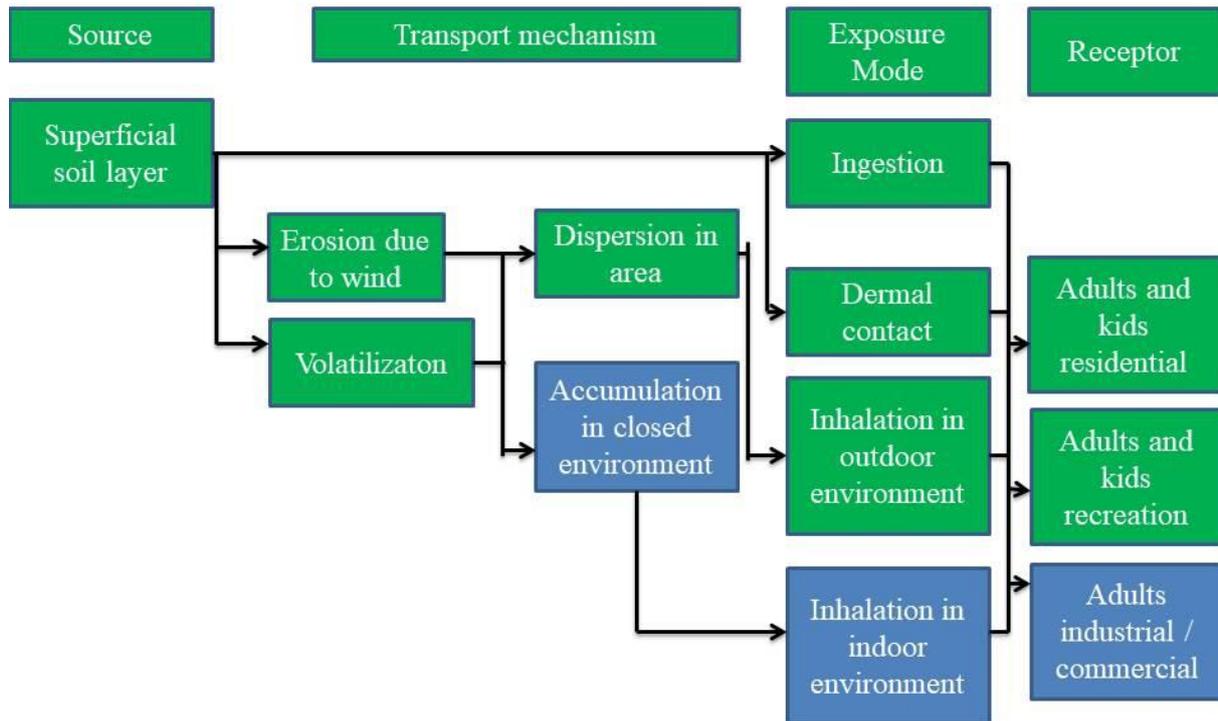
$$(4) RI_{\text{total}} = \sum_{m=1}^n RI_m$$

$RI_{\text{total}} < 1 \times 10^{-5}$ indicates that there is no significant carcinogenic risk. Conversely, if $RI_{\text{total}} > 1 \times 10^{-5}$, the exposed population is likely to experience obvious carcinogenic effects with a probability that tends to increase as the value of RI_{total} increases.

Risk analysis for human health was done using the site specific conceptual model (**Fig. 6**). The source, receptor, and exposure frequency considered for **Campello Monti** and **Gorno** are described below:

- Distributed EW that forms the layer in contaminated area was considered to be superficial soil and the source of the contamination.
- Residents living in the study area were considered the receptors of metals through soil ingestion, dust inhalation and dermal contact from superficial soils, whereas residents living at a distance from the source are only exposed to contaminants through dust inhalation. The distance of off-site human receptors was considered to be 100 m. At Campello Monti, the exposure frequencies were adjusted after considering the exposures of children and adults in recreational areas. The exposure frequency for residential areas was also considered, due to the close proximity of waste dumps to the residential population of Campello Monti. While, for Gorno the exposure frequencies were adjusted only for recreational activities. The number of outdoor hours for recreational activities were set to three hours per day .

Figure 6 - Site specific conceptual model developed after site investigations at Campello Monti and Gorno (the active sources, pathways and receptors highlighted in green while the boxes in blue shows pathways and receptors not active for site) (Mehta et al. 2018, modified).



The results of risk analysis in Campello Monti (Mehta et al., 2018) showed that there is an unacceptable risks to residents. There was presence of carcinogenic risk ($RI > 1 \times 10^{-6}$) due to arsenic in Campello Monti , which had an RI equal to 2.73×10^{-6} . The Hazard Index was found to be 1.35 which is > 1 for Campello Monti. The major risk contributors were Ni and Co (**Table 4**).

The results of risk analysis at Gorno (**Table 4**) depicted that humans using the area for the recreational activities were exposed to human health risks due to contaminants in EW. There was presence of carcinogenic risk ($RI > 1 \times 10^{-6}$) due to arsenic, which had an RI equal to 72.2×10^{-6} . Hazard Quotient was greater than 1, at site due to arsenic, cadmium, thallium, and zinc. The presence of arsenic was found to cause non-cancer toxic risk with HQ of 1.30. The HQ for cadmium, thallium, and zinc was found to be 3.34, 3.27 and 2.50 respectively. The hazard index was found to be 11.7 for Gorno. Risk due to ingestion and dermal contact was found to be an important contributor to overall carcinogenic risk and toxic non-carcinogenic risk at both the sites.

The presence of potential risks to human health at both the sites leads to the fact, that the future use and intervention activities of the material should consider mitigation activities to reduce the risk to acceptable levels.

Table 4- Potential human health risks at Campello Monti and Gorno

Metal	Superficial layer, Campello Monti	Superficial layer, Gorno
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	CRS* [mg/kg]	Human health risk		CRS [mg/kg]	Human health risk	
		Carcinogenic Risk(RI)	Hazard Quotient (HQ)		Carcinogenic Risk (RI)	Hazard Quotient (HQ)
Antimony	3.80	---	0.04	30.38	---	0.99
Arsenic	1.05	2.73×10^{-6}	0.05	28.09	7.22×10^{-5}	1.3
Beryllium	0.08	3.28×10^{-11}	3.51×10^{-4}	0.47	3.96×10^{-11}	3.29×10^{-3}
Cadmium	0.05	1.74×10^{-11}	9.62×10^{-4}	130.20	7.74×10^{-12}	3.34
Cobalt	18.91	---	0.8	1.46	---	0.06
Chromium (total)	160.40	---	3.05×10^{-3}	4.60	---	4.55×10^{-5}
Nickel	426.60	2.88×10^{-8}	0.3	3.67	3.18×10^{-11}	2.44×10^{-3}
Lead	3.89	---	9.73×10^{-3}	22.22	---	0.084
Copper	172.80	---	0.06	83.08	---	0.02
Selenium	0.02	---	5.26×10^{-5}	0.02	---	---
Thallium	0.01	---	0.03	1.72	---	3.27
Vanadium	12.5	---	0.04	30.58	---	0.10
Zinc	9.87	---	4.37×10^{-4}	57079.00	---	2.5

Footnotes - *CRS denotes concentration of contaminant in source (mg/kg)

5. Conclusions

To decide if EW exploitation is sustainable or not, the REEP methodology, described in the paper, can be applied. To test and validate this methodology, two different mining sites in the North of Italy have been selected: Campello Monti (mining site for Ni exploitation) and Gorno (mining basin for Zn-Pb exploitation). Looking at the results arising from the REEP methodology application to these two case studies, it has to be highlighted that:

- **Campello Monti** shows Ni, Cu, Co enrichment in the OR and lower in WR. The volumes of the WR and OR facilities are quite small and the accessibility to the area is possible only 6 months per year. The area is scarcely populated, and tourism is present only few months during the summer. On the other side, the results of the risk analysis (**Tab. 4**) show the

presence of carcinogenic risk ($RI > 1 \times 10^{-6}$) due to arsenic, characterised by an RI equal to 2.73×10^{-6} .

- **Gorno** shows Zn, Ga, Cd in the WR and baryte and Pb in the tailings. The volume of the WR and tailings facilities are quite big and the area shows good infrastructures for transport and for installing new dressing plants. Furthermore, the area (pertaining to Brembana, Seriana and Riso valleys), is quite populated and shows a touristic connotation. On the other side, the results of risk analysis (**Tab. 4**) show that there was presence of unacceptable risks to residents. There was presence of carcinogenic risk ($RI > 1 \times 10^{-6}$) due to arsenic in Gorno, which had an RI equal to 72.2×10^{-6} .

On the basis of the first results arising from the application of REEP methodology, Campello Monti is recognisable as an area not to investigate further for EW facility exploitation. But it has to be noticed that there is a cancerogenic risk associated to As, and that Ni market value is increasing more and more. Thus, it is possible to think about collecting waste from the investigated area and dispose them into a landfill with no other kinds of waste, to be accessible, on the one side, as “new integrative resource” for Ni exploitation, and to reduce, on the other side, the environmental risks present in Campello Monti area.

On the contrary, Gorno can be indicated as a site to be investigated further: thus, focused field surveys, material characterisation and environmental impacts evaluation thinking about different scenarios have to be carried out. In case the company, interested in CRM/SRM exploitation from EW facilities, will decide to move on with deeper investigation phase, focusing on the calculation of real exploitable volume, deeper EW characterisation, risk analysis connected to the new potential exploitation phase (both at mine and dressing plant level), real value estimation (including the potential earning from RM/CRM exploitation from waste and costs due to exploitation activities, environmental issues, health safety, social issue, etc.).

The REEP approach would be useful also for future primary mining exploitations, thinking about the recovery of each fraction produced during the dressing activity and thinking about storing the residual waste in a mapped and known facilities in order to be, on the one hand, easily monitored and, on the other hand, accessible for future exploitation. This approach can be named “sustainable mining”.

6. Observations for future investigation

As introduced, to think about RM/CRM exploitation from waste, in case the REEP approach gives a positive feedback, a wider analysis of economic, environmental and social issues is needed.

The increment of the market value of a commodity, potentially present in the investigated EW facility, can lead people to think about the recovery of CRM/SRM from landfill, but a specific **economic** evaluation is needed, in particular:

- an economic study of the market of CRM/SRM and by-products exploitable from the selected facilities is fundamental to appreciate if such exploitation can be profitable or not. In particular, depending on the RM market value and on the quantity and quality of RM present in the investigated EW facilities, it is possible to estimate the economic value of the “new ore-body” (intended as the EW facility). The evaluation of the accessible resources and of the percentage of exploitable CRM/SRM and by-products is fundamental;
- the costs connected to the exploration, characterisation, authorisation, exploitation, treatment, waste management and commercialization phases have to be evaluated;
- the costs due to environmental, safety and social issues have to be estimated, together with the decrement in environmental rehabilitation costs and saving of disposal costs;
- the value of the areas near the EW facilities should improve after their exploitation, mainly if these areas show tourism potential. Indeed, those areas, at the end of the exploitation activity, will boost their value due to the fact that rehabilitated land can be used for citizens’ interests (eg. recreational activities) or for private interests (eg. industrial areas, building areas, area for new landfilling).

The CRM/SRM recovery from EW facilities scenario can show both positive and negative effects on the **environment** and on **safety**: negative mainly in the short-mid time and positive if considering the mid-long time.

- Positive impacts: the exploitation of EW facilities, in the long run, guarantees the removal of a potential source of soil and water pollution and of hazardous materials which can cause health diseases. Indeed, the removal of waste decreases the presence in the groundwater of pollutants (heavy metals and chemical agents), due to leaching and migration of waste. Furthermore, the removal of waste from an area diminishes the chance of surface water and rain to transport the potentially polluted fine fraction to other areas, with a consequent reduction of the impacts on surface water and soil. The removal of the pollution source, exposes the area to weather agents and the use of proper instruments to avoid water and soil pollution has to be guaranteed (monitoring activities and realization of a net and a basin for water transport and storage). Furthermore, if the area is going to be used as new landfill area, it is fundamental to guarantee the necessary actions to avoid the leakage of pollutants (for example construction of an impermeable

layer, realization of a proper drainage, and capping – both temporarily during the working phase and definitively after the closure of the landfill);

- Negative impacts: the mobilization of pollutants present in the waste (mainly heavy metals and chemical agents used during dressing activities – eg. cyanides, lubricants, etc.) can cause water and soil pollution in the short to mid-term. These negative effects are mainly connected to OR and tailings, which present a fine distribution, with a consequent capacity to hold pollutants, and are often confined within ponds and basins, sometimes covered by an impermeable layer. Furthermore, air pollution due to mining activities, and in particular connected to excavation, transport within the mining area, can be present. Such air pollution is linked to dust and fine powder produced during exploitation, which may have negative impacts on human health: eg. asbestos fibers, silica powder, etc., and to the CO₂ emissions connected to machineries employed in the mining yard. The dust production can be properly managed on the basis of a well programmed operation (dust abatement systems, monitoring, etc.). Finally, the mining of EW facilities can cause new potential impacts connected to machineries employed for excavation, transport and dressing activities; in particular oils and “fine particles” connected to mechanic shovels, heavy metals and chemical agents present in tailings in case of exploitation using water jets and pumping, lubricants connected to machinery present in the dressing plant, “new tailings” waste, exiting the treatment process, to be managed using best practice, etc.

All these potential impacts have to be estimated and monitored and proper devices have to be adopted.

As for the **social issue**, it has to be considered that, after exploiting the EW facilities, the cleared space can be reused as recreational area, industrial area, etc. and visual impact connected to an EW facility can be reduced/removed. The absence (or limited presence) of EW facilities after waste exploitation guarantees a lower constraint to future mine/quarry development, with increased chances for working activities. On the other side, at the short-mid term scale, the presence of mining activities causes the traffic improvement due to the increment of transport activities in the area, this is commonly not positive for citizens.

Finally, to face the EW recovery from landfill, a clarification about the legislation to follow is needed. To exploit CRM/RM/SRM from EW facility do we have to follow the legislation for ore-deposit exploration and exploitation or the one about waste management, or both? This issue has to be discussed and a proper regulation has to be set to pass from a “teoretical way to recover CRM/SRM from landfill” to a “real sustainable way to exploit CRM/SRM from EW-orebodies”.

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