Analysis of Zinc Concentration from Acid Mine Drainage (AMD) in the Ceredigion Region, Wales: An Assessment of the Rheidol and Ystwyth River's Contamination Sources.

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Abstract

The contamination of the water resources of the United Kingdom is a big priority for the Environment Agency. The better understanding of the conditions that lead to said contamination is key for recognizing the potential for remediation and mitigation measures for the water bodies.

This project will focus in the assessment of the ecological status of the rivers Rheidol and Ystwyth which are under a great environmental stress due to the pollution on their water courses by the discharge of mine drainage from abandoned mine sites. It is the responsibility of the Natural Resources Wales Agency to provide the means necessary to ensure the restoration of the environment in said area and ensure it remains that way.

With special attention for heavy metals present in the rivers, Zn in particular, the project shall recognize the pollution sources and perform strategic analysis to identify the possible measures to be taken in the future.

Under the scope of the objectives of the European Union Water Framework Directive of 2000 the project will demonstrate the potential and most important the need for remediation.

Declaration of Original Work

The work presented in this thesis is the result of independent investigation. Where my work is indebted to the work of others, I have made appropriate acknowledgements.

And:

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning;

Nor any portion of the work referred to in this dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Juan Pablo Maldonado Rueda

June 5th 2017

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1. Introduction.

The current situation of the Afon¹ Rheidol and Afon Ystwyth, in the Ceredigion region of Western Wales, United Kingdom, regarding levels of contamination due to the historical mining activities requires special attention (Rees, 2004). The implications and distresses on the environmental conditions and the hydrological resources of the Welsh region due to such pollution are greatly relevant to the British Environmental Agency (Mayes and Jarvis, 2012).

This research project will seek and enable the understanding of these conditions; and will serve to recognize the potential for remediation and mitigation measures for the rivers in a logical manner.

The project will assess the conditions of the hydrological resources of the Afon Rheidol and Afon Ystwyth; with an assessment of their water quality, to determine the environmental impact of the Cwm Rheidol and Cwm Ystwyth mines² -located at river bank accordingly-. As it will be described, the project will focus on the concentration of Zinc (Zn) in the water, as it is the contaminant with the highest load found in the rivers, in contrast with environmental regulations in Wales, the United Kingdom and the European Commission (Natural Resources Wales, 2013).

The rationale for this project is based on the idea that the Environment should no longer endure, alone³, from the alterations caused over the years by anthropogenic activities. As a previous epicenter of industrial activities, especially those related to the exploitation of underground-materials, the Cwm Rheidol and Cwm Ystwyth typify a region with a need for demanding countermeasures.

Such justification for the project clearly sets a relation with the purpose of the Water Framework Directive as defined in said document as: *"To establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater which prevents further deterioration and protects and enhances the status of aquatic*

¹ "Afon" is the Welsh Word for "River" and will be used throughout this report (Griffiths and Jones, 1995).

² "Cwm" is the Welsh Word for "Valley" (Griffiths and Jones, 1995). In this case, the term Cwm refers to a Mine site and will be used throughout this report e.g. Cwm Rheidol = Rheidol Mine.

³ The Environment's recovery and preservation is a task for both Mankind and nature (Pinchot, 1910).

ecosystems and, with regard to their water needs, terrestrial ecosystems and wetlands directly depending on the aquatic ecosystems" (Water Framework Directive, 2000).

The theoretical justification of the project relies in two principles, at first the principle of Environmental Conservation, presented by Pinchot as early as of 1910. Pinchot's speech presents the concept of managerial conservation which evokes *"planned and orderly development and conservation of natural resources*". Such conservation must be sustained for the sake of, not only the future generations wellbeing, but also for the present generation's right to the fullest necessary use of these resources (Pinchot, 1910).

Secondly, together with the ideas of Pinchot, the principle of Intergenerational Equity, presented the in the Burtland report in 1987. Principle which demands constant "development to meet the needs of the present without compromising, and actively ensuring, the ability of future generations to meet their own needs" (World Commission on Environment and Development, 1987).

Both principles are embedded in the concept of sustainable development and therefore provide support and motif to the project.



Figure 1 The Ceredigion Region in Wales (Office for National Statistics, 2017)

1.1 Acidic Mine Drainage.

1.1.1 Historical Background.

1.1.1.1 The Ceredigion region, Mining and the production of AMD.

Located in the Northern side of Wales, the Ceredigion county encompasses a vast region of approximately 1,795 sq. km; the region has an approximate population of 74,642 -last record from 2015-, which represents the second lowest population density in Wales (Office for National Statistics, 2017). With over 100-km-long coastline and the Cambrian Mountain rage sparsely populated, the region covers large areas afforded with protected status due to their exceptional environmental qualities (McDonagh, *et al*, 2015).



Figure 2 Map of the Ceredigion Region (Developed with Digimap®⁴)

The Ceredigion region has been historically identified as a mining region since the Bronze Age, its metal bearing lodes have been exploited for Silver, Lead, Cooper, Zinc and Gold.

⁴ Digimap is a collection of EDINA services that deliver maps and map data of Great Britain to UK tertiary education. EDINA is a centre for digital expertise and online service delivery. The University of Edinburgh (EDINA, 2017).

Relative to the massive exploitation of these resources, there are currently several abandoned mining sites which residuum consists of exposed waste at surface and mine water discharges from underground works (Johnston, 2004).

The agency in charge of the management and protection of the Welsh environmental resources, Natural Resources Wales, establishes that there are 92 water bodies in the Ceredigion region categorized as rivers (Natural Resources Wales, 2013); a rough number of 70 of these rivers are identified to be affecting protected areas.

The extensive works in the Western Wales region, and specifically those of the Ceredigion Ore fields during the 17th and 19th centuries, concentrated numerous mine sites (See Figure 3); which are now a day being identified as sites of significant impact to watercourses (Johnston, 2004). In the late 1990's this condition contributed to the failure of at least 108 Km of river curses to meet Welsh's water quality standards (Mullinger, 2004b).



Figure 3 Location map of the main former non-coal mining districts of the UK (Adapted) © Crown Copyright and database right 2007. Ordnance Survey license number 100026380 (Mayes *et al.*, 2009).

Figure 3 shows the location of mine sites in the Ceredigion region and allows to notice the high concentration of mine sites, as compared to other regions of the United Kingdom.

This project will focus specifically in two rivers located in the Ceredigion region: The Afon Rheidol and the Afon Ystwyth; both finding confluence and connection to the Irish Sea at the Cardigan Bay, nearby the population Welsh of Aberystwyth (See figure 4) (Office for National Statistics, 2017).



Figure 4 Representation of the Afon Rheidol and Afon Ystwyth from the mine sites to the tidal limit at Cardigan Bay -on the left- (Developed with Digimap®⁵)

In terms of the Zn sources for the rivers; the Afon Ystwyth receives most of its contamination from: The Cwm Ystwyth, through the Pugh's Adit and the Nant y Felin⁶; and the Cwm Frongoch through the Frongoch Stream and its confluence with the Nant

⁵ Digimap is a collection of EDINA services that deliver maps and map data of Great Britain to UK tertiary education. EDINA is a centre for digital expertise and online service delivery. The University of Edinburgh (EDINA, 2017).

⁶ "Nant" is the Welsh Word for "Brook or Stream" (University of Wales Trinity Saint David). In this case, the term Nant y Felin refers to the "Kingside Adit".

Cell (See Figure 5). This creates a network of approximately 64 kilometers, including at least 6 "WFD Cycle 2 River Waterbodies" (Anscombe, 2014), that connects the Afon Ystwyth with different mines throughout its course, from the Cwm Ystwyth, as the Upper Ystwyth, to the Cardigan Bay at the Irish Sea (Mullinger, 2004a).



Figure 5 Map of the Afon Ystwyth with connections to different mines (Adapted) (Erichsen Jones, 1958)

Due to the different inputs from the mines described in this catchment system (see Figure 5), the Afon Ystwyth fails River Quality Standards for Zn for at least 47 kilometers. The chart presented in Figure 6 shows the distribution of the Zn daily budget among the main sources of contribution of the river (Mullinger, 2004a).



Figure 6 Zn Contributions at the Afon Ystwyth (Mullinger, 2004)

With over a half of the Zinc budget; The Cwm Ystwyth and the Cwm Frongoch are the main Acid Mine Drainage -AMD- providers in the region and there are likely to cause adverse effects on the aquatic environment (Stokes, 2012).

For the case of the Afon Rheidol, the main pollution sources have been identified to be Adit No. 6 and Adit No. 9 from the Cwm Rheidol which provide highly contaminated AMD.



Figure 7. Conceptual source-pathway-receptor model (Atkins, 2006).

Figure 7 describes a conceptual source-pathway-receptor model of both Adits in the drainage network that finds its endpoint in the Afon Rheidol. From the model, it is observed that Adit 6 connects four mine sites adjacent to the Cwm Rheidol: The Llwynteifi Mine; The Bwlchgwyn Mine; The Penrhiw Mine; and the Ystumtuen Mine. Adit 6 collects leakage from each of the mines and conducts the drainage towards the Afon Rheidol (Edwards and Potter, 2007).

Before clearing the drainage into the river, the AMD from Adit 6 and Adit 9⁷ is diverted into a Limestone filter for Zn removal and afterwards discharged to the Afon Rheidol. However there is evidence that a substantial volume of the adits waters bypass the filter bed due to percolation and reaches the river basin through groundwater (Edwards and Potter, 2007).

It is important to note that throughout the Afon Rheidol course there are other connections to abandoned mines, however, the AMD flow to the river around the area is mainly caused by these two Adits (Williams and Stokes, 2012).

1.1.1.2 Mining conditions and characteristics.

For the case of the Cwm Rheidol, the Ordovician and Silurian polymetallic mineralization, principally Pb-Zn were the most productive in terms of metal production; as well, Galena (PbS) and Sphalerite (Zn,Fe)S were the two principal Ore Sulphides (Rees, 2004).



Figure 8 Section of the Ceredigion Region showing the A. Rheidol and A. Ystwyth systems and their associated mine network (Fuge *et al.*, 1991).

⁷ Adit 9 is located bellow, and performs the same as Adit 6 in terms of collection and conduction of AMD.

According to the Natural Resources Wales agency (2016), the construction of Adits No. 6 and No. 9 by the late 19th century enabled the expansion of the drainage network and connection of the entire mining complex with the Cwm Rheidol, this allowed mobilization of the extracted ore through the Afon Rheidol and later processing to the Valley of Rheidol Railway to be carried on to Aberystwyth (Natural Resources Wales, 2016a). This suggests that the introduction of the contaminants to the Afon Rheidol was of customary practice for a lengthy period of extraction in the region.

Figure 8 shows the distribution of mines along the Afon Rheidol and Afon Ystwyth and provides a depiction of network that was created in the 19th century.

The Cwm Ystwyth was abandoned, around 1950, with its remaining including a large opencast, shafts, and adits. The mine is located nearly 6 kilometers away from the Pont rhyd-y-groes village in the Ceredigion (See Figure 8); with about 250Ha of coverage, the mine exploited three mineral lodes, namely Comet, Kingside and Mitchell (Natural Resources Wales, 2016b).

For the case of the Frongoch mine, as stated by Palumbo *et al* (2009) the works were described by Moissenet, as early as 1866: *"A series of workshops arranged on a slope at the mine and powered by water; in which the crushing, jigging and separation of the ore were carried out hydraulically by gravity separation to concentrate the Pb and Zn minerals. The tails were discharged from the final stage Lisburn buddle to waste"*. This is evidence of the similarity of the Afon Ystwyth pollution to the common practice in the Afon Rheidol and the Cwm Rheidol waste disposal, where the waste was directed to the river without any attempt of a primary treatment (Palumbo-Roe *et al.*, 2009).

1.2 Scientific Background.

1.2.1 Acid Mine Drainage and Surface Water.

1.2.1.1 About Acid Mine Drainage.

The production of Acid Mine Drainage (AMD) is given by the exposure of Sulphidebearing material to O_2 and H_2O . Although the process of generation of AMD occurs naturally, through the increment of exposed Sulphides in the surface, mining carries a significant role for the generation of AMD. With the oxidation of the Sulphides into dissolved iron, sulphate and hydrogen (Akcil and Koldas, 2006) and the precipitation of iron in water bodies, comes along the dissolution of heavy metals such as Cu, Pb, Zn into the ground or surface waters.

High concentrations of Zn in AMD for the case of the Ceredigion region result from the oxidation of Sphalerite [Zn,Fe]S and Pyrite [FeS₂] (Younger, *et al.*, 2002). Elevated concentrations of Zn in surface water and ground water can preclude their use as drinking water or aquatic habitat.

1.2.1.2 Measurement of AMD in Surface water: Acid Mine Drainage Index

The introduction of the Acid Mine-Drainage Index (AMDI) adapted by Gray (1996) allows the detection and quantification of contamination caused by AMD, it is calculated using seven parameters in a modified arithmetic weighted index which basically represents the relative strength of AMD in surface Waters.

The AMDI weights the impact of the following parameters: pH, Sulphate, Fe, Zn, Al, Cu and Cd; then the assessment index system applies a rating system and a set of equations that allow quantifying the toxicity of each these parameters. Finally, the value provided as the AMDI on a scale of 0 to 100 -where 0 is the worst possible and 100 is the best possible- defines the quality of the water in terms of the impact by AMD (Gray, 1996).

The study by Gray (1996) for the Avoca mines in County Wicklow, Ireland, considered a wide range of water sources for the AMDI generation, both upstream and downstream from the mine sites, including: surface runoff; temporary and permanent ponds; springs; and adits discharge. Comparison of the AMDI in different areas of the affected site indicated the usefulness of the index in discriminating between types of AMD affected waters.

1.2.2 Zinc concentrations in the Afon Rheidol and Afon Ystwyth.

The UK Technical Advisory Group, UKTAG commissioned in 2010 a programme to derive Environmental Quality Standards (EQSs) for substances failing under Annex VIII of the WFD. In its 2012 report "Proposed EQS for Water Framework Directive Annex VIII substances: Zinc" it comments in the properties and fate of Zn in water as follows:

"Zinc is a naturally occurring element that exists mainly as sulphide, silicates and carbonates. Zinc plays an essential role in organisms, where its internal concentration can be regulated to a limited extent depending on the concentrations to which an organism is exposed. Effects of deficiency or toxicity may occur if the concentrations deviate from those that the organism can regulate".

"In water, zinc exists in the +2-oxidation state in forms that are dependent on physicochemical parameters, such as pH, hardness and the content of dissolved organic carbon" (Dawn Maycock, Adam Peters, 2012).

In consideration of this basis, it has been established that levels of Zn for salmonid waters (in freshwater), in relation to hardness of the water and should follow the values shown in table 1 (Fuge *et al.*, 1991).

CaCO3 Hardness	Zinc
100 mg/L	0.3 mg/L
50 mg/L	0.2 mg/L
10 mg/L	.03 mg/L

Table 1 Levels of Zinc concentration for salmonid waters in relation to hardness (Fuge et al., 1991)

1.2.2.1 Zn concentrations from AMD at Afon Rheidol.

For the case of the Cwm Rheidol and the introduction of AMD to the Afon Rheidol.

According to Fuge *et al* (1991) there are high concentrations of Zn in the AMD discharging from Adits No. 9 and No. 6 into the Afon Rheidol. In the early 1960's all the drainage from the Adits and tips of the Cwm Rheidol were channelled and conducted through a series of three beds limestone chips filter (Jones and Howells, 1975).

The filter was designed to raise the pH of the water and cause precipitation of most of the heavy metals for the purpose of introducing a hydro-electric scheme in the Rheidol catchment (Fuge *et al.*, 1991).

The following table shows estimates of the Zn concentration in the AMD coming directly from the Adits and going in and out of the filter:

	Lower Adit (No.9)	Upper Adit (No.6)	Filter Inlet	Filter Outlet
рН	2.8-3.0	3.2-3.7	3.2-3.5	3.5-3.8
Zn (mg/L)	38.0-72.0	9.8-12.4	12.0-16.1	10.0-13.9

Table 2 Analytical data for AMD, Cwm Rheidol (Fuge et al., 1991) (Adapted).

It is observed that the Zn concentration due to the filter could be reduced with a rate of up to 15%; However, evidence quoted from Jones and Howells (1975); Fuge (1972) and Fuge et al. (1991) shows that the levels of Zn after to the filtering might had increased over the years (See Table 2).

Another issue regarding the amount of Zn going into the water is that despite the efforts of channelling the AMD for filtering; It is clear from the exiting literature that certain volume of it reaches the River via springs and percolation (Fuge *et al.*, 1991).

Year		Filter Inlet	Filter Outlet
1969	рН	3.5	6.0
1969	Zn (mg/L)	22.5	2.6
1971	рН	3.1	6.3
1971	Zn (mg/L)	23.7	15.3

1973	рН	3.2	3.6
	Zn (mg/L)	50.0	45.0
1982	рН	3.8	3.9
1902	Zn (mg/L)	19.0	17.0
1988	рН	3.4	3.4
	Zn (mg/L)	46.8	29.5

Table 3 Variation of Water chemistry and efficiency of the limestone filter through time, Cwm Rheidol (Fuge *et al.*, 1991) (Adapted).

With the current monitoring technology, and due to the fluctuation of AMD production from the mine, it is not feasible to estimate the exact volume of the AMD that enters the river. Nevertheless, it is possible to measure the amount of dissolved Zn that is present in the river. The following table presents data on the influence of the AMD in the Afon Rheidol water quality regarding Zn:

	Afon Rheidol above mine area	Afon Rheidol 2.5 km below mine area	Afon Rheidol 16 km below mine area
рН	6.1-6.8	5.9-6.2	5.5-6.4
Zinc (µg/L)	81-97	254-285	80-171

Table 4 Influence of AMD from Cwm Rheidol on water quality in the Afon Rheidol (Fuge et al., 1991) (Adapted).

From Table 3, it is evident that the river presents a major increase in the concentration of Zn right after the mine area. On the other side, it can be implied that the decreasing levels of Zn are consequence of the morphological characteristics of the river that generate variations in the Flow ⁸, including the incorporation of tributary water bodies or adjacent catchments; or the change in the cross section of the river.

1.2.2.2 Zn concentrations from AMD at Afon Ystwyth.

For the case of the Cwm Ystwyth and the introduction of AMD to the Afon Ystwyth, Natural Resources Wales released information in 2016 about the concentrations of Zn in the river, with values of 9.1 μ g/L upstream from the mine and of 330 μ g/L downstream from the mine. Although these are not as considerably high as those expressed for the Afon Rheidol, these concentrations do cause the river to fail European Water Framework Directive (WFD) (Natural Resources Wales, 2016b).

The following table contains data from a monitoring project performed by the Natural Resources Wales agency in June 2012, it shows the concentrations of Zn in the Afon Ystwyth prior to the Cwm Ystwyth as well as the Zn concentrations of the AMD coming from the Adits and the concentration of Zn after the mine site:

	Pugh's Adit	Gill's Adit	Afon Ystwyth upstream mine	Afon Ystwyth downstream mine
Flow (L/sec)	9.6	3.2	980	2,209
рН	6.5	6.4	6.4	6.4
Zn (µg/L)	23,085	4,244	9.1	330
Zn (kg/yr)	6,070	384	12	21,217

Table 5 Influence of AMD from Cwm Ystwyth on water quality in the Afon Ystwyth (Natural Resources Wales,2016b) (Adapted).

⁸ Flow is referred here as a hydraulic/hydrological measure of the relation between speed (at movement) of a fluid and the area that the fluid covers while at movement, in this case it represents the speed of the river over the cross section of the river, therefore Flow= Velocity/Area with units of (Volume/Time) (Smith, 2003).

From Table 4, it is evident that the river presents a major increase in the concentration of Zn right after the Cwm Ystwyth area. As presented in Figure 6, there is also a large contribution of Zn from the Frongoch mine located in the North vicinity of the Afon Ystwyth and connecting to it through the Nant Cell and the Nant Magwr (See Figure 5). The load input of Zn provided by the Frongoch tributary through the Nant Cell is reported to be around 1,700 Kg/yr while the Nant Magwr provides an approximate of 7,800 Kg/yr to the river (Stokes, 2012).

1.2.3 Consequences of the AMD in the Ceredigion region.

1.2.3.1 AMD from Cwm Rheidol and Cwm Ystwyth complexes.

It has been recognized that the main causes of soil infertility in the Ceredigion region are strongly related to the surface drainage from mine waste heaps; the re-deposition of slime dust; the discharges of mine Adits; and the flood deposition of Pb and Zn (Palumbo-Roe *et al*, 2009).



Figure 9 Water Framework Directive: Reasons for Failure for Water Bodies in Ceredigion (Natural Resources Wales, 2013)

The chart in Figure 9 shows the different reasons for water bodies at the Ceredigion region that are failing to meet WFD objectives, in it, the yellow fraction, assigned to the abandoned mines and contaminated land, together with the orange section, assigned to acidification and related with AMD, cover a third of the pie. By interpretation of this, it is

shown that 1 out of every 3 water bodies that fail the WFD objectives, do so because of the effects and presence of AMD.

There is evidence that the Zn concentrations in the water bodies has impacts in the fish species, causing: damage to gill tissue; increased sensitivity to low dissolved oxygen levels; blackening of tissue among other (Environment Agency Wales, 2002).

In terms of the drinking water, it has been reported that there are traces of Pb, Cu and Zn contamination due to the dissolution of pipe materials by acid water; this does not affect only the sectors with no pH adjustment (private supplies majorly) but also occurs in public supplies. The contamination of the sources for potable water in the region is probable to be linked with the mixture of contaminated groundwater from the mine areas.

1.3 Remediation actions.

1.3.1 Initial remediation measures.

For the case of the Cwm Ystwyth, Monitored Natural Attenuation⁹ has been established as the method for remediation (Jarvis *et al.*, 2014).

On the other side, the following list provides a description of what the different remediation measures that have place in the Cwm Rheidol throughout time, starting around the 1960's with engineering biological-physical methods and going remediation measures

- The development of a Three Bed Limestone filters -1960s- (Edwards and Potter, 2007).

- The Cwm Rheidol Metal Mines Remediation Project- Phase 1 -2007- (Edwards and Potter, 2007)

According to the project outline there were three key actions involved in the generation of a report for the remediation plan:

⁹ According to the European groundwater and contaminated land remediation information system EUGRIS: Monitored Natural attenuation (MNA) is the monitoring of the effects of naturally occurring physical, chemical, and biological processes or any combination of these processes to reduce the load, concentration, flux or toxicity of polluting substances in groundwater in order to obtain a sustainable remediation objective (EUGRIS, 2005).

- Detection and reduction of surface waters into the mines.
- Lab-scale studies along with the installation of a pilot plant to assess the feasibility of water treatment using a passive treatment system.
- Water quality, flow and ecological monitoring for outcomes measuring and to provide baseline data for following parts of the project.

- Diversion of water incoming the shafts -2007-:

- Prevention and reduction of the volume of contaminated discharge (Natural Resources Wales, 2016a).

- Drainage of Adit No. 9 to reduce mine-water blowout -2008- (Natural Resources Wales, 2016a).

- Piping of the Adits discharges to prevent soils erosion and therefore incorporation of more metals into the water-flow -2009- (Natural Resources Wales, 2016a). The discharges were diverted to a pilot-scale Vertical Flow Pond (VFP) passive treatment system (Jarvis *et al.*, 2014)

As established by Jarvis *et al* (2014) the most recent approaches for the mitigation of AMD in the Cwm Rheidol Region are related with passive treatment systems related with Anaerobic Reactors; which encourage bacterial sulphate reduction in organic substrates.

1.4 Environmental Policy Background.

A review of the conditions of the mine sites in comparison with the criteria of the report "A methodology for identification and prioritization of abandoned non-coal mines in England and Wales" from the Environmental Agency Wales is necessary to assess the priority status and conditions of both the Cwm Rheidol and Cwm Ystwyth regarding pollution (Mayes and Jarvis, 2012). This serves useful in the process of identification of plausible and possible treatment conditions for mine drainage remediation for the rivers.

As well, evaluation of the impacts on the water environment of the region I required, based on the "Hazards and risk management at abandoned non-coal mine site" report from the Environmental Agency Wales. The historical framework for water pollution/quality legislation in the United Kingdom dates as early as to the 1870's with the *Rivers Pollution Prevention Act of 1876*. The following timeline presents the past and existing legislation:



Figure 10 Timeline for the Water Pollution/ Quality Legislation in the United Kingdom.

The Rivers Prevention Pollution Act in 1951 required licensing of all new industrial or sewage discharges to inland waters; however, existing discharges did not required license unless altered. In 1961 the previous version of the act was modified to include other discharges only to become obsolete by 1974 with the Control of Pollution Act (Bell, and McGillivray, 2000).

It was until 1976 that one of the first EU directives regarding water pollution was set into order; the Dangerous Substances Directive whose purpose was to eliminate or reduce the presence of various substances; such substances were separated and classified into two lists: the Grey list that included substances to be regulated by the Member States setting their own Environmental Quality Standards; and the Black list, which included substances to be eliminated or regulated using the discharge consent system (ECC, 1976).

As an outcome, the system separated 129 identified substances into two parameters based on their EQS (regardless of their list): the standards which Member States must consider as guidelines and those which are to be considered as imperative.

The Water Act of 1989 brought along the creation of the National Rivers Authority as a wide regulatory agency focused on tackling water pollution. The Water Act introduced the procedure of setting water quality standards and objectives dependent on the classification and use of the controlled waters. This served as a step towards the 1991 Water Resources Act which is considered to have consolidated water pollution law (Bell, and McGillivray, 2000).

The Water Resources Act instated punitive measures for the cases of pollution of controlled waters guided by a series of consents gained from the National Rivers Authority. However, and relevant to this project, abandoned mines' pollution was not included in the Act until its amendment in the 1995 Environment Act (Wolf *et al.*, 2002).

The Environment Act intended that from 2000 any operator could no longer abandon a mine without giving a previous notice to the Environment Agency. Unfortunately, this last amendment still does not cover historically abandoned mines. Additionally, the discharge consent scheme under the Water Resources Act, 1991 only applied to discharges from identifiable point sources, therefore, diffuse pollution cannot be as easily controlled (Wolf *et al.*, 2002).

The Water Framework Directive (2000/60/EC) introduced a single system of coordinated objectives to be met through the generation of integrated river basin management plans (Wilby *et al.*, 2006). The Directive seeks the protection of the water resources of every Member State of the EU through its Environmental Objectives; the ones considered for this project include:

-Prevent deterioration of the status of all surface and ground water bodies;

-Restore, improve and maintain all water bodies with the purpose of achieving *good ecological and chemical status* by 2015; the first of 3 six years planning cycles;

-Reduce or eliminate pollution from priority substances and cease discharges, emissions and loss of priority hazardous substances.

Article 16 of the 2000 Water Framework Directive replaces the Dangerous Substances Directive and identifies priority substances and many of this are designated as priority hazardous substances. Also in 2000, the EU introduced the COM (2006)397 Directive on environmental quality standards in the field of water policy, which served as amendment of the 2000/60/EC Water Framework Directive and presented a series of EQS, still current, for hazardous substances with the aim of a higher level of protection against risk to the aquatic environment (ECC, 2006).

As a result from all of these measures (and relevant to this research project), the Environment Agency Wales developed a River Basin Management Plan detailing the current status of every water body in the Welsh territory, and the action plan to be followed to comply with the 2000 Water Framework Directive (Mayes *et al.*, 2009) (Johnston, 2004). This management plan details actions for improvement and remediation of water bodies with relation to metal mines and acid mine drainage:

- The implementation of best practice controls and remediation of abandoned mine sites by 2015.
- The development of a project to investigate and remediate mine sites in Wales.
- The generation of agreements with local metal mine partner organizations for investigation of discharges from abandoned metal mines, as well as solutions to restore pollution levels to meet EQSs.
- The coordination of research and development of suitable and integrated remediation options in accordance with the Metal Mine Strategy for Wales.

The water status designated to the water bodies is classified at 5 levels (high, good, moderate, poor and bad) considering chemical, ecological and morphological aspects of the river basin. In the case of failure of the "good ecological status" target from a water body, the Environment Agency is responsible for establishing a focalized programme with the actions required to deliver environmental improvements by the next six-year planning

cycle (2015, 2021, 2027), and ensuring the continuity of such actions until there is no further deterioration.

1.4.1 Environmental Quality Standards applicable.

The following table present information of the applicable standards according to the corresponding directive for Zn concentration in water bodies:

-United Kingdom Technical Advisory Group on the Water Framework Directive (UKTAG) specifically its report -Proposal for Environmental Quality Standards- focused on water bodies' classification (Dawn Maycock, Adam Peters, 2012).

Water	Exposure	Annual Statistic	UKTAG standard
Fresh	Long-term	Mean	8-125 µg/l total
Salt	Long-term	Mean	40 µg/l total
*The existing freshwater standard depends on the hardness of the water.			

Table 6 Environmental Quality Standards for Zinc (Adapted) (UKTAG, 2012)

1.4.2 Natural Resources Wales Agency: Historical database for comparison.

The Natural Resources Wales Agency, as part of its primary tasks to follow the Water Framework Directive 2000 objectives, has developed monitoring schemes *-Abandoned Mines Project-* for each of the rivers in the country that have been identified as sites with potential environmental impact from the past mining activities. These schemes vary according to the conditions of the river and their ecological status and are intended to provide useful data for the development of strategic activities with remediation and prevention purposes.

As part of this, the Agency has developed a dataset with all the information of the Afon Rheidol and Afon Ystwyth for almost 40 years of monitoring activities. The database provides water quality data in different stations along each river and allows to understand the variation in the chemical and physical conditions of the river. The current project has selected detailed data from these databases as the primary source of information for the assessment of the quality of the rivers in terms of pollution related to Acid Mine Drainage, particularly that related to Zinc contamination. All this information was requested to and delivered by the Natural Resources Wales Agency and it has been published as Appendix.02 of the 2012 report on the WFD Investigation: Abandoned Mines Project (Stokes, 2012; Williams, T. and Stokes, 2012).

The following tables and figures provide a view of the sites considered from each of the rivers of the project as provided by the Agency:

ID	Station Name	National Grid
		Reference UK
1	RHEIDOL U/S CWM RHEIDOL MINE	SN 73040 78040
2	CWM RHEIDOL MINE LOWER ADIT 9	SN 72950 78200
3	CWM RHEIDOL MINE ADIT 6	
	DISCHARGE	SN 73000 78300
4	RHEIDOL: BELOW CWM RHEIDOL MI	SN 72725 78178
5	NANT HARVEST HALL:	SN 72485 78235
6	ABOVE RHEIDOL UNITED	SN 71600 78300
7	RHEIDOL UNITED STREAM	SN 71400 78300
8	RHEIDOL ELECTROFISHING SITE R5	SN 71300 78500
9	NANT BWA DRAIN: TRIBUTARY OF RH	SN 71300 78800
10	RHEIDOL:100YDS D/S ABERFFRWD	SN 69300 79400
11	RIVER RHEIDOL AT TYCAM	SN 68039 79196
12	RHEIDOL E, FISHING R2 CAPEL BAN	SN 65000 79800

13	RHEIDOL AT GLAN YR AFON	SN 61234 80484
14	RHEIDOL: PENYBONT BRIDGE	SN5944080327

Table 7 Afon Rheidol Stations (sample points) (Williams, T. and Stokes, 2012).



Figure 11 Afon Rheidol Stations (sample points) See Annex.1 for detailed version (Developed with UK Mobile Grid Reference Finder © 2011) (Williams, T. and Stokes, 2012).

ID	Station Name	National Grid
		Reference UK
1	YSTWYTH: ESGAIR-WEN BRIDGE	SN 82712 75488
2	NANT PENYGWNDWN CONF WITH AFON YSTWYTH	SN 81354 74744
3	AFON YSTWYTH - UNNAMED TRIB AT CONF	SN 81409 74747
4	NANT GARW AT ROAD CULVERT	SN 81450 74850
5	YSTWYTH U/S CWM Y MINE TY MAWR BRIDGE	SN 81472 74764

6	NANT STWC AT ROAD CULVERT	SN 81200 74850
7	NANT YR ONNEN AT ROAD BRIDGE U/S CONF	SN 80963 74805
8	AFON YSTWYTH AFTER CONFLUNCE NANT CWM	SN 81019 74780
9	AFON YSTWYTH AFTER CONF NANT YR ONNEN	SN 80962 74753
10	NANT Y WATCYN U.S. OF MINE WASTE	SN 80539 74809
11	NANT Y WATCYN D/S OF MINE WASTE	SN 80572 74628
12	NANT Y GWAITH U/S POTENTIAL LOSS GROUND	SN 80407 74729
13	KINGSIDE ADIT UPWELLING	SN 80426 74518
14	AFON YSTWYTH U/S NANT Y GWAITH	SN 80497 74482
15	AFON YSTWYTH D/S NANT Y GWAITH U/S K'BRD	SN 80353 74441
16	AFON YSTWYTH D/S CONF UNAMED TRIB	SN 80059 74354
17	R. YSTWYTH AT CWMYSTWYTH	SN 78885 73756
	GAUGING STATION	
18	NANT MILWYN AT CWMYSTWYTH	SN 78899 73717
19	YSTWYTH: PONTRHYDYGROES BRIDG	SN 74100 72700
20	LEVEL FAWR DISCHARGE, PONTRHYD	SN 73900 72200
21	FRONGOCH STREAM D/S OF NANT CELL	SN 73533 72942

22	NANT BRITHYLL (NANT YR HEN FEL	SN 72915 71843
23	YSTWYTH: FOOTBRIDGE GROGWINIO	SN 71520 72020
24	YSTWYTH: LLANAFAN BRIDGE:	SN 68694 71388
25	SYCHNANT NEAR PENYBONT FORD (N	SN 68420 71020
26	AFON MAGWR NEAR ABERMAGWR BRID	SN 66526 73870
27	CREUDDYN (AFON LLANFIHANGEL)	SN 64200 75500
28	R. YSTWYTH AT RHYDYFELIN ROAD B	SN 58871 78796

Table 8 Afon Ystwyth Stations (sample points) (Williams, T. and Stokes, 2012)



Figure 12 Afon Ystwyth Stations (sample points) See Annex.1 for detailed version (Developed with UK Mobile Grid Reference Finder © 2011) (Williams, T. and Stokes, 2012).

These tables contain every Station selected for the project, the databases from the Natural Resources Wales Agency were adapted to fit the scope of the project; this due to the large amount of data provided by the Agency.

The database provided by the Agency presents information about many "parameters" for water quality and ecological status designation, including: pH; Hardness (mg/l); Flow (m³/s) or (l/s); Temperature of the Water; Zinc (μ g/l); Sulphate SO₄; Iron as Fe (μ g/l); Aluminum (μ g/l); Cooper (μ g/l); Cadmium (μ g/l); Lead (μ g/l); Sodium (mg/l); Potassium

(mg/l); Magnesium (mg/l); Calcium (mg/l); Organic Carbon (mg/l); Chromium (μg/l); Arsenic (μg/l); Manganese (μg/l); Nickel (μg/l); Lithium (μg/l); Silver (μg/l); among others.

2. Aims & Objectives.

2.1 Aims.

The following has been established as the original hypothesis for the research. *"The Cwm Rheidol and Cwm Ystwyth mine sites are contaminating the Afon Rheidol and Afon Ystwyth causing them to exceed required regulatory levels for Zinc".*

In accordance the previous statement, the main aim of the project is to perform an assessment of the environmental quality of the Rivers Rheidol and Ystwyth through water quality analysis, focusing in Zn, in comparison with the Environmental Quality Standards established by the UKTAG in accordance with the European Water Framework Directive 2000.

It is expected from this project to establish the sources of this contamination of zinc contamination in the Afon Rheidol and Afon Ystwyth.

2.2 Objectives.

2.2.1 Primary objectives.

- a) Evaluate the pollution of the river through water quality analysis and evaluate how this compares to historical data.
- b) Perform comparison between water quality analysis results and WFD Standards, with consideration of contrast between the two rivers.
- c) Identify links between potential impacts of the River and mitigation practices from the applicable/corresponding Directives (Mining Waste and Water Framework Directives, Wales Environment Agency, United Kingdom Environment Agency).

2.2.2 Secondary objectives.

a) Identify the mechanism of transportation for the contaminant and how these affect the river as a system.

b) Identify remediation methods, both performed and eligible, for improvement of water quality. This will include the evaluation of potential engineering scale projects.

3. Methodology & Results.

3.1 Historical database from the Natural Resources Wales Agency.

As described in Section 1.4.2, there are a set of Stations, for each of the rivers of the project, selected to conduct the assessment of water quality related to the presence of Acid Mine Drainage and the Zinc concentration. Initially there was certain preparation of the data for analytical purposes, afterwards a brief statistical analysis was conducted in order to establish significance of the data prior the analysis and finally there was an assessment of the Zinc concentrations in the rivers against the ruling EQSs.

3.1.1 Database preparation for analysis.

Arrangement of the data into organized spreadsheets was necessary to allow a suitable visualization of the information for each of the Stations. The geographical location of the Stations was also important so it could be clear which of the Stations required more attention and how the data on Zn concentrations needed to be laid out for the analysis.

Data was arranged so the Stations closer to the mine sites were the first on the analysis and those at tidal limit were the last, such arrangement would facilitate the representation of the river basin flow while performing the metal concentration assessment.

During this preparation stage, it was noted that the datasets have certain discrepancies in the presentation of the date from both historically and between the different Stations, therefore it was decided to perform a regular normalization of the data to enable statistical testing to ensure its validity.

3.1.1.1 Normalization of data for Statistical Analysis: Statistical Significance Verification.

As part of the process of normalization of the dataset, it was decided to analyse the metal concentrations based in yearly averages given the amount of data and the variability of

the concentration values within the years. The calculation of yearly mean values allowed to narrow the available data and enabled representation of the concentration as intended.

The normalized data was then employed to conduct a test for statistical significance; a verification through the ANOVA test would demonstrate the differences between the mean values of the concentrations of Zn through time and proof the need for analysis.

The null hypothesis for the ANOVA test was that: *the mean values of the concentrations for the different Stations through time are equal at a 95% level of confidence*. The results of the test performed with the Afon Rheidol data are described in the following table:

Source of				_		_
Variation	SS	đf	MS	F	p-value	Fcrit.
Between groups	320500.5	6	53416.75	12.57	1 _E -11	2.1525
Within groups	718059.3	169	4248.87			
Total	1038559.8	175				

Table 9 ANOVA test: Variance Analysis for the Afon Rheidol data for selected Stations (See Appendix 2)

As observed in the table, the calculated p-value is well below a 0.05 value for approval of the null hypothesis, and therefore, it is rejected. This was expected due to the large variability in the concentration values and the lack of continuity of the data for some of the Stations throughout time (See Appendix 2). With this result, the difference between the mean values appears to be significant; and therefore, the Zinc concentrations at the Stations must be evaluated against the whole outlook of the river and compared with every other Station.

For the case of the Afon Ystwyth the ANOVA test was conducted in a different way, due to the lack of historical data in several Stations the test focused on the two years that provided the most information for the selected Stations: 2007 and 2008. Consequently, the null hypothesis would be that: *the mean values of the concentrations for the years*

2007 and 2008 at all the Stations are equal at a 95% level of confidence. The test results are shown in the following table:

Source of						
Variation	SS	df	MS	F	p-value	F _{crit} .
Between groups	1164924.2	1	1164924.2	1.18	.2835	4.0785
Within groups	40442342.3	41	986398.5		·	<u>.</u>
Total	41607266.5	42				

Table 10 ANOVA test: Variance Analysis for the Afon Ystwyth data for 2007 and 2008 (See Appendix 2)

As observed in the table, the calculated p-value for this case is higher than the 0.05 value for approval of the null hypothesis and therefore it can be accepted. This was expected due to parity of the values calculated for the couple of years and in consideration of the continuity of the data. The positive outcome of this second test presents itself resourceful for the analysis of the Afon Ystwyth.

The information provided by the Agency was not as extensive for the case of the flow rates (I/s), therefore, it was established that they should be used, together with the Zinc concentrations (μ g/I) to calculate the Zinc loads (Kg/yr) for the eligible Stations; and that the analysis of those loads should be performed, first, by monthly average given the variability of the measures within the months, and afterwards by calculating the yearly mean values.

The equation for calculating the Annual Zinc Load is:

Zinc Load (Ton/year) = Flow $(m^3/s) * Zn (\mu g/l) * 1000 (l/m3)/1 * 10^6 (\mu g/Ton) * 315360000 (s/year)$

Derived from the results of the ANOVA tests, it was clear that the Zinc loads were to remain represented by yearly mean values for the case of the Afon Rheidol; and solely represented for 2007 and 2008 by the mean values of each Station.

3.1.2 Analysis for Zn Concentrations and Flow rate.

Once the validity and usability of the data has been tested and its boundaries and limitations have been recognized the analysis of the data was in order. The analytical review was performed through a series of charts that allowed (as previously commented) visualization of the historic frame of the data and enabled qualitative analysis of the Zn concentrations along the river basin and at the mine sites.

The following represent the results for the Afon Rheidol data on Zinc concentration and Zinc Load:



Figure 13 Zinc Concentration along Afon Rheidol [μ g/l] yearly trend.

The chart shows that there is a decrease in the concentration of Zinc throughout time and along the river (flowing direction from left to right); and that the concentration of Zinc is related to the Zinc input from the mine, considering the raise at 78178 (right after the mine).



Figure 14 Zinc Concentration [µg/l] over time: Mine-Tidal limit

The graph shows the concentration of Zinc over time in different stations, the 78178 being the one right after the Cwm Rheidol site (initial); and the 80327 at Aberyswyth (final). In addition, it can be observed that there are similar tendencies in the values throughout the years and that the fluctuations of Zinc at the last station follows certain pattern driven by the concentrations in the initial station (as expected).



Figure 15 Zinc Concentration over the last two Stations of Cwm Rheidol

The graph shows how the concentrations on the last two Stations do not vary significantly over time (from one station to the other) and therefore there is the possibility to treat the water from that point as there is no evident influence from other sources of AMD.



Figure 16 Relation between Flow and Zn Load in the 80327 Station



Figure 17 Zn Concentration (µg/l) for the 80327 Station

From figure 16, It can be observed that the flow at the 80327 Station appears to have increased over the years, with a raise on the year of 1999-2000, a slight decrease in

2002-2003 and then again raising from 2006-2007. This has clear influence in the Zinc Load (Tons); although the Zn concentration appears to have reduced in figure17, the Zn load remains with high values due to the increment of flow. Therefore, it can be inferred that the increase in the water flow is coming from the tributaries and those are enriched in Zn, preventing dilution of the existing Zn from the Cwm Rheidol.

The following represent the results for the Afon Ystwyth data on Zinc concentration and Zinc Load:



Figure 18 Zn Concentration (μ g/I) for Afon Ystwyth in the years 2007 and 2008

As it can be seen in figure 18 the concentration of Zn for the Afon Ystwyth is highly altered by the presence of the Cwm Ystwyth mine site. The graph shows a strong relation between the two years presented and there appears to be a pattern followed by the concentrations of Zn in 2008.

Unfortunately, the information provided by the Agency was not entirely beneficial for the analysis of the concentration in the Afon Ystwyth as the dataset presents long periods of time without monitoring information or, as seen in figure 17 for the case of 74518 some of the values were too erratic in terms of what the data was expected to show.

4. Discussion.

4.1 Comparison of Zn Concentration levels between the two rivers and against the WFD Regulations.

It is clear from every piece of information that the Agency provided and other literature that the levels of contamination of the rivers are increasing once the river reaches the mine site areas. From the data analysis, it was easy to signal the Stations were the levels of Zn raise and it is also clear that the rate of decrement of the pollution is not comparable to the rate of increment at the sites.

Although the concentration of Zinc may present certain decrease at different Stations, for both rivers the reality is that the Zinc load measured at the tidal limit continues to increase and does not follow a decreasing trend.

In terms of the EQSs, both rivers fail to comply with the regulation. Although it is true that the existing levels of Zinc prior the mine sites are already elevated due to natural presence of Zinc or other minor sources of Acid Mine Drainage. It is clear that the levels that the water reaches at the Cwm Rheidol and Cwm Ystwyth are with no doubt over exceeding the current legislation and the activities performed so far have not had a major role in the remediation or attenuation of this conditions.

4.2 Assessment of Zn Concentration against current Legislation levels.

The Agency has indicated that both sites (in many occasions) have a "Failing" ecological status, and this not only for Zn but for other biological and chemical parameter and the presence of other heavy metals. It appears that due to the lack of consensus from the various stakeholders for assigning effective remediation measures the status and condition of the rivers will remain the same, regardless of that stipulated by the WFD 2000.

The Monitored Natural Attenuation scheme that is currently in place for most of the waterbodies in the UK does not finish to proof sufficient and a technological approach is required to tackle the challenge of meeting the good ecological status for every water body by the next cycle in 2021.

Measures like the construction of AMD treatment plans before its discharge to the controlled water should be considered as priority as well as engineering works to prevent water from coming into contact with the contaminants in the first place. Research for unconventional remediation techniques, and those based in sustainable practices must be continued to increase to achieve progressive change.

5. Conclusion.

- The Afon Ystwyth and Afon Rheidol rivers in the Ceredigion are in constant pollution from AMD discharged from the mine sites that exist along their basins.
- The levels of pollution in these rivers exceed those that are indicated by Local regulation and by the European legislation in place.
- The main contaminant in the rivers is the metal Zn, which concentrations can go up to 800 μg/l while the legislation requires those levels to be under 125 μg/l in the most extreme cases.
- The need for strengthening the monitoring schemes for these rivers has been established as critical. This was proven by the lack of information for the Afon Ystwyth.
- There is evidence that the concentration of Zn can be reduced with biological treatment plants and other passive treatment technologies that do not require major investment for success.
- The Local authorities are urged to take action to reverse the situation and allow the water resources of the region to be clean and safe for every species and for the sake of the environmental wellbeing.

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Annex.1









Appendix 2

Zinc Concentration values (Yearly mean values) in μ g/l for the main Stations of the Afon Rheidol. From the table, it is clear that the values are quite varied from one Station to the other and that there are many voids in time for the values to be considered as equal (at a dataset scale) regardless of the similarity of their values and the intrinsic dependence from one Station to the other as it represents the river flow path.

			Zn [µg	/i] (Total Mean)			
Year	SN 73040 78039	SN 72725 78177	SN 69300 79399	SN 68039 79195	SN 65000 79799	SN 61234 80483	SN 59440 80320
1977	73.57	205.57					167.02
1978	78.61	254.60	267.00	131.30			144.43
1979	87.08	205.44		132.27			136.10
1980	83.46	232.61		130.40			128.77
1981	68.75	191.21		130.66			130.96
1982	67.39	214.35		124.52	123.63		124.31
1983	72.73	191.85		119.27			118.21
1984	71.47	184.46		153.52			95.46
1985	76.00	200.56		93.75			123.67
1986	75.30	141.87		114.83			130.70
1987	72.90	165.86	115.74				103.10
1988	67.67	153.57	98.90	106.40			150.50
1989	141.25	314.57					114.05
1990	70.50	208.75	80.50	110.75			125.33
1991	76.67	250.33		113.71			114.14
1992	52.50	111.50	39.00				95.67
1993	67.28	148.84	104.00	97.17	108.33		104.63
1994	47.55	130.50	86.25	95.78	96.44		92.17
1995	44.00	137.00	73.00	76.00	78.00		86.38
1996	59.75	162.20		117.01			114.53
1997		531.94		113.59			104.73
1998	66.13	150.36		83.10			93.61
1999		142.12		81.20			89.41
2000		115.24		77.99			72.69
2001		812.80		89.82			79.15
2002		172.75		87.75		84.42	84.57
2003	48.67	149.58		88.64		91.40	86.09
2004	48.98	135.39		82.63		98.99	93.33
2005	49.04	128.33		81.84		91.18	91.66
2006	53.23	135.05		89.31		89.80	91.03
2007	53.88	135.50	143.40	101.46		94.06	89.07
2008	62.38	121.96		75.23		84.38	80.13
2009	73.74	126.90		86.13		75.25	85.22
2010	64.30	134.53	43.90	80.79		85.15	82.24
2011	43.92	120.10	70.80	77.92	73.60	73.36	80.54
2012	39.93	101.82	69.30	70.13	108.19	70.64	69.06
2013	40.71	116.47					75.97
2014	46.99	105.73					78.90
2015	44.84	101.55					73.86
2016	37.75	102.53					97.20
VFRAGE	63.68	186.16	99.32	100.46	98.03	85.33	102.46

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