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Selenium and Other Trace Element Mobility in Waste Products and Weathered Sediments at Parys Mountain Copper Mine, Anglesey, UK

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Abstract: The Parys Mountain copper mining district (Anglesey, North Wales) hosts exposed pyritic bedrock, solid mine waste spoil heaps, and acid drainage (ochre sediment) deposits. Both natural and waste deposits show elevated trace element concentrations, including selenium (Se), at abundances of both economic and environmental consideration. Elevated concentrations of semi-metals such as Se in waste smelts highlight the potential for economic reserves in this and similar base metal mining sites. Selenium is sourced from the pyritic bedrock and concentrations are retained in red weathering smelt soils, but lost in bedrock-weathered soils and clays. Selenium correlates with Te, Au, Bi, Cd, Hg, Pb, S, and Sb across bedrock and weathered deposits. Man-made mine waste deposits show enrichment of As, Bi, Cu, Sb, and Te, with Fe oxide-rich smelt materials containing high Pb, up to 1.5 wt %, and Au contents, up to 1.2 ppm. The trace elements As, Co, Cu, and Pb are retained from bedrock to all sediments, including high Cu content in Fe oxide-rich ochre sediments. The high abundance and mobility of trace elements in sediments and waters should be considered as potential pollutants to the area, and also as a source for economic reserves of previously extracted and new strategic commodities.

Keywords: Parys Mountain; ochre; selenium; pyrite; gold; copper

1. Introduction

Historic mining sites and associated tailings can be a significant source of polymetallic contamination, resulting in potentially toxic levels of metals posing a risk to surface and groundwater systems [1]. Sulphide-mineral oxidation within current and former mine sites is a significant environmental threat faced by the mining industry worldwide [2]. Elements such as Se, Te, As, Cd, Hg, and Pb are notable pollutants in waste sites due to their widespread and intense occurrence, and can be damaging to ecological and human health, affecting livestock, soils, and groundwater systems [3–11]. Conversely, the need for new low-carbon energies and technologies has led to an increase in demand for many critical raw materials such as Se [12–16]. Historic mining sites previously focused upon base or precious raw materials may now contain economic concentrations of these other trace elements. Therefore, trace element enrichment at historic mining sites poses both a potential environmental threat and an economic opportunity. Selenium is typically found in association with Cu mines as a by-product recovery from anode slimes [15,16], and Cu mining districts may show Se enrichment. The objective of this study is to quantify the distribution of Se and other economically and environmentally significant trace element concentrations in the natural and mining waste products of Parys Mountain Cu mining district, Anglesey, North Wales, and to evaluate the geochemical controls on the distribution of these trace elements. This includes (1) a geochemical characterisation of the bedrock, smelt materials, weathering soils, and acid mine drainage (ochre) sediments, (2) identification of trace element source and controls on element liberation and fixation in the Parys Mountain Cu mining district, and (3) determination of any resource potential and environmental threats posed by trace elements at Parys Mountain. Due to its increasing economic and environmental importance [10,11,14–16], Se will be the focus of this study, as well as elements with chemical affinities to Se (e.g., Au, Cu, Pb, As, Te). Understanding the distribution of Se and the geochemical processes that control trace element enrichment in natural and waste products of mine tailings is important for predicting and managing soil and water quality in such extensive areas.

2. Study Area

Parys Mountain (Mynydd Parys; National Grid Reference: SH441904) is a historic Cu mining site on the island of Anglesey, north-west Wales, UK (Figures 1–3; [17–22]). The site has a long history of mining, as far back as the early Bronze Age [17,18]. The western part of the mountain is currently (2017) under operation licence by Anglesey Mining Plc. Two prominent historic Cu mines, the Mona and Parys mines, are centred on Parys Mountain (Figures 2 and 3). Evidence suggests that Parys Mountain was subjected to fire setting techniques during the Bronze Age in order to extract Cu for crude tools [17–19]. It has also been suggested that Romans mined Parys Mountain for Cu and Pb [19]. The site became one of the world's largest copper mines in the 1780s, with ore recovered from a number of open pits and underground workings up to 150 m below the surface. Between 1768 and 1904, an estimated 3.5 million tonnes of ore were removed to yield 130,000 tonnes of Cu metal [20]. From 1810, significant underground workings were opened, and by 1900, all significant mining activity had ceased [20]. Drilling programs took place from 1961 to 1990. An overall geological reserve of 4,114,000 remaining tonnes has been proposed, with estimated grades of 1.43% Cu, 1.2% Pb, 2.4% Zn, 20 g/t Ag, and 0.3 g/t Au [20].

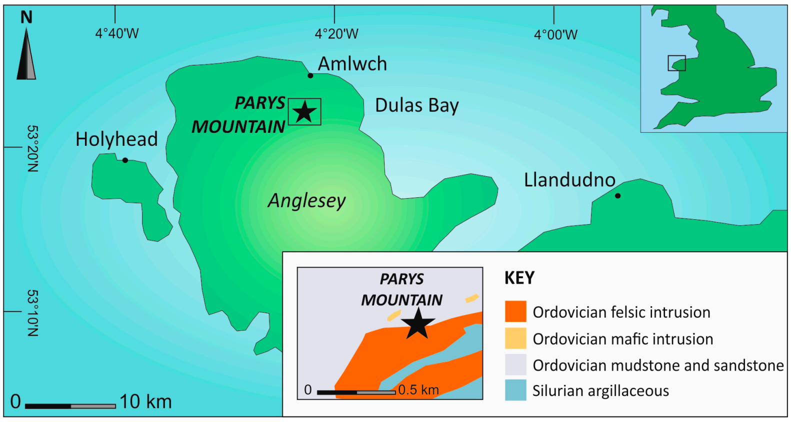

Figure 1. Location of Parys Mountain on the island of Anglesey (North Wales, UK) and, bottom inset, simplified geological map of Parys Mountain and surrounding area (adapted from [17–22]).

The disposition of the main geological units (Figure 1) resulted from the folding of the initial sequence of mudstone overlain by rhyolite and shales into a large anticline-syncline structure with an east-west strike and a dip to the north, with the north limb overturned to the south. Mineralisation at Parys Mountain is Ordovician volcanogenic massive sulphide (VMS) deposits of Kuroko type [21–25]. The country rock is made up of folded Ordovician–Silurian sandstones and mudstones, rhyolitic lavas and pyroclastic deposits, mafic and felsic intrusions, and minor basaltic lavas [21,25]. Quartz veins host abundant pyrite (Figure 4), associated with Ordovician–Silurian sea floor hydrothermal activity [21–24]. Veins rich in Cu were remobilised during subsequent tectonic activity [23–25].

As a consequence of the extensive mining history, the area hosts a number of natural and solid waste deposits enriched in trace elements. Natural deposits include exposed bedrock, soils, and streams, while waste deposits include smelt soils and muds, mine drainage systems, and associated Fe(III) (oxy)hydroxide (ochre) stream sediment deposits [23,24,26–31]. Previous studies at Parys Mountain have generally focused on the uptake, retention, and environmental impact associated with toxic metal contamination on bioaccumulation and plants [31–35], and environmental contamination of muds and stream waters of a select suite of major and trace element concentrations [26–28,36]. Weathering of waste spoil heaps and bedrock, and subsequent oxidation of sulphides, has led to the development of acidic waters that drain into rivers, smaller connected streams, standing water bodies, and eventually Dulas Bay (Figure 1). Ochre sediment precipitation occurs in these streams and run-off systems (Figure 2), principally containing Fe(III) (oxy)hydroxides and enriched trace elements [37].

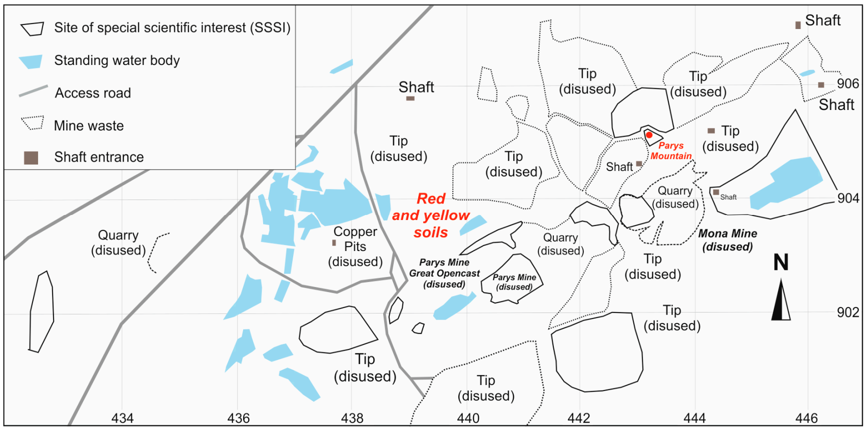

Figure 2. 1:4000 scale map of Parys Mountain former workings (including the Parys Mine and Mona Mine), disused tips, and quarries (adapted from [19]).

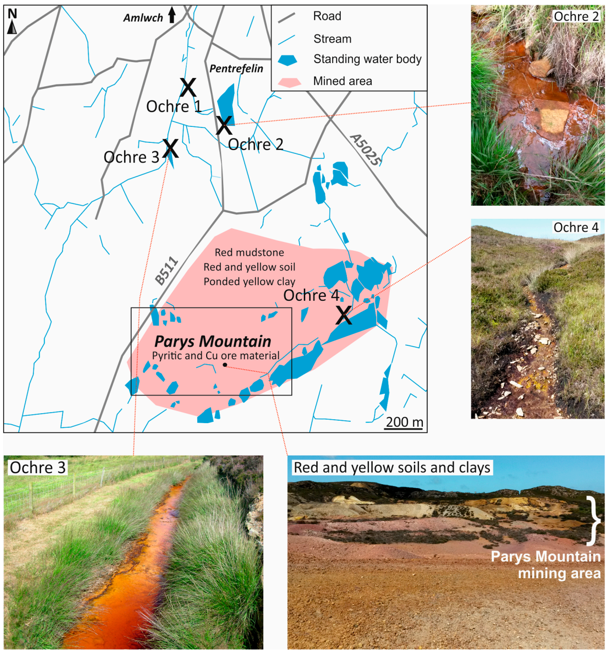

Figure 3. Parys Mountain former workings (light red area on map), and associated natural and mine waste deposits, including ochre-bearing streams, yellow weathered soils, and red smelts. Numerous connected streams and water bodies also shown on map.

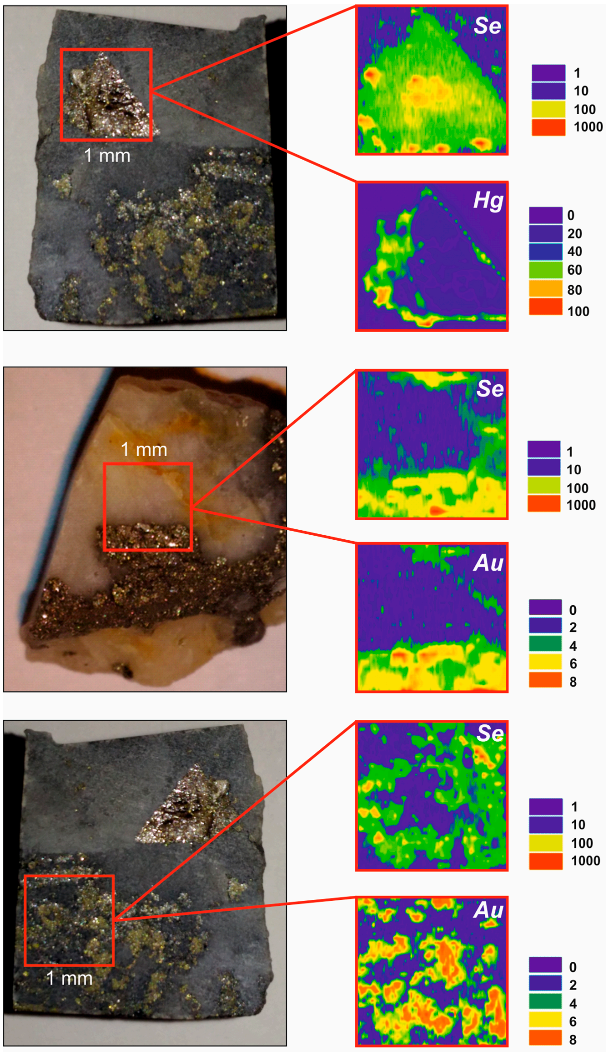

Figure 4. Element maps (LA-ICP-MS) of pyrite in bedrock (red box representing ~1 mm length and width), rich in associated major and trace elements, including Se, Fe, Au (all commonly in the core), and Hg (in the later rim). Enrichment depicted by colour scale (low blue to high red; semi-quantitative data in ppm).

3. Materials and Methods

3.1. Sampling

Whole rock, sediment, and water samples were collected from Parys Mountain under the guidance and supervision of the volunteers of the Parys Underground Group. Targeted samples included:

- Natural deposits: sulphidic bedrock (n = 4) and weathering soil (n = 8). Weathering soil formed from the natural weathering of bedrock deposits.
- Waste deposits: red smelt muds and soils (n = 7) and ochre sediments (n = 8). Red muds and soils formed from weathering of waste material from sintering, refining, and beneficiation activities, while ochre sediments formed from precipitation of Fe(III) (oxy)hydroxides from mine drainage systems.
- Underground pool water (n = 1) and surface stream water samples from mine drainage systems (n = 3) were also collected.

3.2. Scanning Electron Microscopy

Whole rock and sediment samples were examined using an ISI ABT-55 scanning electron microscope (SEM) (Kevex, Thermo Fisher Scientific, Waltham, MA, USA) with Link Analytical 10/55S EDAX (EDS) (Link An, High Wycombe, UK) facility for mineralogical determination.

3.3. Laser Ablation

Trace element analysis of polished blocks was performed by using a New Wave laser ablation system UP213 nm (New Wave Research, Fremont, CA, USA) coupled to an inductively coupled plasma-mass spectrometry (ICP-MS) Agilent 7900 (Agilent Technologies, Tokyo, Japan). The laser beam was fired with a spot size of 100 μm moving in straight line, a 10 Hz repetition rate, and at 50 $\mu m \cdot s^{-1}$ ablation speed with 1 $J \cdot cm^2$ energy. Before ablation, a warm-up of 15 s was applied with 15 s delay between each ablation. Settings parameters were optimised daily by using a NIST Glass 612 (NIST, Gaithersburg, MD, USA) to obtain the maximum sensitivity and to ensure low oxide formation. In order to remove possible interferences which could affect Se measurement, a reaction cell was used with hydrogen gas (between 3.0 and 3.5 mL/min optimisation to decrease Se background). MASS-1 Synthetic Polymetal Sulfide (USGS, Reston, VA, USA) was used to provide a semi-quantification by calculating the ratio concentration ($\mu g \cdot g^{-1}$)/counts per seconds, and multiplying this ratio by the sample counts. Certified and informative values are available by request through the US Geological Survey website.

3.4. Whole Rock and Sediment Geochemistry

Whole rock and sediment samples were analysed by both inductively coupled plasma atomic emission spectroscopy (ICP-AES) and solution ICP-MS. Elements of interest include As, Au, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, and Te. Samples of ~30 g were individually milled and homogenised, and 0.5 g were digested with aqua regia in a graphite heating block. The residue was diluted with deionised water (18 MΩ cm), mixed, and analysed using a Varian 725 instrument at ALS Minerals (Loughrea; method ID: ME-MS41). Results were corrected for spectral inter-element interferences from the sample matrix, solvent medium, and plasma gas. The limits of detection/resolution for elements of interest are shown in Supplementary Materials. Errors for whole rock for ICP-MS were calculated based on certified and achieved values for certified reference materials, shown in Table S3. Geological Certified Reference Materials (CRMs) utilised included MRGeo08 (mid-range multi-element CRM), GBM908-10 (base metal CRM), OGGeo08 (ore grade multi-element CRM), and GEOMS-03 (multi-element CRM). Results for CRM analysis were within the anticipated target range for each metal and standard. Duplicate analyses produced reported values within the acceptable range for laboratory duplicates, with an average relative percent difference of 4%.

Total organic carbon (TOC) and S contents were measured using a LECO CS225 elemental analyser to a precision of ±0.05%. Analyses were run concurrently with standards 501-024 (Leco Instruments, Saint Joseph, MI, USA; 3.23% ± 0.03% C, 0.047% ± 0.003% S, instrument uncertainty ±0.05% C, ±0.002% S) and BCS-CRM 362 (Bureau of Analysed Samples Ltd., Middlesbrough, UK, 1.48% S). The repeatability (based on 3 repeats of standards and blanks) of samples was consistently within 1%.

3.5. Water Chemistry

Four water samples (three acid mine drainage streams and one underground mine pool) were collected for water chemistry analysis. Sample collection was performed using acid-cleaned plastic bottles and stored at 4 °C in the dark before analyses. The samples were centrifuged for 5 min at 4500 rpm. A 10 mL supernatant was collected and spiked with 100 μL HNO_3 (70%, analytical reagent grade, Fisher Scientific, Hampton, NH, USA) and 100 μL H_2O_2 (32%, analytical reagent grade, Fisher Scientific) to reach a 1 wt % final concentration of H_2O_2 and HNO_3 in the solution. All the samples were analysed in triplicates. Analysis was performed by ICP-MS (7900, Agilent Technology, Santa Clara, CA, USA). Procedure parameters are presented in Table S4. Lense parameters were optimised daily by using a solution of 1 $\mu g \cdot L^{-1}$ of gallium, yttrium, thallium, and cerium to ensure the best detection limit. Hydrogen (3.5 mL min^{-1}) or Helium (4.3 mL min^{-1}) were used in the reaction cell to reduce the background and to remove possible interferences. Standards solutions were prepared at a concentration of 0, 0.05, 0.1, 1, 10, 50, and 100 $\mu g \cdot L^{-1}$ using multi-element standard solutions (VWR) and deionised water. Standards were used as external calibration for quantification. Germanium (20 $\mu g \cdot L^{-1}$) was added online as an internal standard during the entire analysis to correct the effect of possible instrument drift or fluctuations in the plasma. The analysis for sample Ochre 4 was repeated with a dilution factor of two to ensure that cobalt, cadmium, and nickel measurements fit in the calibration curve. As a quality control, the samples were spiked with a standard multi-elements solution to reach an addition of 10 $\mu g \cdot L^{-1}$ and a recovery was calculated between 90% and 110%. Water samples were also measured for acidity (pH level) using an electrode pH meter.

4. Results

4.1. Sample Descriptions

Massive sulphide bedrock deposits provide a source for Se, ore materials, and other trace elements in the region (Figure 4). In the ground immediately surrounding Parys Mountain, two waste materials were identified and widespread to a depth of 0.3 m: a smelt, identified as a red mud layer, and a weathered smelt, identified as a coarser red soil. The red mud and soil represent a processing residue from roasted ores, i.e., a smelted material (Figure 5). Partially lithified red mud smelts (RMS) represent solid raw waste material from sintering, refining, and beneficiation activities. The RMS is a heterogeneous fine fraction residue and contains quartz, Ti- and Al-oxides, pyrite, hematite, goethite and minor elemental S, baryte, galena, and sphalerite, identified by SEM. Deposits of RMS are typical of Al refineries (e.g., Bauxite red muds) but have been known to show affinities for As, Cu, and S mining wastes [38–41]. Coarser red weathering smelt soils (RWSS) are also typical in Cu mining wasteland areas [39,42,43], produced by weathering of smelt and bedrock. Parys Mountain RWSS contain more Fe oxides and pyrite than the RMS. Quartz and sandy components are retained in both RMS and RWSS, often with an altered appearance and numerous Fe oxide and pyrite inclusions. Iron oxides and elemental S are produced from the smelting of pyrite. Pyrite often shows an altered, weathered texture, and/or a rim comprising S, Si, Fe, and Al (identified using SEM-EDS). Other minor components of bedrock, soils, and smelts include gypsum, limonite, jarosite, monazite, sericite, and chlorite.

Standing pools of mine water (produced during extraction activity) are evident at the surface of Parys Mountain and also underground. Yellow soils and clays are thicker and more widespread, formed from natural weathering of the bedrock, unrelated to sintering, refining, and beneficiation activities. Yellow soils and clays contain quartz, pyrite, gypsum, limonite, jarosite, and monazite (SEM-EDS analysis). Mine drainage from the former workings are deposited in nearby natural stream systems, with precipitation of Fe(III) (oxy)hydroxides in drainage channels, resulting in yellow-orange ochre sediment deposits. Four ochre-bearing streams were sampled on Parys Mountain and the surrounding areas for ochre sediment and stream water (where present): a dried ochre deposit (Ochre 1—ochre sediment only), two ochre-bearing streams on the slopes to the north of former workings (Ochre 2 and Ochre 3), and an ochre-bearing stream on top of the former workings (Ochre 4) (Figure 2).

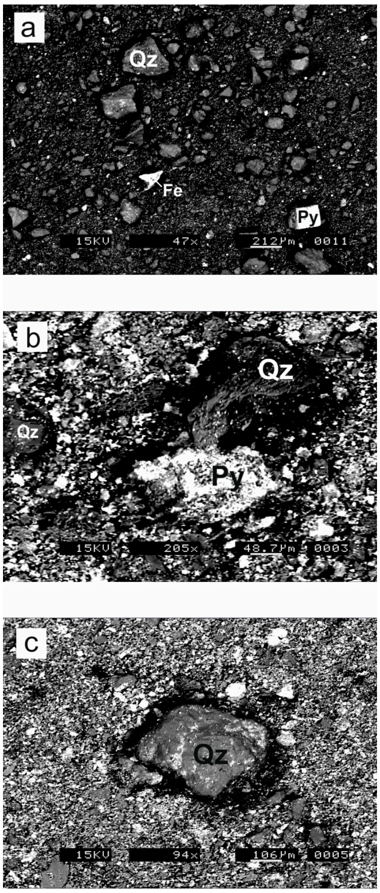

Figure 5. Microscopic (SEM) images of Parys Mountain mine waste red mud smelts (RMS) and red weathering smelt soils (RWSS). (**a**) Typical composition of RMS, including quartz (Qz), pyrite (Py), hematite, and goethite (Fe). (**b**) Red weathering smelt soil comprised of abundant Fe oxide minerals (bright), altered pyrite, and quartz. (**c**) Quartz with numerous Fe oxide inclusions in red weathering smelt soil.

4.2. Whole Rock and Sediment Geochemistry (ICP-AES and ICP-MS)

All results are shown in Tables S1 and S2. Both natural and smelt deposits are enriched compared to world average values [44–47] (Table S1; Figure 6), typically by 2–3 orders of magnitude. Overall, there is a general decrease in average concentrations of Co, S, and Te from the bedrock source to the final weathered products (Figure 7). Concentrations of Cu, Fe, Mo, Ni, and TOC increase from source to ochre sediments, while As and Cd vary across samples (Figure 7). There are high average concentrations of As, Bi, Hg, Mo, Pb, Sb, Se, and Te in weathered smelt materials. Excluding TOC, which is inherently enriched in weathered products due to vegetation and biological processes, the highest enrichment factor for any element is Pb in weathered smelt, which is enriched by a factor of 82.1 compared to the bedrock concentrations. Lead is enriched in all weathered products compared to the bedrock. Mercury and Sb are also highly enriched in weathered smelt (67.7 and 32.6 respectively) compared to the bedrock.

Sulphidic bedrock and RWSS show high Te levels (0.7–1.6 ppm), significantly enriched compared to the world average continental crust and soils. Both Se and Te are depleted by the stage where materials are weathered to soils and ochre sediments, but a notable portion remains throughout weathering. In RWSS, Se is higher than the bedrock, while much of the high Te concentrations are also retained from the bedrock but are relatively depleted in the weathering products. A comparison of Se and Te (Figure 8a) indicates a positive correlation, with some exceptions (RMS). In ochre sediments, Se is more variable, but Te is generally low.

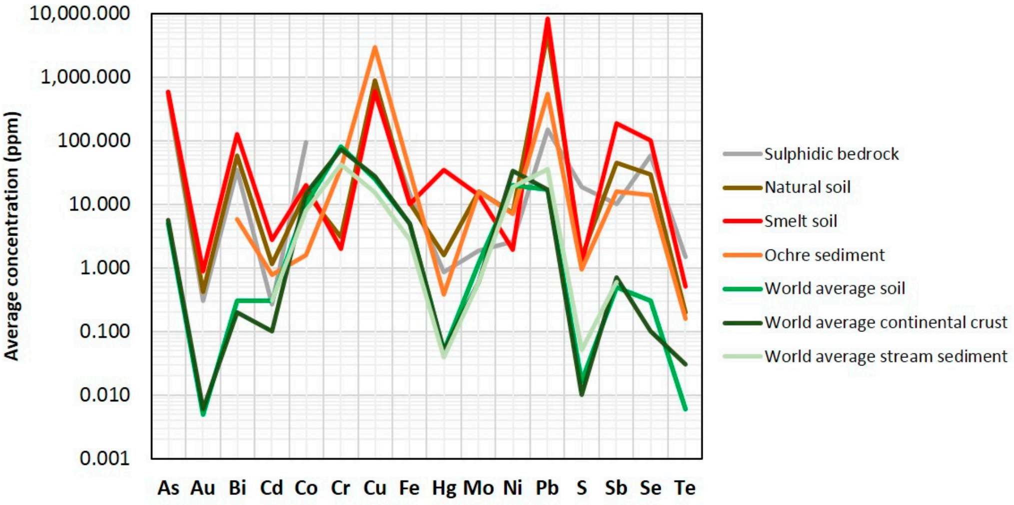

Figure 6. Enrichment of natural and mine waste Parys Mountain trace element concentrations compared to world average compositions. Error calculations for each element shown in Table S3.

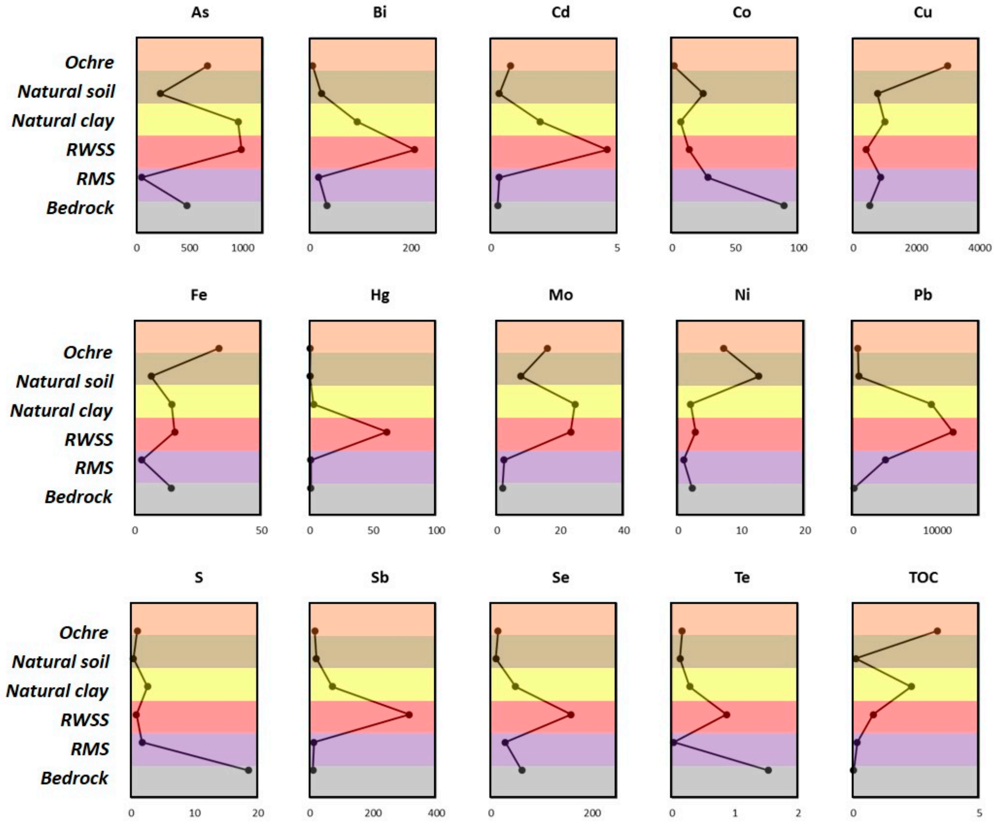

Figure 7. Profiles illustrating changes in concentration of trace elements from pyritic bedrock source to weathered smelts, natural soils/clays, and ochre sediments. Units as shown in Table S1.

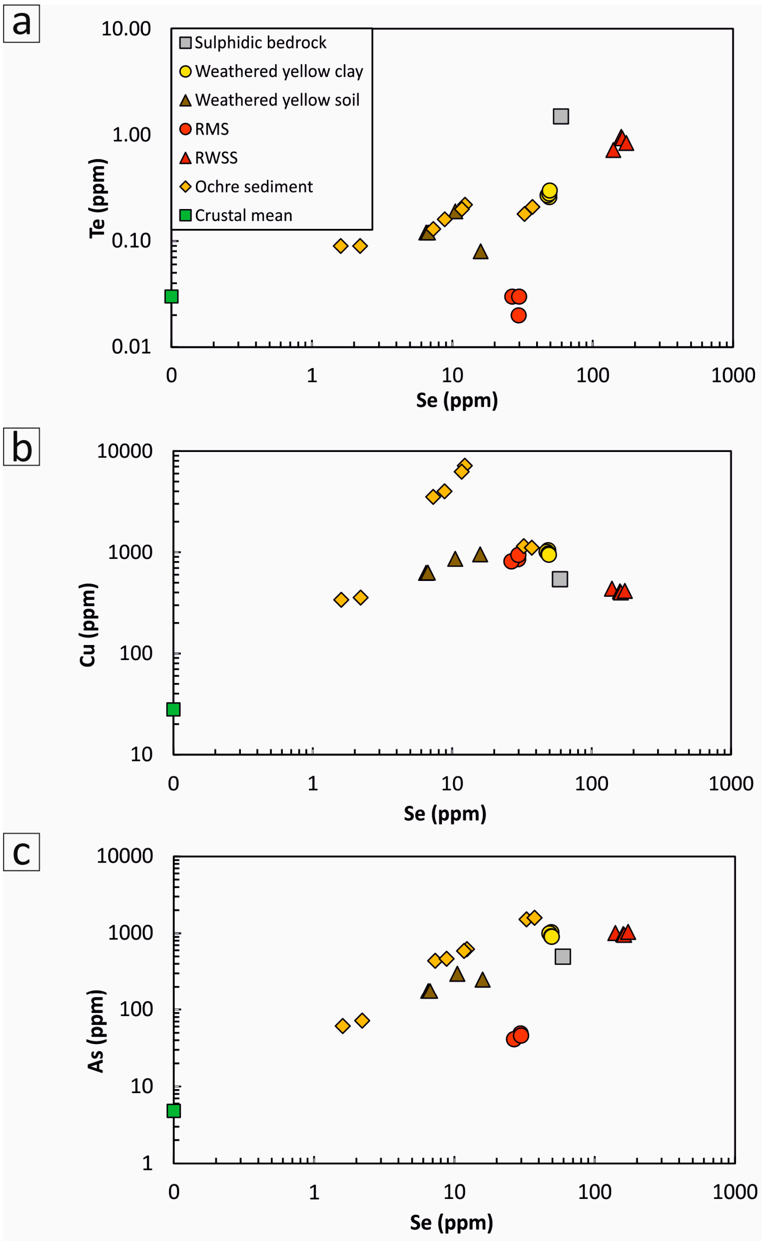

Figure 8. Cross-plots of Se vs. (**a**) Te; (**b**) Cu; and (**c**) As concentrations for all samples. Error calculations for each element shown in Table S3.

Sulphidic bedrock contains 0.3 ppm of Au. Across all samples, Au shows minor correlation with Se, Bi, Cd, and Hg (Figure 9). Correlation coefficients for all trace elements and statistical significance of Au correlation coefficients are shown in Table S5. There is also a strong correlation between S and Au (r correlation value of -0.82). Smelt samples show high Au content (up to 1.2 ppm), as well as natural yellow clays (0.4–0.5 ppm Au content). Ochre sediments and yellow soils do not host Au above level of detection. Given the presence of Au in whole rock, waste, and weathered samples, it is possible to identify potential Au pathfinder elements across Parys Mountain samples, as previous studies have shown that Se and Te can also act as Au pathfinder elements [48–53]. Figure 9 shows that Se, Bi, Cd, and Hg have a positive correlation with Au, and can act as pathfinder elements for Au in natural and waste soils and clays at Parys Mountain.

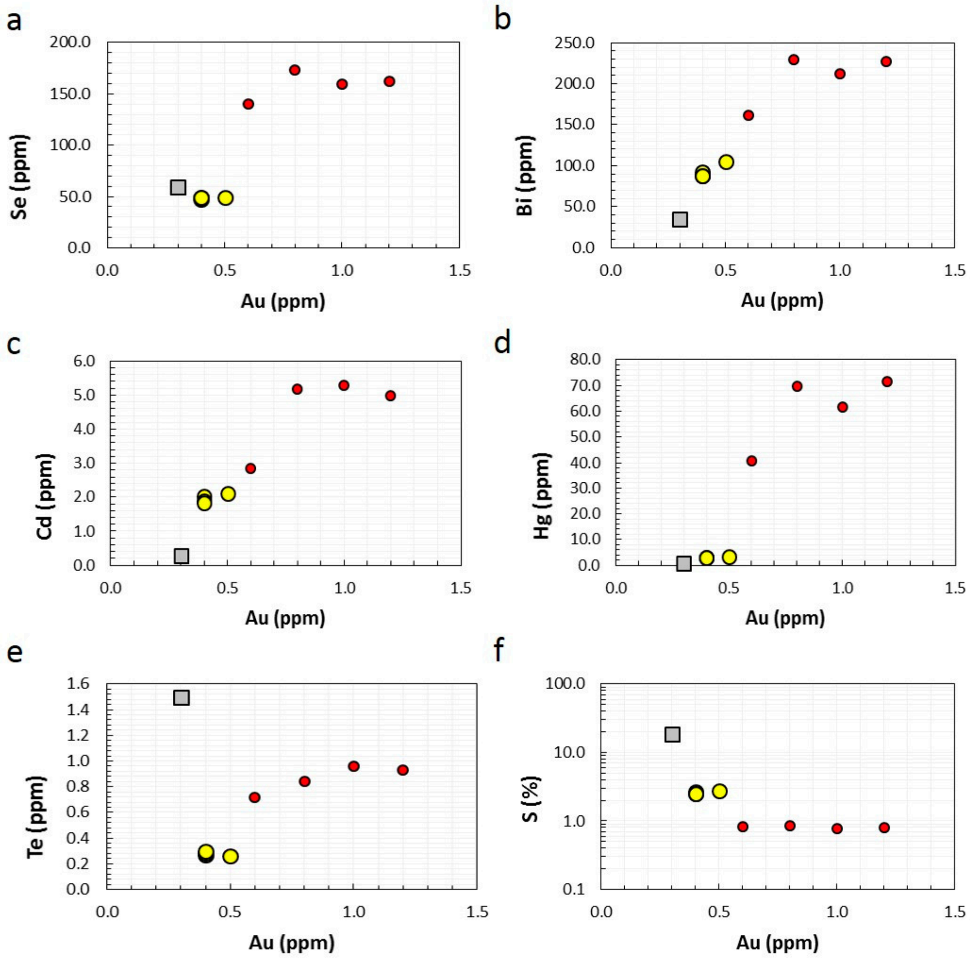

Figure 9. Cross-plots of Au vs. (**a**) Se; (**b**) Bi; (**c**) Cd; (d) Hg; (**e**) Te; and (**f**) S for all samples containing Au above LOD (symbol key from Figure 8). Correlation and statistical significance shown Table S5.

Highly sulphidic (up to 18.6%) and Fe-rich (14.7%) bedrock deposits are enriched in As (495 ppm), Bi (35 ppm), Cu (543 ppm), Pb (149 ppm), Se (60 ppm), and Te (1.5 ppm). Sulphur is higher in natural clays (2.5–2.8%), sediment from Ochre 4 (2.3–2.4%), and smelts (1.7–1.8%), while other samples are low in S (<0.8%). Waste deposits show enrichment of As, Bi, Cu, Sb, and Se compared to natural deposits and bedrock (Figure 6). Ochre sediments and RWSS show As concentrations up to 1590 ppm and 1040 ppm respectively. The RWSS samples show the highest Bi content of all deposits (up to 230 ppm), the highest Hg content (70 ppm), Pb (up to 1.5%), Sb (351 ppm), and Se (173 ppm). Trace elements Te, S, and Co are depleted from the bedrock to both natural and waste deposits. In ochre sediments, Fe, S, As, Bi, Hg, Mo, Sb, and Se decrease away from the bedrock, while Cu and Cr show a more sporadic spatial occurrence across ochre sediments, including higher concentrations away from the bedrock (Table S2). Conversely, Co is concentrated in the ochre sediments further away from the bedrock and former workings. Ochre sediments show the highest Cu content of all deposits, including concentrations higher than bedrock and smelts (up to 7140 ppm in Ochre 3).

4.3. Water Chemistry

Underground mine pool water shows an acidic pH of 2.3, with elevated trace element concentrations compared to the world average stream water trace element content [54] (Figure 10). Mine pool water shows an As content of 1113 $\mu g \cdot L^{-1}$, significantly enriched compared to an average stream water content of 2 $\mu g \cdot L^{-1}$ (Figures 10 and 11). Mine pool water also hosts enriched Cr (247 $\mu g \cdot L^{-1}$), Se (55.6 $\mu g \cdot L^{-1}$), and Ni (151 $\mu g \cdot L^{-1}$), and also retains minor Te content (0.19 $\mu g \cdot L^{-1}$).

Ochre 4 run-off waters show an acidic pH (2.5), while Ochres 2 and 3 show a more neutral pH (6.6 and 6 respectively). Trace element concentrations in these ochre-bearing stream water samples decrease away from Parys Mountain (Figure 11), with the exception of Pb which is higher in Ochre 3 (14.6 µg·L^{-1}).

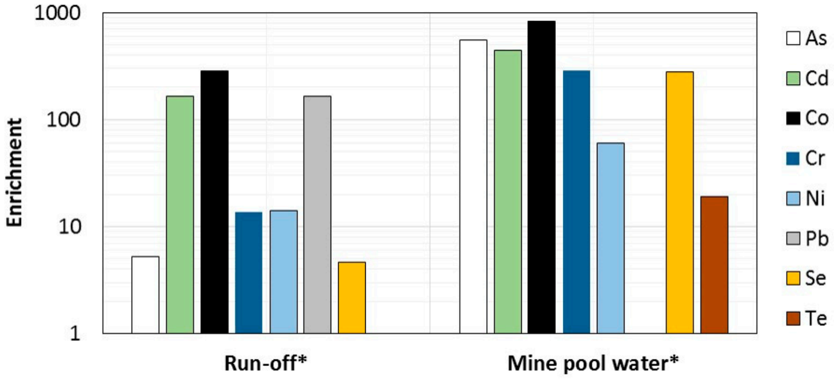

Figure 10. Trace element enrichment (*compared to world average stream water compositions) of ochre-bearing stream water (run-off) and underground (mine pool water) samples.

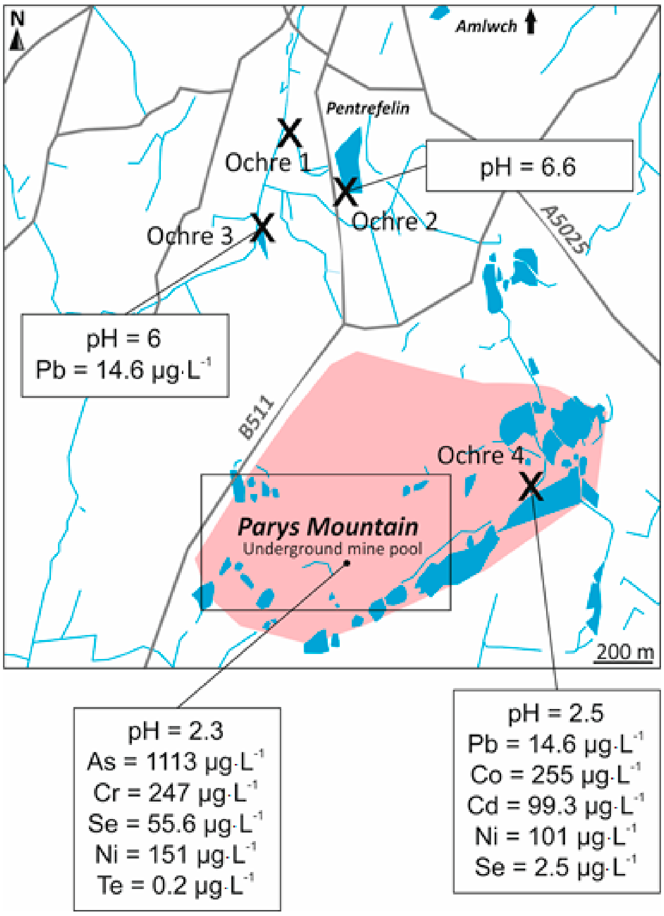

Figure 11. Water pH and select trace element concentrations at Parys Mountain underground mining pool water and ochre-bearing streams (Ochres 2, 3, and 4).

5. Discussion

5.1. Trace element Liberation and Fixation

Pyrite oxidation is considered the main source for polymetallic contamination and trace element enrichment in weathered sediments at Parys Mountain. Minor mineral phases in bedrock samples such as limonite, jarosite, and sericite may also be a source of Se, as well as Fe, S, Au, and Pb. Minor mineral phases may also be a source of trace elements, including gypsum (Cd, Cr), monazite (Pb, Au), and chlorite (Fe, No, Cu, Pb). However, due to their low abundance in the bedrock with respect to pyrite content, minor phases contribute smaller amounts of trace elements to natural and man-made deposits.

Oxidation of exposed pyrite can liberate trace elements [55–59] from the rapidly exhumed bedrock ore. The initial liberation and enrichment of all waste and natural deposits resulted from active pyrite oxidation, leaching, and release of trace elements, sulphates, and other heavy metals [60–62]. Notably high As, Bi, Hg, Mo, Pb, Sb, and Se in weathered smelt materials indicate that these represent a mine-related geochemical signature, directly related to the pyritic bedrock. Elements such as As, Cr, Se, Ni, Cd, and Pb are enriched in mine pool water and stream water samples, indicating that these elements are present in the form of water-soluble compounds and are readily liberated from the source. Acidic pH levels also promoted Cu, Pb, As, and Ni mobility [5–8], resulting in higher concentrations in weathered soils and ochre sediments at Parys Mountain. Elements which show low enrichment or an overall decrease in concentrations from bedrock source to weathered sediments (e.g., S, Co, and Te) were likely non-reactive and not liberated during oxidation and any processes of dissolution. More alkaline conditions (pH levels 7 or above) may increase Se concentrations in water, which contributes to the notable absence of Se in ochre sediments and run-off deposits compared to high-Se smelts. Selenate (Se IV), the most mobile form of Se that can be leached to groundwaters, is unlikely to migrate to deeper groundwaters underlying acidic soils [63], which may also explain the concentrated distribution of Se at Parys Mountain.

High concentrations of trace elements in RWSS may be related to the close proximity to the bedrock source (i.e., elements with a low mobility), with more mobile elements accumulating in more distal ochre sediments. High concentrations of a number of trace elements in RWSS (As, Bi, Cd, Hg, Mo, Pb, Sb, Se, and Te) and ochre sediments (As, Cu, Fe, and Mo) may also be related to the changes in mineralogy of the deposit types, with adsorption and fixation of trace elements related to Fe-oxide minerals. The RWSS show the highest abundance of Fe-oxide mineral phases, while ochre sediments contain abundant orange-brown Fe(III) (oxy)hydroxides, indicating the oxidising conditions of both environments. Sorption of trace elements onto Fe(III) (oxy)hydroxides is a potentially important control on the transport and attenuation of (hydr)oxyanion forming elements, and can act as a sink for elements such as Se, As, Ni, and Sb [64–66]. Retention of trace elements on Fe oxides may be possible due to immobilisation processes, with trace elements strongly adsorbed by Fe oxides. This retention has been previously identified with goethite over the entire pH range and by magnetite in the neutral-to-alkaline range [67–69]. Ochre-bearing streams at Parys Mountain exhibit pH ranges from acidic to neutral, and both goethite and magnetite have been identified in weathered soils and clays. Therefore, weathered materials containing abundant Fe oxides act as a sink for trace elements, resulting in trace element enrichment compared to the source and other sediments containing lower abundances of Fe oxides. As ochre deposits are made up of almost entirely Fe(III) (oxy)hydroxide precipitate phases, the whole rock results of ochre sediments give an indication of the magnitude of adsorption and fixation of trace elements by Fe oxides. As well as Fe and Se, results in Figure 7 and Table S2 also suggest a strong fixation of As, Cd, Cu, Mo, Ni, Pb, and Sb in Fe oxides.

5.2. Economic Considerations

Parys Mountain is still an actively licensed mining site, and several surveys have been made on the tonnage potential and resource grade on the bedrock in the area since the 1980s. Anglesey Mining estimated a geological resource of 6.5 million tonnes, with 2.15 million tonnes containing 0.36% Cu, 2.11% Pb, and 0.42 g/t Au [19,20,70]. Results from this study suggest that there may be potentially economic resources in the weathered products from the bedrock, both in the RWSS and the ochre sediments. The area in the immediate vicinity of the previously worked Parys Mountain Great Opencast and Mona mines shows expansive areas of RWSS, streams, and ochre sediments. These weathered deposits contain concentrations of trace elements above the lowest cut-off grades utilised by recent and ongoing mining operations worldwide [71–78]. Adopting the lowest cut-off grades from recent ore mining projects [71–77], for a workable area of 0.556 km^3 surrounding the former mines, with a depth of 0.3 m and topsoil density of 1.2 tonnes/m^3, some conservative estimates of resource potential of Se and other resources in RWSS have been calculated. Cobalt, Sb, and Te resource estimates are not given at Parys Mountain due to their lower than cut-off level abundance. These calculations indicate that there is a potential 45 tonnes of Se in the RWSS. However, the average Se content of 158.6 ppm in these deposits is below the lowest Se cut-off grade of 400 ppm [78]. While this suggests that extraction of Se at Parys Mountain is not feasible, the elevated concentrations of Se in smelts may highlight the potential for economic reserves in similar base metal mining sites around the world, particularly VMS-hosted deposits and weathered sulphidic orebodies. It is also vital to record these estimates for future consideration, as the demand for these elements is expected to increase [10–16] and cut-off grades may alter accordingly.

Parys Mountain hosts potentially economic Au deposits. There are several examples of recent and ongoing Au mining projects that operate assuming a cut-off grade of 0.2 to 0.4 g/t [19,20,70]. Previously reported grades of Au at Parys Mountain include the aforementioned estimates of 0.3 to 0.42 g/t [19,20]. The sulphidic bedrock samples measured here agree with these estimations of Au content (0.3 ppm), while natural yellow soils, RMS, and ochre sediments do not show Au levels above detection limit. However, natural yellow clays show Au content up to 0.5 ppm, and RWSS show Au concentrations of up to 1.2 ppm. These results indicate that Au content at Parys Mountain may be higher than previously thought and, in RWSS, there could be a potentially untapped source and target. Selenium can act as a pathfinder element in Au exploration worldwide in selenide-containing epithermal Au–Ag and massive sulphide deposits [49,51,52,79]. Tellurium can also fix Au in telluride-bearing Au ore deposits in a range of settings [51,53,79]. Both Se and Te correlate with Au at Parys Mountain, as well as other elements typically associated with Au such as Pb, Ni, Sb, Hg, Bi, and Cd, indicating that these trace elements can act as Au pathfinders at Parys Mountain. The Au concentrations of 0.3 to 1.2 ppm indicate a potentially higher Au grade in other similar areas of Parys Mountain, which are yet to be investigated. Resource calculations here show that Parys Mountain RWSS contain a potential 0.26 tonnes of Au.

Other elements that show concentrations higher than typical cut-off grades include Pb in RWSS, with an average of 1.18% in Parys Mountain RWSS compared to a cut-off grade of 1% [77], and Cu and Fe in ochre sediments (Cu = 0.29% average concentration in ochre sediments compared to a cut-off value of 0.15% [76], and Fe = 33.32% average concentration in ochre sediments compared to a cut-off value of 27.78% [74]). Resource estimate for Pb in RWSS is 3346 tonnes. However, estimates of workable ochre sediment tonnage are difficult to define. Very modest estimates based on stream area calculations in close proximity to the Parys Mountain site (Figure 2 streams only; not including standing water bodies) and a potential sediment depth of up to 0.1 m give 1.83 tonnes of Cu or, more significantly, 211 tonnes of Fe in stream ochre sediments. Hyper concentrated mine pools and ochre-bearing streams at Parys Mountain could also be used in sewage treatment as flocculating agents, similar to projects from Buxton colliery, Derbyshire, UK, and Falun Cu mine complex, Sweden [62], and the high Fe ochre sediment content could potentially be harvested from the contaminated stream sediments and mine waters. This has been achieved at the Marchand Mine project, Pennsylvania, where Fe sludge has been removed and recovered from the contaminated Sewickley Creek and the Youghiogheny River for use as a crude pigment [80].

5.3. Environmental Implications

All the discussed trace elements with the exception of Cr and Ni show concentrations above the world averages in continental crust, soils, stream sediments, and stream waters. In some cases, concentrations are 2–3 orders of magnitude higher than world averages. This is to be anticipated in an area of such extensive historic former workings, and what is essentially still a working mining site. However, the high and seemingly mobile Se and other trace element contents in sediment and water should be monitored as the area has numerous interconnected streams, rivers, and water bodies, connecting to more extensive water systems on Anglesey leading to Amlwch and the sea, as well as local rural communities and agricultural land.

Results and observations indicate that the main source of pollution at Parys Mountain is subaerial mine-waste tips, with their high content of sulphide minerals. A well-known concern to former and operational mining sites worldwide is contamination of soils and groundwaters from Se, particularly in U mining sites [11,81,82]. The release of Se during extraction can have environmental ramifications, affecting livestock [3,4,7,10,83–85]. Elevated water-soluble trace elements such as Cd, Co, Cu and Pb at Parys Mountain are also typically higher than previously determined maximum permitted levels by various studies and governing bodies [86,87]. Compositionally similar and extensively extracted base metal sulphide ore deposits in Norway have been classified as "significantly" or "highly" polluted as a result of mining activities releasing Cu, Zn, Fe, Pb, and Cd [62,88,89]. The soil guideline values [90] for inorganic As is 640 ppm for commercial land use, and levels for residential and allotment land use is lower. Parys Mountain deposits show consistently higher concentrations of As across deposits than the guideline values. Similarly, Parys Mountain shows higher concentrations of Hg than the soil guideline levels of 26 ppm.

In former mine workings across Europe, including sites associated with sulphide mineralisation, technosols have been developed and utilised in order to reduce the threat of contamination posed by tailings [1,90,91]. Technosols are man-made soils, often made up of stock materials such as carbonates, biochars, and crop residues, and have been shown to reduce acidity, immobilise metals, and improve soil quality, fertility, and structure. This can result in increased microbial biomass activity and development of vegetation. These factors have helped to decrease the hazards for human health and the environment in the affected areas. Due to the high abundance of Cu-Pb across Parys Mountain deposits, these two elements should be monitored, along with other enriched and potentially harmful trace elements such as Se, Hg, Cd, and Mo.

6. Conclusions

Natural deposits and former site workings at Parys Mountain host enriched concentrations of critical trace elements such as Se. A number of trace elements are enriched and retained across samples from natural sources and weathered soil or clay products, to smelts, ochre sediments, and water bodies. Iron oxide-rich waste deposits are more enriched in Se and other trace elements than natural deposits. Selenium and other elements have been mobilised from the pyrite in the bedrock source and retained in high concentrations in Fe oxide-rich RWSS, weathered soils, and ochre sediments. Selenium correlates with the enrichment of other trace elements, including Te, Au, Bi, Cd, Hg, Pb, S, and Sb. Parys Mountain also hosts potentially economic Au deposits, and Se (as well as Te, Pb, Ni, Sb, Hg, Bi, and Cd) can be used as geochemical pathfinder elements for Au enrichment in the area. There are also potentially economic Cu and Pb reserves in weathered materials. Potentially toxic amounts of As, Se, Pb, Cd, and Cu have been identified in some Parys Mountain deposits, and should continue to be monitored as contaminants in local soil and groundwater systems.

Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/7/11/229/s1, Table S1: Trace element content of natural bedrock, soils, and water run-off at Parys Mountain mining district. World average soil, crust, stream sediment, and stream water compositions also shown (Salminen et al. [46] and references therein); Table S2: Trace element concentrations of mine waste smelt deposits, ochre sediments, and mine water associated with the Parys Mountain mining district; Table S3: Calculated error for whole rock

(rock, sediments, soils) for inductively couple plasma-mass spectrometry (ICP-MS), based on certified and achieved values for certified reference materials; Table S4: ICP-MS instrument settings used for water sample analysis, Table S5: Correlation coefficients for all trace elements, and significance of a correlation coefficient (determined by *t*-test confidence level of linear relationships in Microsoft Excel) between Au vs. Bi, Cd, Hg, Ni, Pb, S, Se, and Te. Statistically significant correlation coefficients: $p < 0.05$.

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