Implications of Historical Mining on the Geochemistry of Ryans Field , Cornwall, UK.

Tom Swanson

B.Eng 3 Industrial Geology

Camborne School of Mines, University of Exeter, Redruth, Cornwall, TR15 3SE

Supervisor: Dr D. Pirrie

Abstract.

Ryans Field is a 15 acre, RSPB managed field in the south east of Hayle Estuary, cut of from the estuary in the 1930's by construction of a causeway, isolating the field from tidal flooding in all but spring tides. Hard rock mining in the catchment has been extensive since the 1300's, and since then, Hayle Estuary has received and concentrated the mobilised particulate waste from these mines. The result is an approximately 0.75 m thick unit of laminated to unbedded, highly contaminated, clay and silt dominated sediment. The southern end of the field contains dredged waste from a nearby tin streaming program, with elevated levels of contamination (eg. Sn 11841 ppm, As 8765 ppm, Cu 8179 ppm). A small stream in the north of the field drains Mellanear Mine, with concentrations of Zn in the sediment reaching 7%, Cu 6%, and As 1.5%, within a discreet plume. The majority of the field has been ploughed, or disturbed by other physical processes, causing significant remobilisation of previously inert particulate waste. SEM analysis reveals high concentrations of cassiterite and sulphides, the later of which are undergoing extensive alteration. In addition, the presence of diverse diagenetic minerals suggests remobilisation and chemical precipitation of contaminants within sediment pore fluids.

Contents Page

Chapter 1 : Introduction

1.1 Estuarine Contamination

Estuaries are dynamic sedimentary systems. Topographically positioned to receive mobile contaminants moving down gradient within a fluvial catchment, they can act as a sink, preserving a record of both past and present contamination. Cornish estuaries like the Fal, Fowey, Camel, Ganel, Helford and Hayle estuaries are all known to be highly contaminated (Pirrie et al. 1997), as they all have fluvial catchment areas within zones of historically intense metalliferous extraction. Contaminants are liberated in solution or as particulates from associated mining, eventually being deposited and stored within the estuarine sediment. It is possible to relate particulate contamination to the associated mine product/processes, as proven within the Fal Estuary with respect to polymetallic hard rock mining during the late 1800's (e.g Pirrie et al. 1997, Hughes 1999).

By analysing the species, distribution and concentration of the contaminants, essential data can be derived concerning the appropriate management of the site in question. The impact of mine waste on natural systems is severe, and Cornish estuaries are unfortunate enough to contain world class levels of contamination. With metal mining in Cornwall currently non-existent, estuarine systems are continuing to be polluted by the poorly managed waste from mines which ceased in operation hundreds of years ago. Fortunately, no industrial processes of a similar nature occur within the Hayle catchment area, so the impact of mine waste is not obscured or worsened by subsequent contaminataion.

This report contains a geochemical and mineralogical appraisal of metallic contamination of the RSPB managed site at Ryans field, within the Hayle Estuary.

1.2 Area of Study

This report is concerned with the Hayle Estuary, an RSPB managed, nationally acclaimed reserve. Fringed by the town of Hayle and the villages of Lelant and Phillack, the estuary is very popular for bird watching, fishing and walking. The estuary is located in south west Cornwall, on the north Cornwall coast (Figures 1 and 2).

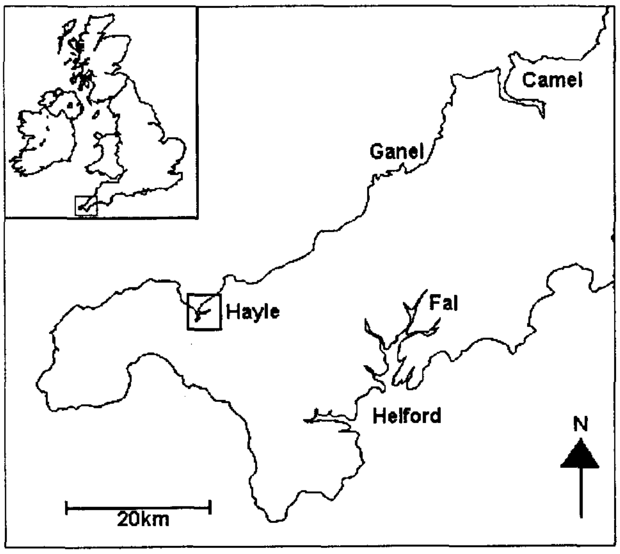

Figure 1 displays the national and regional setting of the estuary.

The estuary comprises of two distinct branches, Copperhouse to the north east, and Hayle to the south west. This report is concerned with the larger, Hayle branch. The Hayle branch is located to receive inflow from four fluvial catchments, Hayle, Trencrom, Canonstown and Lelant, that drain an area in excess of 70 km^2 (Pirrie et al. 2002). The northern end of the Hayle branch features a small harbour and deep water channel, that flows out into St. Ives Bay. Historically, Hayle was a locally important port where copper ore was exported, and coal imported.

In the south east of the Hayle branch, separated from the main body of the estuary by a raised platform featuring the main access road to Hayle, is Ryans Field (Fig. 2). The field is approximately 200 m by 300 m, and occupies 15 acres of poorly vegetated wetland, which is partly flooded during spring tides.

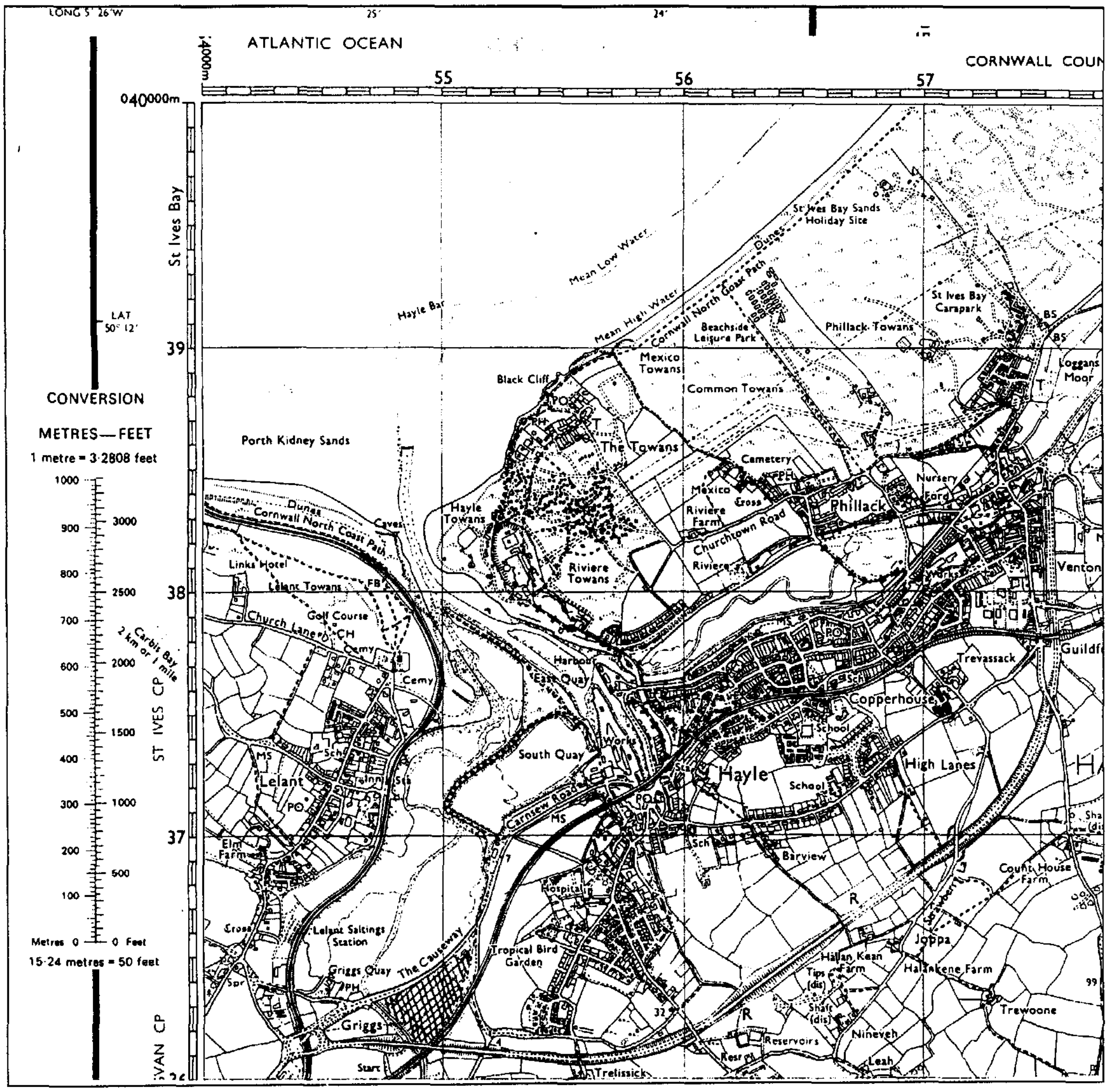

Figure 2 is taken from an ordnance survey map, and displays the town of Hayle and the villages of Lelant, Philack, and The Towans. Ryans Field is shaded, and is located in the south west of the map.

1.3 : Regional Geology

The catchment area for the Hayle estuary is 70 km^2 (Pirrie et al.1999). The large catchment area is attributed to the low lying estuary being fringed by three topographically elevated granite plutons. The regional geology surrounding the Hayle estuary is complex. The area is dominated by low-lying Devonian metasediments, punctuated by topographically elevated granites, unconformably overlain by Tertiary and Quaternary sediments.

The estuary lies upon Devonian metasediments of the Gramscatho Basin, which are assigned to the Porthtowan and Mylor Slate formations (Fig 3). However, the estuaries catchment area also incorporates the Lands End Granite to the west, the Tregonning-Godolphin Granite to the south, and the Carnmenellis Granite to the east.

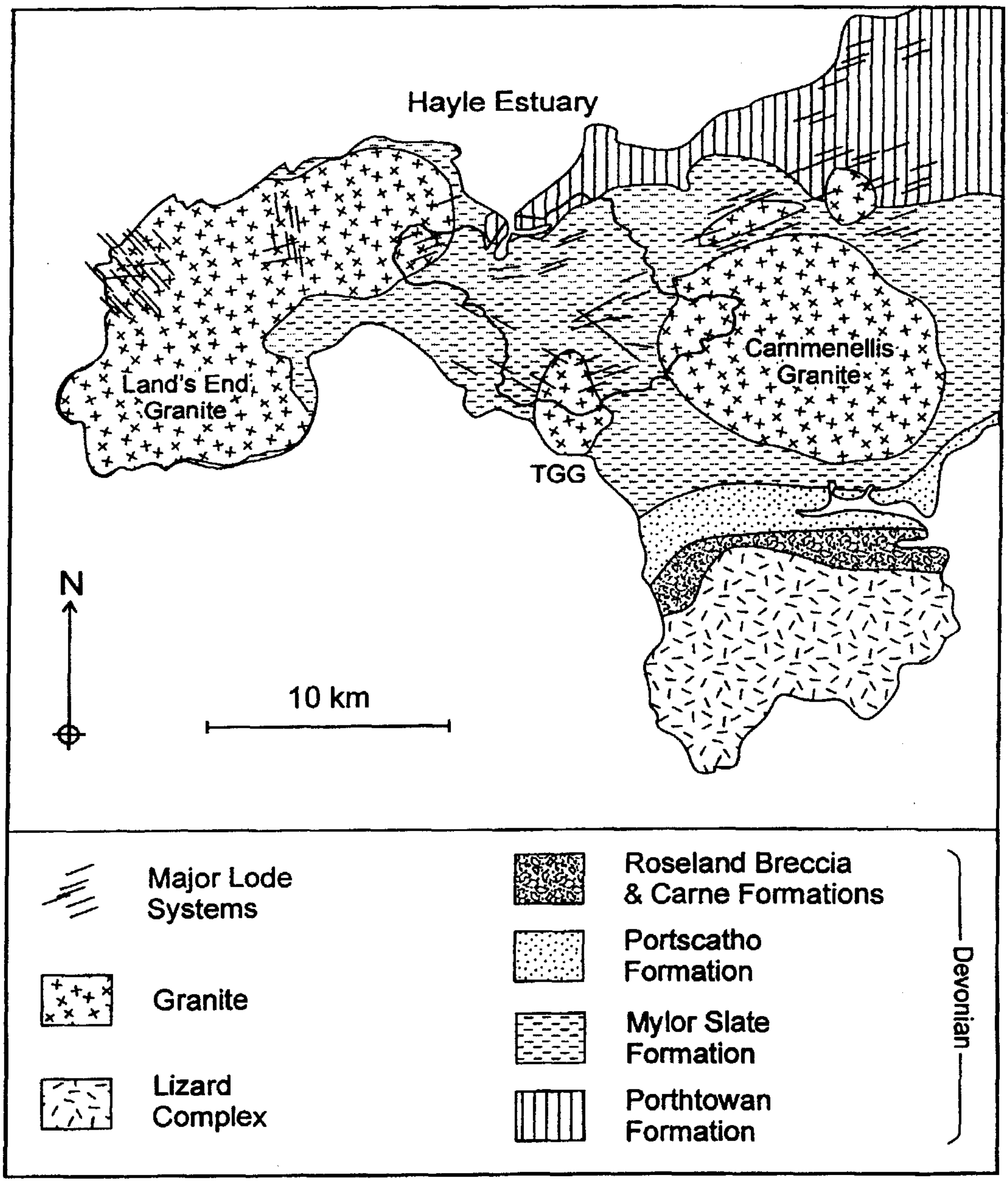

Figure 3. Geology of south west Cornwall (Rollinson et al. Submitted).

The Mylor Slate formation is Famennian in age, and overlies the older Porthtowan Formation. Predominate strata are pale green to white, silty laminae (Goode and Taylor 1988). Infrequent thin to medium bedded, muddy fine sands and slump deposits are also recognised (Selwood et al. 1998). Metabasites (greenstones), account for approximately 10-20% of the formation to the east of St. Ives, and in a NE-SW zone between Penzance and Camborne (Selwood et al. 1998). The metabasites are altered basalts, due to regional lower greenschist facies metamorphism during the Variscan Orogeny (Pirrie et al. 2002).

The granite outcrops are part of the Cornubian Batholith, and are all interconnected at depth (Goode and Taylor 1988). The Lands End Granite is the youngest of the plutons (Clarke et al. 1993). It is comprised of biotite granite, with feldspar phenocrysts reaching up to 200 mm in size. Recent mapping however, has shown that is made up of discrete bodies of both fine grained and coarse grained granite (Goode and Taylor 1988). The Tregonning Granite crops out in a comparatively small composite pluton. The southern area is coprised of topaz granite, post dated by a smaller mass of biotite granite in the northern zone of the pluton (Selwood et al. 1998). The Carnmenellis Granite is defined by its regular outcrop shape, and narrow metamorphic aureole (<1 km). The granite is a porphyritic, coarse grained, muscovite biotite granite (Leveridge et al. 1990). Although coarse grained, phenocryst size is markedly smaller than in the Lands End Granites.

The catchment area of the Hayle Estuary is extensively mineralised. Directly between three granite plutons, the area boasts textbook examples of both high temperature minerals (cassiterite, wolframite, and arsenopyrite), and lower temperature minerals (sulphides of Cu, Zn, and Pb). Fracture patterns within the region vary, and between Penzance and Redruth the older main stage high temperature hydrothermal veins (locally termed lodes) trend WSW-ENE (Goode and Taylor 1988, Pirrie et al. 2002). These lodes characteristically swell and pinch, and vary considerably both laterally and vertically. It is from these lodes that the bulk of the Sn, Cu, As and W was extracted, with the dominant main stage ore minerals being cassiterite and arsenopyrite (Selwood et al. 1998, Pirrie et al. 2002). Permian dewatering of the Plymouth Basin brought about the final significant stage of mineralisation within the Cornubian Batholith, a process that occurred for approximately 30 million years. Trending at approximate right angles to the main stage lodes, these locally termed 'cross course' veins trend NW/SE in the Hayle catchment, and comprise chalcopyrite, sphalerite and galena (as well as Ag, Sb and U bearing ores).

Unconformably overlying the eroded Mylor Slate Formation, are the St Erth Beds. These Pliocene deposits are the most researched of the Tertiary deposits in West Cornwall, and contain a prolific and diverse fauna. Goode and Taylor (1988) recorded 35 species of gastropod, and 20 species of bivalve within the marine sands. Overlying the sands are complex fluvial conglomerates consisting of clays, sands, gravels and head deposits.

Quaternary sediments, typically comprising raised beach deposits, overlain by Devensian periglacial slope deposits crop out in the area. Quaternary sediments are also found within the estuarine catchment area are head deposits (Godrevy), buried channels (Hayle Estuary), and blown sand (St Ives Bay dune system). Previous boreholes taken from the Hayle Estuary recorded 34 m of sediment before reaching the country bedrock (Goode and Taylor, 1988)

1.4 Mining History

Metalliferous minerals have been exploited in south west Cornwall since the Bronze age. Early workings were predominately alluvial tin placer deposits, and lodes in coastal exposures (Goode and Taylor 1988), with documented tin streaming being carried out in and around Hayle from the Medieval period onwards (Buckley 1999), and a short period in the 1940's, immediately upstream of Ryans field. Hard rock mining within the Hayle catchment area commenced from about the 13th century, initially for tin, then copper and a wide range of products including arsenic, zinc, lead, silver, tungsten, and uranium (Pirrie et al. 2002). Minor underground mining begun in Roman times, but it was not until the introduction of rock blasting using gunpowder and steam driven pumps (17th and18th centuries) that extensive underground extraction began. The Cornish mining industry was notoriously unpredictable, fluctuating heavily but maintaining a general increase in production. Towards the end of the 19th century and early 20th century, the mining industry collapsed. Copper production fell from a peak of 15,000 tonnes per year in 1860, to almost nil in 1990. Tin production fell from a peak of 10,000 tonnes a year to a few hundred in 1920 (Goode and Taylor 1988). Since the early 20th century the industry has struggled, until finally the last mine closed in 1998.

Hayle Estuary receives sediment from rivers draining an area primarily mined for tin, copper, zinc and lead. The area received recognition as being an important copper mining district (Pirrie et al. 2002), and Rollinson (et al. 2002) recorded over 60 hard rock mines which once operated within the Hayle Estuary catchment area. Ryans Field receives drainage primarily from the Hayle, and to a lesser extent, Canonstown catchment areas, which contain a total of 29 mines. Ryans field also receives drainage from a tributary off Mellanear river, running along Water Lane, the significance of this is discussed in Chapter 7. The last major mine to close within these catchments is the Great Works mine, which extracted tin and copper over a period that spanned five centuries. To deal with the tin and copper being produced and exported from the area, mineral processing plants and smelters were established. In 1704 and 1715, small scale tin blowing houses were established in Angarrick and Rose-an-Grouse. Further industrial development lead to the building of the areas first copper smelter in 1721, in Penpol. In 1758 the area now known as Copperhouse, another copper smelter was built, the black slag from which can be observed in the local buildings and bridges. In 1779 an important iron foundry was established. In 1816 and 1837, two tin smelters were built at Copperhouse and Mellanear, which continued production until 1908. The industry resulted in the supply of a large volume of mine waste sediment and significant contamination of the estuarine sediments in and around Copperhouse pool (Pirrie et al. 1999).

1.5 : Aim of Dissertation

The aim of this dissertation is four fold:

- Record the sedimentology of Ryans field through a series of cores, and analyse for patterns in bedding.
- Identify chemical species representing contaminants within Ryans field.
- Analyse contaminant concentration and distribution, and assess the chemical activity of the system.
- Identify contaminant sources, and assess future contaminant risks.

Chapter 7 : Data Synthesis

Cores taken from Ryans Field reveal a clay-silt dominated sediment persisting from surface to depths of 0.3-0.67 m. The bedding is non-uniform, with a mixed uppermost 0.3 m of sediment. The clay-silts are late Holocene to recent deposits, whist the carbonate sands and head deposits are Holocene and Devensian in age respectively. XRF analysis confirmed the absence of significant contamination within the carbonate sands, and the underlying head deposits. This allows focus to be aimed at the clay-silts within the upper 1 m of the sediment profile. As noted in Chapter 3, five of the eight cores contain laminated clay-silts, which comprise approximately one third of the total sediment. XRF data confirms that the highest contamination occurs within these beds, which are often stained green due to Cu contamination. Also as noted in Chapter 3, there is a probable reason for the lack of persistence of these units, particularly close to the surface can be attributed to the mixing of the sediment, brought about by the aforementioned management techniques. Sand, gravel and large proportions of organics and bioturbation are also observed within the upper 0.3 m of the sediment profile, but the matrix/bulk sediment content is clays and silts. Mixing of the upper units has done little to reduce the contaminant concentration, with high levels persisting up to the surface. It was noted in section 4.3 that a general trend in distribution of contaminants is a peak in metal concentration just 0.05-0.15 m below the surface, followed by a general decline towards the base of the unit. A reasonable assumption is that ploughing has been ineffective in reducing contaminant levels, and (as with the dredged sediment) has possibly reactivated previously inert areas of contamination, which are now concentrated within the upper layers of the sediment.

The laminated clay-silts represent the deposition of mine waste into the estuary over a period of up to 300 years. Transported down-slope as particulates, the minerals/slags create laminated sediment representative of particular times in Hayles history. Each core displays varying degrees of co-variance within its constituent metals, each core showing predictable responses to changes within core sediment (eg. Increasing contaminant grains encountered in typical Cornish mine waste. As a result, the exceptionally high values of industrially important minerals must be derived from mine waste within the fluvial catchment. The presence of smelts and slags is attributed to smelting within the Trencrom and Mellanear catchments, and is significant. The pathways traversed by these grains are likely to be the same as the detrital sulphide grains. This proves the viability of a successfully traversed pathway for particulate waste, from the contaminant source, to the estuary.

Sulphide oxidation is the dominant source for metallic ions liberated into the diagenetic pore fluid, and the existence of ions within solution is controlled by pH. Abundant sulphide alteration and the presence of precipitated diagenetic grains, act as an indicator to the chemical activity of the system.

Chapter 8 : Discussion

8.1 : Contaminant Sources

The distribution of the contaminants ties in superbly with the fields history. Prior to the construction of the causeway in the early 1930's, Ryans Field was strongly tidal, completely flooding on each high tide. As discussed in section 1.4, there have been over 60 hard rock mines in the Hayle Estuary catchment zone since the 13th century. Since the development of hard rock mining in the area, thousands of tonnes of detrital contaminants would have made their way in to the estuary, where the large tides would deposit them around the estuary, or carry them out to sea in suspension.

Realistically, taking into consideration the shear quantity of mines in the catchment zone, and the effective mixing of sediment within the main body of the estuary, attempts to designate specific sources would be inaccurate, and of little value since the isolation of the field in the 1930's. Up until the construction of the causeway, contaminant distribution across the field would have been generally homogenous, with the exception of the dicreet plume in the north east corner. Earlier work by Pirrie et al (2002), reveal a discreet plume in the eastern side of the Hayle Estuary, containing high levels of Cu, As, Zn, and Sn within the surface sediment, originating from the same stream that flows along the northern edge of Ryans Field. Subsurface evidence indicates that this stream is of historic significance to Ryans Field, and surface data indicates that it is of modern significance to both Ryans Field, and the Hayle Estuary.

As such, it is a reasonable assumption to state that the most significant active source of contamination in Ryans Field is this small stream. On construction of the causeway, Ryans Field became isolated from the main body of the estuary, therefore removing a large source of contaminated sediment inflow into the field. Had the Field then been left alone, all contaminated sediment (apart from the northern end of the field), would now be relatively inert, overlain by a thin, less contaminated sediment, that would have developed

developed over the last 70 years. No significant tidal action has minimised physical remobilisation (eg. via migrating tidal channels or heavy tidal flow), and therefore limits chemical remobilisation.

However, subsequent physical and chemical remobilisation of particulate waste has been the result of human intervention. After construction of the causeway, the south western end of the field was used as a saltings dump (for dredged sediment from the bed of the Hayle River), for the tin streaming program that was being carried out up stream during the 1940's. This disturbed the in situ contaminated sediment, with tonnes of sediment of even greater contamination. Surface contour plots reveal the amorphous contaminant plume in the south west of the field to cover the same land as the area used as the saltings dump (Fig. 45). Inspection of the field reveals the saltings to be composed of tonnes of very fine sediment, discoloured green, and of high contamination. More recent misuse of the field came about when the RSPB ploughed the field in the early 1990's. Unknown to them at the time, they were in fact remobilising tonnes of mine waste, lying below the surface within laminated clay-silt beds. Ploughing would have broken up the dense, anoxic sediment, allowing oxidation of detrital contaminants, and increased mobility. The discreet plume of contamination in the north east corner of the field contains the highest levels of contamination. It is precisely positioned over the only part of the field which is undisturbed, and nearest to incoming sediment from the tailings from Mellanear Mine, connected to the field by a small stream called Water Lane, which runs parallel with the northern edge of the field (Fig. 45).

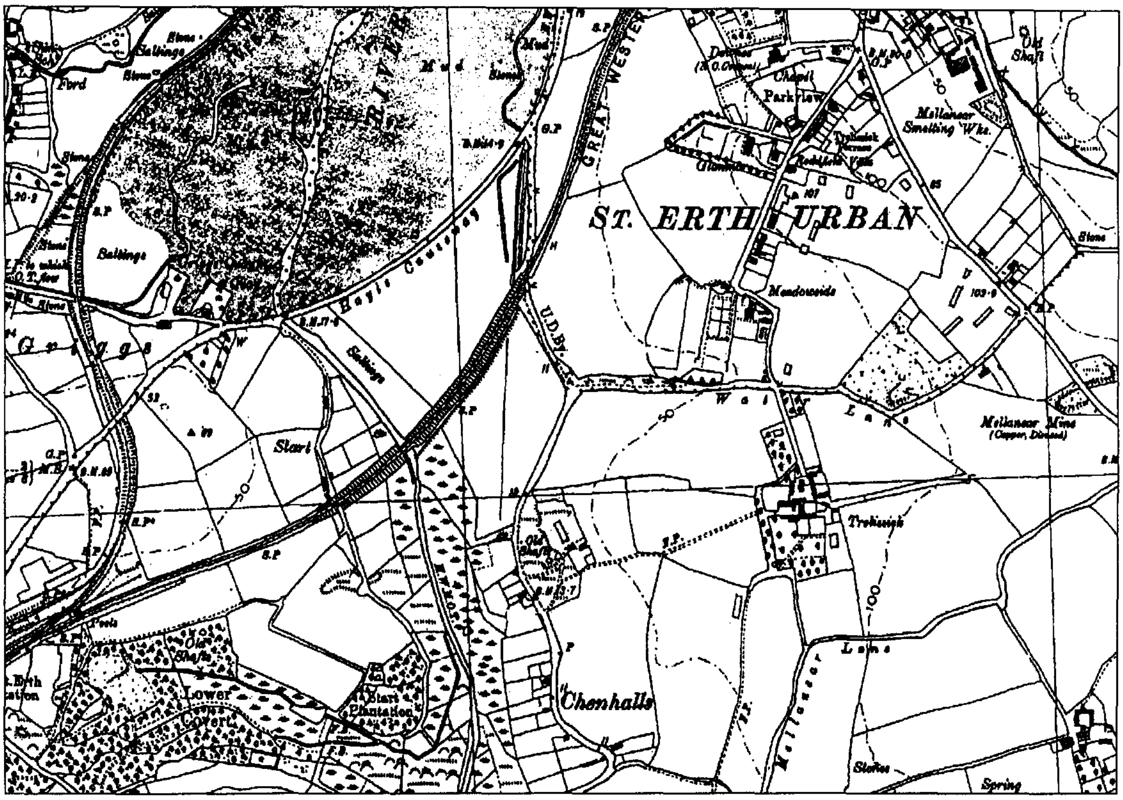

Figure 45. This map was made in 1907. In the east of the map is Mellanear Mine, with the shaded area to the west believed to be the tailings dump. The perimeter of the dump is defined by Water Lane, which runs due west, then north west, where it intercepts the north east tip of Ryans Field and runs along the fields perimeter, and into the Estuary. Inspection of the south west end of the field reveals the area marked 'saltings'.

8.2 : Metal Mobility

Metallic contaminants are present in two phases: as mobilised ions or as detrital grain. Within the Hayle Estuary catchment, these phases must travel from the contaminant source (mine waste), via a pathway (eg. watercourses), before entering the estuary, where they contaminants are deposited or taken out to sea.

8.2.1 : Sources

Release of particulate waste is largely the result of erosional processes, or the direct release of mine waste or tailings into the environment. It is well documented that disturbed, fine sediments like tailings are far more susceptible to these physical processes, and once liberated from the bulk of sediment, the particulate waste is small enough to quickly be transported into the watercourses.

Acid mine drainage (AMD) is a well documented product of mine waste. It is caused by the oxidation of sulphide ores, which in turn releases the highly soluble metallic ions into solution. The product is a highly mobile dissolved contaminant.

8.2.2 : Pathways

The AMD that enters the hydrological system, proceeds gravity controlled on a descent towards the estuary. Typical conduits for metal contaminants are waterways, like streams and rivers. Research carried out by Merefield (1993) proved this when sediment samples from the beds of Tencrom and Hayles rivers and discovered tin concentrations of over 10,000 ppm and Cu concentrations of nearly 3000 ppm. Particulate waste is typically under 63 μm, and as such is transported in suspension. Stokes law dictates that when the energy of a system is no longer of the magnitude capable of sustained movement, deposition occurs. This could be for example, in the lee of a meander (placer deposits), or within the typically low energy environment of an estuary. Whilst being transported, sulphide grains will undergo oxidation, mobilising metallic ions in to solution.

There are several physical and chemical processes operating in a stream that can give rise, directly or indirectly, to attenuation of dissolved pollutants. The four main physical processes are advection, dilution, dispersion and sedimentation. Chemical processes include chemical reaction, precipitation, dispersion and adsorption onto streambed sediments or suspended particles (Salomans). Adsorption is the most important of these processes, and is greatly increased by the rise in pH from the mine waste to a natural system. This decrease in acidity induces adsorption of dissolved metals onto available solid phases, therefore decreasing the amount of 'free' cations. Essentially, the bulk of dissolved pollutants will enter Ryans Field as an adsorbed phase on the surface of particulate pollutants.

8.2.3 Estuarine Mobility

Once deposited within the estuary, particulate remobilisation will only come about via physical processes. However, many physical processes exist within an estuary, like erosion from migrating tidal channels, tidal flow, human intervention, burrowing invertebrates or wading birds. These processes liberate relatively inert sediment back into an oxidising, potentially energetic environment.

When deposited within the estuary, sulphides will degrade, providing appropriate oxygen is available. Essentially, the contaminated sediment is creating its own AMD. The production of AMD will not be the same throughout the sediment, for example, the anoxic laminated clay-silt beds displayed less diagenetic activity than the organic-rich beds, despite being more contaminated. This is due to more oxygen and water being available in the organic rich beds, and therefore a larger quantity of metal rich pore fluid being generated.

The chemical processes that result in the liberation of these metal ions are complex and involve many subsidiary reactions. The exposure of pyrite and other sulphides to atmospheric oxygen and moisture results in one of the most acidic of all known weathering reactions (equation 1), producing iron sulphate, with sulphuric acid as a bi-product:

$$2FeS_2 + 7O_2 + H_20 \Rightarrow 2FeS0_4 + 2H_2S0_4 \qquad \text{(Equation 1)}$$

The product of iron sulphate is a constituent chemical in the oxidation of chalcopyrite (Equation 2).

$$CuFeS_2 + 2Fe_2(SO_4)_3 \Rightarrow CuSO_4 + 5FeSO_4 + 2S \qquad \text{(Equation 2)}$$

Similar reactions occur during the oxidation of sphalerite, which is readily oxidised to produce soluble zinc sulphate ($ZnSO_4$). The generation of AMD within Ryans Field is not desirable to its greater mobility and increase in bioavailability.

8.3 Implications for Site Management

Appropriate site management is subjective, and not the objective of this report. However, remedial measures are required. The contamination is at levels unfit for a nature reserve, or anywhere for that matter. Fortunately, the contaminated sediment is restricted to the clay-silt dominated horizons that are well under a meter thick. The contaminated sediment has been contained, and possibly chemically buffered by the underlying alkaline carbonate sands. Calculations reveal the field to therefore contain approximately 50,000 m^3 of contaminated sediment. Encapsulation within a geomembrane is likely to be the most viable option, and perhaps further investigation in to the stream that drains Mellanear Mines old tailings area, and runs along the northern periphery of Ryans Field would prove essential to appreciate future contamination risks

Chapter 9 : Conclusions

Sediment within Ryans Field excessively exceeds safety levels recommended by the Environment Agency.

XRF analysis reveals a discreet plume of contamination in the north of the field, with elevated levels of contamination (eg. Sn 7%, Cu 6%, and As 1.5%).

The remaining proportion of the field remains highly contaminated with typical values yielding concentrations of Sn at 1%, As at 0.5%, Zn at %, and Cu at 0.5%.

All significant contamination occurs within the clay and silt dominated sediment, and remains severe even at the surface.

Physical and chemical remobilisation of contaminants within the field has increased the bioavailability of the contaminants, and as such represent a genuine risk to the rare birds and other forms of wildlife which make the reserve special.

Ryans Field will receive ongoing contamination from Mellanear Mine draining into the Water Lane stream, from the flooding of the field on spring high tides, and from leached contaminants from the dredged waste which extends to and upstream of Hayle River.

Distribution of the contaminated sediments in relation to their possible remediation is isolated to an approximately 0.75 m thick clay-silt dominated unit, overlying, and almost certainly being buffered by, a clean carbonate sand unit.

The thickness and underlying stratigraphy of the contaminated sediment will ease measures to remedy the situation.

The most effective remedial measures are to either remove the contaminated sediment for disposal in a landfill site/waste facility, or to isolate the sediment in an impermeable geomembrane.