Let me say from the start, I am not categorically opposed to mining, I am however categorically opposed to the type of mining that is proposed by this foreign entity.

I also must state from the beginning that I am not opposed or hold no negative opinions of Canadians but for the sake of clarity we need to note that this is a Canadian company unlike what they appear to represent in their name.

I think it is important to note that the company named "US copper" was previously named "Crown Gold". This name change occurred around the time President Biden announced his new green deal. See Appendix D. The PEA a 235 page document submitted in my previous public comments was produced by this foreign entity and contains the expected production of 21 million oz. of gold and 221 million ounces of silver, which I believe to be the primary purpose for this mine. In other words this is green washing. Copper is not considered a critical resource by the USGS see Appendix B and C. According to the PEA this mine will be arguably the largest open pit mine in the U.S.
93% of open pit mines leak into groundwater resulting in significant water quality impacts, see Appendix E and F.
After these mines are decommissioned they continue to pollute for thousands of years, see Appendix G.
According to the PEA the foreign entity plans to dam up Moonlight Valley to create toxic waste lakes, let that sink in for a sec.
This will be a superfund site like in Shasta county.
This hardly seems like a fair trade for 17 years of mining (See PEA report), that will not significantly benefit the local economy and will negatively impact tourism.

Historically the properties in question have been an underground mining operation, not a surface mining operation.

I am heartened that Plumas county is retaining counsel to inform themselves about the issue at hand.

I encourage all parties to read the PEA report to get a clear understanding of what this mine project really looks like, they are talking about processing 60,000 tons of material a day.

The decisions made here about this issue will reverberate for thousands of years.

A group of concerned citizens of which I am a part has retained retained legal counsel so that we can understand several legal questions and should it be needed represent us moving forward.

We look forward to working together with the county on this issue.

Appendix A

Article 15. Vested Rights Determination

§ 3950. Pursuant to Public Resources Code Sections 2774.4 or 2774.5, where the board exercises and/or assumes some or all of the lead agency's powers, the board shall not conduct vested rights determinations.~~Purpose of Regulations. No person who has obtained a vested right to conduct surface mining operations prior to January 1, 1976 shall be required to secure a permit pursuant to Section 2770 of the Public Resources Code. Any person claiming a vested right to conduct surface mining operations in a jurisdiction where the State Mining and Geology Board (the Board) is lead agency pursuant to section 2774.4 of the Public Resources Code must establish such claim in a public proceeding under this article. In such a proceeding the Claimant shall assume the burden of proof.~~

NOTE

Authority: Sections 2755 ~~and 2775~~, Public Resources Code. Reference: 2774.4 and 2774.5, Public Resources Code.~~Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.~~

~~**§ 3951.** Vested Right(s) - Definition. A "vested right" is the right to conduct a legal nonconforming use of real property if that right existed lawfully before a zoning or other land use restriction became effective and the use is not in conformity with that restriction when it continues thereafter. A vested mining right, in the surface mining context, may include but shall not be limited to: the area of mine operations, the depth of mine operations, the nature of mining activity, the nature of material extracted, and the quantity of material available for extraction. A person shall be deemed to have a vested right or rights to conduct surface mining operations if, prior to January 1, 1976, the person has, in good faith and in reliance upon a permit or other authorization, if the permit or other authorization was required, diligently commenced surface mining operations and incurred substantial liabilities for work and materials necessary for the surface mining operations. Expenses incurred in obtaining the enactment of an ordinance in relation to a particular operation or the issuance of a permit shall not be deemed liabilities for work or materials. Expansion of surface mining operations after January 1, 1976 may be recognized as a vested nonconforming use under the doctrine of "diminishing assets" as set forth in *Hansen Brothers Enterprises, Inc. v. Board of Supervisors* (1996) 12 Cal.4th 533.~~

~~*NOTE*~~

~~*Authority: Sections 2755, 2776 and 2775, Public Resources Code; Hansen Brothers Enterprises, Inc. v. Board of Supervisors (1996) 12 Cal.4th 533.) Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.*~~

~~**§ 3952** Filing of Request for Determination. A claim of vested rights shall be initiated by filing a Request for Determination with the Board. At a minimum the Request for Determination shall include the following information:~~

~~(1) Name, address, and telephone number (and name, address, and telephone number of any agent for contact or service of notice, if different) of Claimant;~~

~~(2) Name, address, and telephone number of the property owner(s) if different than (1) above;~~

~~(3) Name, address, and telephone number of any lessee, lien holder, or other potential claimant to the vested right(s) asserted;~~

~~(4) A map indicating the exact location of the property upon which vested rights are asserted;~~

~~(5) A legal description of such property including township and range, metes and bounds, parcel numbers, or other descriptive methods to specifically identify such property;~~

~~(6) Copies of all documents which Claimant asserts establish title to such property;~~

~~(7) Written statements, with supporting documentation, indicating the basis for claim of a vested right to conduct surface mining operations upon such property;~~

~~(8) Written statements, with supporting documentation, identifying the scope or scale of the vested right claimed;~~

§ 3955 Notice of Pending Determination.
Within 30 business days after the Chairman of the Board, or the Chairman's designee, concludes that the Request for Determination is within the Board's jurisdiction and contains the minimum information required by Section 3952 a notice of pending vested rights determination shall be mailed by the executive officer of the Board to every adjacent landowner identified in the Request for Determination and to the county, city, or regional agency originally holding lead agency status for the identified property and mining operation. A notice of pending vested rights determination shall also be provided to the person claiming vested rights for posting, within 5 days of receipt, upon the property in question in an open and conspicuous place that is reasonably visible to the public and at all points of entry to the property. The notice of pending vested rights determination shall identify the specific property upon which such vested rights are asserted and shall identify the Board as the agency which will be making the determination. The notice shall contain the Board's mailing and electronic addresses and a request that comments be forwarded to the Board. The notice shall remain posted as required through the conclusion of any hearing on the vested rights claim. The notice shall also be immediately noticed and placed on the Board's electronic website. Where the Board determines that additional notice is required, it may require the person claiming vested rights to provide such additional notice.
NOTE
Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

§ 3956 Public Hearing. No vested rights determination will be made by the Board without a public hearing and an opportunity for the vested rights claimant, the original lead agency, and the public to comment.
NOTE
Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

§ 3957 Selection of Hearing Officer. The Board may delegate conduct of a vested rights public hearing to a committee of at least two Board members to be appointed for that hearing by the Chairman of the Board. The Board may also delegate conduct of a vested rights public hearing to an administrative hearing officer or special master. As soon as practicable after the Chairman, or the Chairman's designee, concludes that the Request for Determination is within the Board's jurisdiction and contains the minimum information required by Section 3952, and in no event more than 45 business days from such conclusion, the Board, or a designee of the Board shall decide whether a vested rights public hearing will be conducted by the Board, a committee of the Board, an administrative hearing officer selected by the Board, or a special master selected by the Board.
NOTE
Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

§ 3958 Vested Rights Hearing – Schedule. The Board, its delegated committee, administrative hearing officer or special master shall schedule and hold a public hearing on a vested rights determination no less than 90 business days after the notice of pending vested rights determination was mailed pursuant to Section 3955. In no case shall the hearing be scheduled more than 180 business days after the Chairman, or the Chairman's designee, concludes that the Request for Determination is within the Board's jurisdiction and contains the minimum information required by Section 3952 unless such hearing schedule is agreed to by the party claiming vested rights. The hearing scheduled may be within the county where the vested right is claimed or within the county of the Board's offices (County of Sacramento).
NOTE
Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

NOTE

Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

§ 3962 Vested Rights Hearing Procedure - Continuance. The public hearing may be continued from day to day as necessary to receive all of the statements, information, and testimony identified in Section 3961.

NOTE

Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

§ 3963 Vested Rights Hearing Procedure - Evidence.

Relevant evidence in a proceeding for determination of a claim of vested rights shall be written or oral evidentiary statements or material demonstrating or delimiting the existence, nature and scope of the claimed vested right[s]. Such evidence shall include, but is not limited to, evidence of any permit or authorization to conduct mining operation on the property in question prior to January 1, 1976, evidence of mining activity commenced or pursued pursuant to such permit or authorization, and evidence of any zoning or land use restrictions applicable to the property in question prior to January 1, 1976. As to any land for which Claimant asserts a vested right for expansion of operations, Claimant shall produce evidence demonstrating that the Claimant clearly intended to expand into such areas. Such evidence shall be measured by objective manifestations, and not subjective intent at the time of passage of the law, or laws, affecting Claimant's right to continue surface mining operations without a permit.

NOTE

Authority: Sections 2755 and 2775, Public Resources Code. (See, *Hansen Brothers Enterprises, Inc. v. Board of Supervisors* (1996) 12 Cal.4th 533.) *Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.*

§ 3964 Vested Rights Hearing Procedure - Determination.

Following the public hearing, the Board, if the Board conducted the hearing, or its committee, administrative hearing officer, or special master shall determine whether the Claimant, by a preponderance of the evidence, has demonstrated a claim for vested rights pursuant to Public Resources Code Section 2776. The determination shall identify upon what specific property the vested rights are established and the scope and nature of surface mining operations included within the established vested right or rights. If the public hearing was conducted by a committee of the Board or an administrative hearing officer or special master designated by the Board, the findings and recommendation or proposed decision of the committee of the Board, administrative hearing officer, or special master shall be presented to a quorum of the Board at a regular business meeting, no later than 60 business days after completion of the vested rights public hearing, for consideration and adoption by the full Board. The Board may adopt the recommendation or proposed decision or reject the recommendation or proposed decision and direct the matter back to its delegee for further consideration in light of the discussion before the full Board. The Board may also modify the proposed decision based upon the record before it or make an alternative determination based upon the record or following receipt of additional evidence before the full Board. Following adoption of the Board's final determination notification shall be made by certified mail to the party claiming vested rights and to the local agency originally holding lead agency status. Notification of the final determination of the Board shall also be made by regular mail to any person who commented at, or participated in, the public hearing, any person who has requested such notice, and shall be immediately posted upon the Board's website.

NOTE

Authority: Sections 2755 and 2775, Public Resources Code. Reference: Calvert v. County of Yuba, (2007) 145 Cal. App. 4th 613.

Article 16. Mining Ordinances

§ 4000. Certification and Recertification of Mining Ordinances.

(a) Upon adoption of a new mining ordinance, or amendment of an existing mining ordinance, a lead agency shall, within 30 days of such action, provide written notice of the complete text of the resulting mining ordinance to the State Mining and Geology Board, to enable the Board to review the ordinance in accordance with Public Resources Code Sections 2774.3, 2774.5(a) and 2774.5(b).

(b) Where a lead agency has not provided the Board with timely notice of the complete text of its mining ordinance, consistent with subparagraph (a) herein, the mining ordinance shall not be considered to be in accordance with state policy until the mining ordinance is certified by the Board as being in accordance with state policy.

(c) In any jurisdiction in which the lead agency does not have a certified mining ordinance, the board assumes full authority of all lead agency's powers under Public Resources Code Sections 2710-2796 and Public Resources Code Section 2207 for all surface mining operations until the time the board certifies a lead agency's mining ordinance. Nothing in this section shall be construed as authorizing the board to issue a permit for the conduct of mining operations or issue vested rights determinations.

(d) Notwithstanding subsection (c) of this Article, lead agencies with previously certified mining ordinances retain lead agency authority while the board conducts a review of the amended ordinance pursuant to Public Resources Code Sections 2774.3, 2774.5(a) and 2774.5(b).

NOTE

Authority cited: Section 2755, Public Resources Code. Reference: Sections 2756, 2758, 2759, 2774.3, and 2774.5~~(a), 2774.5(b) and 2774.5(c),~~ Public Resources Code.

HISTORY

1. New article 16 (section 4000) and section filed 1-13-2014; operative 4-1-2014 (Register 2014, No. 3

USGS rejects push to make copper a 'critical' mineral

By Hannah Northey | 05/23/2023 04:25 PM EDT

Copper rods used to machine parts are stacked on a shelf at Makerite Manufacturing in Roscoe, Ill., in 2019. Getty Images

The U.S. Geological Survey is rebuffing bipartisan calls from lawmakers to add copper to its list of critical minerals, a classification that's catapulted in importance as the nation races to compete with China on development of renewable energy technology and boost electric vehicle adoption.

David Applegate, who directs the USGS, told Sen. Kyrsten Sinema (I-Ariz.) in an April 13 letter (https://subscriber.politicopro.com/eenews/f/eenews/?id=00000188-4953-d998-ab8f-fb5f223b0000) and Republican Rep. Bob Latta of Ohio on May 1 (https://subscriber.politicopro.com/eenews/f/eenews/?id=00000188-4952-d998-ab8f-fb5f8eb00000) that vulnerabilities in the nation's copper supplies are reduced by domestic resources, trade deals and other supplies.

"While copper is clearly an essential mineral commodity, its supply chain vulnerabilities are mitigated by domestic capacity, trade with reliable partners, and significant secondary capacity," Applegate wrote in the letters. "As a result, the USGS does not believe that the available information on copper supply and demand justifies an out-of-cycle addition to the list at this time."

Sinema did not immediately respond when asked for comment, but Craig Wheeler, a spokesperson for Latta, said there's still bipartisan, bicameral support for designating copper as critical and significant data that highlights the benefits for the U.S.

"The congressman continues to believe that it's within the secretary's power to acknowledge this reality and designate copper as a critical mineral," said Wheeler.

The congressional push over the status of copper highlights how much is at stake in the rush to source up and incentivize development of supply chains to feed EV production and clean energy technology. Should copper be labeled "critical," projects aime[d] at mining and processing the material could potentially be prioritized by the federal government and benefit from laws like the

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Appendix C

NATIONAL NEWS RELEASE

U.S. Geological Survey Releases 2022 List of Criti Minerals

By **Communications and Publishing**

February 22, 2022

and current policy priorities.

"Mineral criticality is not static, but changes over time," said Steven M. Fortier, USGS National Minerals Information Center director. "The 2022 list of critical minerals was created using the most recent available data for non-fuel mineral commodities. However, we're always analyzing mineral markets and developing new methods to determine the various and evolving critical mineral supply chain risks."

Prior to publishing the 2022 list of critical minerals, the USGS completed a thorough review of more than 1,000 comments received from the public, stakeholders and local and state officials. These comments were received in response to the draft critical minerals list the USGS released for public comment in November 2021.

"The USGS appreciates the input we received from the public and stakeholders," Fortier said. "In addition to reviewing each comment for the current methodology, we are also identifying opportunities to include some of the suggestions we received in the next update of the critical minerals list methodology."

The list of critical minerals will be the focus of USGS research quantifying critical mineral potential within the U.S. In President Biden's Bipartisan Infrastructure Law, the USGS received funding for its Earth Mapping Resource Initiative, which will update the Nation's mapping of these minerals, including those still in the ground and those present in mine wastes.

The Energy Act of 2020 directed the USGS to update the list of critical minerals, and the list is timely to provide guidance for use of the Bipartisan Infrastructure Law funds, both for the USGS and other agencies.

The 2022 list of critical minerals includes the following — click a mineral's name to find relevant statistics and publications:

- Aluminum, used in almost all sectors of the economy
- Antimony, used in lead-acid batteries and flame retardants
- Arsenic, used in semi-conductors
- Barite, used in hydrocarbon production.
- Beryllium, used as an alloying agent in aerospace and defense industries

- Nickel, used to make stainless steel, superalloys, and rechargeable batteries
- Niobium, used mostly in steel and superalloys
- Palladium, used in catalytic converters and as a catalyst agent
- Platinum, used in catalytic converters
- Praseodymium, used in permanent magnets, batteries, aerospace alloys, ceramics, and colorants
- Rhodium, used in catalytic converters, electrical components, and as a catalyst
- Rubidium, used for research and development in electronics
- Ruthenium, used as catalysts, as well as electrical contacts and chip resistors in computers
- Samarium, used in permanent magnets, as an absorber in nuclear reactors, and in cancer treatments
- Scandium, used for alloys, ceramics, and fuel cells
- Tantalum, used in electronic components, mostly capacitors and in superalloys
- Tellurium, used in solar cells, thermoelectric devices, and as alloying additive
- Terbium, used in permanent magnets, fiber optics, lasers, and solid-state devices
- Thulium, used in various metal alloys and in lasers
- Tin, used as protective coatings and alloys for steel
- Titanium, used as a white pigment or metal alloys
- Tungsten, primarily used to make wear-resistant metals
- Vanadium, primarily used as alloying agent for iron and steel
- Ytterbium, used for catalysts, scintillometers, lasers, and metallurgy
- Yttrium, used for ceramic, catalysts, lasers, metallurgy, and phosphors
- Zinc, primarily used in metallurgy to produce galvanized steel
- Zirconium, used in the high-temperature ceramics and corrosion-resistant alloys.

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COMPANY HISTORY

2018

- The Moonlight property option was exercised and fully paid for in March.
- The PEA on the Moonlight deposit was filed on SEDAR in April.

2019

- Crown prepared drill program to define oxide resource at Moonlight.

2020

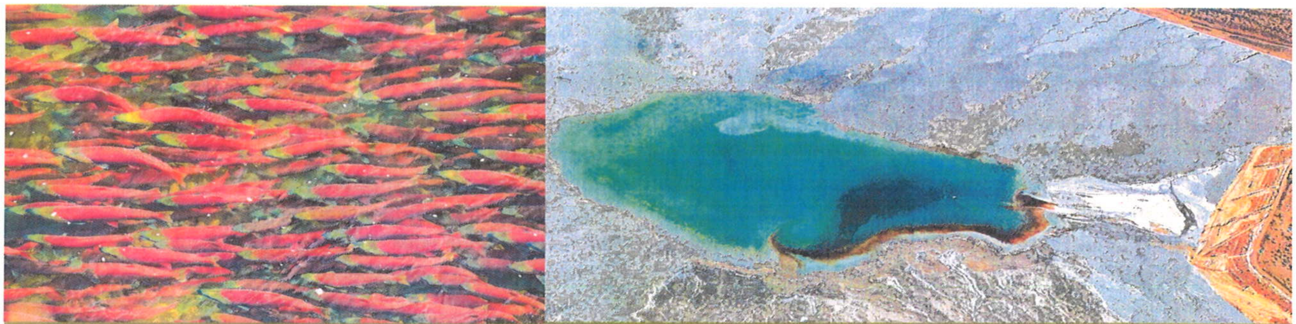
- Crown prepared drill program at Superior to identify silver and gold credits.

2021

- Company announces name change to US Copper Corp.
- US Copper to undertake drill program of 7 holes at Superior and Engels.

Appendix D

Appendix E



U.S. OPERATING COPPER MINES:

FAILURE TO CAPTURE & TREAT WASTEWATER

BY BONNIE GESTRING, MAY 2019

In 2012, Earthworks released a report documenting the failure to capture and treat mine wastewater at U.S. operating copper mines accounting for 89% of U.S. copper production.[1] The report found that 92% failed to capture and control mine wastewater, resulting in significant water quality impacts. This is an update to that effort. We reviewed government and industry documents for fifteen operating open-pit copper mines, representing 99% of U.S. copper production in 2015 – the most recent data on copper production available from the U.S. Geological Survey (see Table 1). **Our research found similar results: 14 out of 15 (93%) failed to capture and control wastewater, resulting in significant water quality impacts (see Table 2).** These unauthorized wastewater releases occurred from a number of different sources including uncontrolled seepage from tailings impoundments, waste rock piles, open pits, or other mine facilities, or failure of water treatment facilities, pipeline failures or other accidental releases.

TABLE 1:
Copper production from top 15 (as of 2015) U.S. open-pit copper mines (most recent data available from USGS).[2]

MINE	PRODUCTION (metric tons)
Morenci	481,000
Chino	142,000
Safford	91,600
Bagdad	95,300
Bingham Canyon	92,000
Sierrita	85,700
Ray	75,100
Pinto Valley	60,400
Mission Complex	68,300
Robinson	56,800
Tyrone	38,100
Continental pit	31,000
Phoenix	21,100
Miami	19,500
Silver Bell	19,300
Total (99% of U.S. production)	**1,377,000**
U.S. Total Copper Production	**1,380,000**

EARTHWORKS

MINE	DOCUMENTATION OF WASTEWATER CAPTURE AND TREATMENT FAILURE
Chino (cont'd)	the main pit. In the South Mine area, groundwater has exceeded standards for manganese and cadmium at Middle Whitewater Creek, Hurley and Lake One, and has exceeded standards for copper at Lake One. A 2012 assessment of groundwater impacts concluded that contaminated seepage from the mine will require water treatment in perpetuity.[14] In 2009, the State of New Mexico reached a settlement of $279,000 with the Chino Mine after the release of one million gallons of process solution that overflowed a containment sump and travelled more than 2 ½ miles down a surface water tributary near the mine in 2007.[15]A 2003 ecological risk assessment reported elevated concentrations of the hazardous substances copper and zinc in surface water from five different drainages at the Chino Mine, including Hanover/Whitewater Creek, Bayard Canyon, Bolton Draw, the unnamed drainage between Bolton Draw and Lampbright Draw and Lambright Draw.[16] The areal extent of injured alluvial and regional groundwater at the Chino Mine is 13,935 acres.
Safford	No documentation of unauthorized seepage or releases of unauthorized wastewater.
Bagdad	There have been numerous spills, including a broken pipeline in 2009 causing a release of 2.3 million gallons of sulfuric acid into the surrounding soils,[17] and a 1999 report of 12,000 gallons of process water with residual chlorine spilled into Bridle Creek.[18] According to a 2006 study, a tailings impoundment at the Bagdad Mine failed in 1991 and discharged to Copper Creek. Elevated concentrations of mercury, phenols, ammonia, copper and acidity occurred in Boulder and Copper creeks, resulting in a fish kill.[19] Water quality monitoring from 1998-2002 in Boulder Creek found water quality exceedances for arsenic, lead, mercury, and selenium. In Burro Creek, there were water quality exceedances for copper and mercury. In Butte Creek, there were water quality exceedances for mercury and selenium. In 1996, the EPA and the state of Arizona announced that Cyprus Bagdad Copper Corp., a subsidiary of Cyprus Mineral Corp., paid penalties totaling $760,000 for discharging contaminated water from the Bagdad Copper Mine.[20] The discharges involved various facilities including tailings ponds, leach dumps, and a sewage treatment plant.[21] According to an EPA report, seepage of pregnant leach solution from the Copper Creek Leaching System was discovered in a receiving pool in Boulder Creek in 1991.[22] Studies indicated that instead of being contained by the Copper Creek Flood Basin, the heavily contaminated solution seeped under the dam. The concentration of total copper in samples collected in the pool in Boulder Creek were as high as 76.4 mg/l. On March 29, 1993, U.S. EPA issued a Finding of Violation and Order against Cyprus.[23]
Bingham Canyon	Wastewater from the mine has escaped the site's collection system, contaminating groundwater with acid, metals and sulfates. The groundwater plume extends towards the Jordan River and covers and extensive area – contaminating the drinking water aquifer used by Salt Lake City residents.[24] Water treatment will be required in perpetuity.[25] In February 2008, the United States Fish and Wildlife Service took legal action against Kennecott for the release of hazardous substances from the mine's facilities, including selenium, copper, arsenic, lead, zinc and cadmium.[26] Groundwater contaminated by mine operations has been released from the mine site through artesian springs into areas that serve as fish and wildlife habitats. According to the federal biologists, the release of these hazardous pollutants has harmed natural resources, including migratory birds and their support ecosystems, which includes wetlands, marshes, freshwater wildlife habitats, playas and riparian areas and freshwater ponds.[27] The 2002 Record of Decision for the Kennecott North Zone Site, which includes the Magma tailings impoundment, describes leaching of contaminants through the berm and into

MINE	DOCUMENTATION OF WASTEWATER CAPTURE AND TREATMENT FAILURE
Ray Mine (cont'd)	According to a 2012 ecological risk assessment by the State of Arizona, "The site of injury stretches from the Ray Mine and the Hayden Facility, to the Gila River from the Ashurst- Hayden Diversion Dam, upstream past the confluence of the San Pedro and Gila Rivers, and for a distance of 5 miles up each of those rivers beyond the confluence and to Mineral Creek from its confluence with the Gila River upstream to a point one mile above the Big Box Canyon Dam."[41] The most substantial injuries occurred in the reach of Mineral Creek that extends from the tunnel outlet to the Gila River. The report finds that, "Dissolved copper concentrations in the surface water of this reach have been recorded up to 130 times surface water quality standards that will sustain aquatic life, and sediment copper concentrations have been recorded to exceed up to 22 times the level beyond which injury is inflicted on sediment-dwelling organisms (MacDonald et al. 2000)."[42] These concentrations of copper caused a complete loss of aquatic life in this reach. Overall, the report found that, "ecosystem services lost in the 117 acres that include Mineral Creek and its associated riparian habitat were estimated to be 100% from 1981- 2005, and up to 50% from 2005 to the present (Lipton 2009). Hazardous releases also affected the aquatic and riparian portions of the Gila River near the Ray Mine/Hayden Smelter Complex, including approximately 2,930 acres upstream of Mineral Creek to the confluence with the San Pedro River, and approximately 1,620 acres downstream of Mineral Creek to the Ashurst-Hayden Dam. The most substantial loss of ecosystem services in these areas occurred during the three years following the release of 300,000 tons of tailings in 1993, when ecosystem service losses were estimated at 10-25% (Lipton 2009)."[43]
Pinto Valley	In 2010, a report of a storm event that caused 5,362 tons of tailings to spill onto soil and Pinto Creek, including 214 pounds of arsenic and 11 pounds of lead.[44] According to the report, 500 cubic yards were released into water. Pinto Creek is a tributary to Roosevelt Lake. In 2007, a release of impounded storm and seepage water occurred due to a flange separation in a tailings line. The unexpected release washed out a section of the secondary containment, which allowed it to escape. An estimated 45,000 gallons of stormwater and tailings seepage reported to an unnamed tributary of Pinto Creek.[45] In 2007, the facility noticed that the action leakage rate for the Gold Gulch pond had been exceeded, documenting a leak in the pond. In February 2008 a wind and storm event ripped the top portion of the liner, requiring major repair, which was completed in February – March 2008.[46] The ALR exceedances continued on an intermittent basis throughout the remainder of 2008 and 2009. The leak rate was 26 gallons/minute on the day of the inspection. Since 1989, extreme storm events caused releases of copper bearing sediments and liquids to Pinto Creek from Pinto Valley operations. These releases resulted from partial tailings dam failures, pipeline breaks, seepage flows, conveyance blockages, and storm water overflows. Recent significant release events occurred in August 1989, July 1990, January 1991, August to September 1991, January to February 1993, and October 1997. In each of these events, materials were released in quantities sufficient to impact Pinto Creek or its tributaries."[47] Based on EPA's review of discharge monitoring reports between January 1990 and September 1991, Magma (now Pinto Valley) reportedly discharged effluent to Pinto Creek or its tributaries in excess of allowable effluent limitations on numerous occasions, and/or did not collect and analyze samples, in violation of permit conditions.[48] According to the report, during the first episode, approximately 3,000 gallons of effluent containing total suspended solids and copper of unknown concentrations was discharged from the ditch. A similar discharge of 24,000 gallons occurred on September 5, 1991. An estimated 39,000 gallons of effluent in exceedance of Arizona Surface Water Quality Standards and Aquifer Water Quality Standards for copper, zinc, and lead were discharged from the ditch on September 23, 1991.[49]

MINE	DOCUMENTATION OF WASTEWATER CAPTURE AND TREATMENT FAILURE
Tyrone (cont'd)	pathways at the Sites, including process water leaks and spills; tailings spills; dryfall from smelter emissions; windblown materials; runoff, infiltration, or percolation from tailings and waste stockpiles; and transport through erosional processes. Whitewater Creek and Mangas Creek are two important waterways at the Chino and Tyrone mines, respectively, where the riparian and associated streambed habitats have been exposed to hazardous substances from multiple sources. Those sources include direct inputs of contaminated water from the mines, tailings pond breaches during high-volume storm events, and deposition or spills of tailings directly into the streambed areas.[63] There have been multiple spills of tailings, releasing hazardous substances. The largest event occurred at the No. 3 tailings dam in 1980, releasing 2.6 million cubic yards of tailings into the Mangas Valley.[64] Tailings flowed 8 kilometers downstream and inundated farmland. The failure occurred as the result of a dam wall breach. In 2001, 5 tons of tailings spilled into the Mangas Wash from the stormwater containment dike at the tailings dam.[65]
Continental Pit	According to the Butte groundwater injury assessment report for the State of Montana's Natural Resource Damage Program, the walls of the Berkeley and Continental Pits were a source of groundwater contamination in the Butte Mine Flooding Operable Unit of the Superfund Site along with leaking solutions from the Yankee Doodle Tailings Pond.[66] Groundwater contamination is extensive, requiring the City of Butte to pipe its drinking water in from other watersheds. At current operations, mine tailings from the Continental Pit mine are placed in the Yankee Doodle tailings impoundment, which also contains the mine waste from previous mining at the Berkeley Pit. The tailings impoundment is unlined, and seepage from the impoundment travels through faults and fractures into the Berkeley Pit. When mining ceases, seepage from the tailings impoundment will continue to contribute contaminated water to the Berkeley pit. A consent decree requires contaminated water from the Berkeley Pit to be collected and treated in perpetuity.[67]
Phoenix	In 2002, groundwater from the gold tailings facility contain elevated concentrations of chloride, sodium, and sulfate, which is the result of a solute plume originating from the Gold Tailings facility – a copper and gold tailings storage facility.[68] In 2005, seepage of low pH and poor-quality solution emanating from a portion of the southern toe of the North Fortitude Waste Rock Facility was identified in June and formally inspected in August. Flow emanates from two locations along a 300-foot width of the toe and ultimately migrates to a natural drainage and eventually into the pit. In 2006, seepage of a small quantity of low pH and poor-quality water was discovered at the toe of the Box Canyon Waste Rock Facility following an intense precipitation event. Flow was estimated at 2 gallons per minute.
Miami	The Miami Mine, currently owned by Freeport McMoran, was formerly the Inspiration Mine owned and operated by the Inspiration Consolidated Copper Co. In 1986, the U.S. EPA issued a finding of violation and order under the Clean Water Act to the Inspiration Consolidated Copper Co. for discharges of acidic process solutions from Webster Lake (a large process solution impoundment) to Miami Wash and for acidic, metal contaminated groundwater surfacing near the confluence of Miami Wash and Pinal Creek.[69] Acidic water from this lake and other mining related sources generated a 15-kilometer-long plume of acidic groundwater in the alluvial aquifer.[70] In 1989, the Pinal Creek Site, which includes the Miami Mine, was placed on the WQARF Priority list.[71] The WQARF program is the state equivalent of the Federal "superfund" program. The Pinal Creek site was listed under the Arizona Water Quality Assurance Revolving Fund program for contamination in the shallow alluvial aquifers within the Pinal Creek drainage. According to the State of Arizona, "Releases of contaminants have occurred from all of the major mining sites from a variety of different sources, including, but not limited to, process solution

[21] Id.
[22] US EPA, Damage Cases and Environmental Releases from Mine and Mineral Processing sites, 1997.
[23] Id.
[24] Interstate Technology and Regulatory Council Mining Waste Team, Bingham Canyon Wastewater Treatment Plant, Kennecott South Zone, August 2010,
International Conference on Acid Rock Drainage, March 26–30, St. Louis, MO. Available at: https://www.itrcweb.org/miningwaste-guidance/cs48_kennecott_south.pdf
[25] Borden, R.K, Peacey, V. and Vinton, B. 2006. "Groundwater response to the end of forty years of copper heap leach operations, Bingham Canyon, Utah. 2006. " Proceedings, 7th International Conference on Acid Rock Drainage, March 26–30, St. Louis, MO. Available at: http://www.imwa.info/docs/imwa_2006/0214-Borden-AU.pdf
[26] United States v. Kennecott Utah Copper Corporation. Complaint Case: 2:08cv00122. February 14, 2008.
[27] United States v. Kennecott Utah Copper Corporation. Complaint Case: 2:08cv00122. February 14, 2008.
www.fws.gov/.../r_r_Kennecott_Utah_Copper_ComplaintFinal.pdf
[28] US EPA, Kennecott North ROD, September 2002.
[29] Arizona Department of Environmental Quality, Phelps Dodge Sierrita Aquifer Protection Permit, Fact Sheet, Publication No. FS-05-17. Available at:
https://legacy.azdeq.gov/environ/water/download/phelps.pdf
[30] Id.
[31] US EPA, Damage Cases and Environmental Releases from Mines and Mineral Processing Sites, 1997.
[32] Id.
[33] Id.
[34] Id.
[35] Personal Communication, Peter Jagow, Compliance inspector, Arizona DEQ, July 10, 2012, based on February 2012 inspection.
[36] Arizona Department of Environmental Quality, Notice of Violation, Case ID #130170, May 9, 2012.
[37] Arizona Department of Environmental Quality, Inspection Report, May 6, 2011.
[38] Arizona Department of Environmental Quality, Inspection Report, May 6, 2011.
[39] State of Arizona and US Department of Interior, "Draft Restoration Plan and Environmental Assessment for the Hazardous Substances Releases from the Hayden Smelter and Ray Mine Facilities," February 2012.
[40] Arizona Department of Environmental Quality, Notice of Violation, Case ID 79745, July 12, 2007.
[41] Id.
[42] Id.
[43] Id.
[44] National Response Center Incident No. 929841.
[45] BHP Billiton, Follow Up Report, Environmental Release, National Response Center, Letter to EPA, October 31, 2007.
[46] US EPA, Region 9, Total Maximum Daily Load for Copper into Pinto Creek, Arizona, April 2001. p. 11.
[47] Ibid. p. 14.
[48] US EPA, Damage Cases and Environmental Releases from Mine and Mineral Processing sites, 1997. p. 32.
[49] Ibid.
[50] US EPA, Region 9 Total Maximum Daily Load for Copper into Pinto Creek, Arizona, April 2001. P. 14
[51] US Fish and Wildlife Service, Environmental Contaminants Program website, Pinto Creek Restoration, News and Activities, Arizona. Posted on December 22, 1999.
[52] National Response Center, Incident No. 986438.
[53] Arizona Daily Star, "Tailings spill blamed on Asarco valve issue" August 5, 2011. Available at:
https://tucson.com/business/local/tailings-spill-blamed-on-asarco-valve-issue/article_fea75159-fcb9-5b7f-a9d2-7f6422e9b8db.html
[54] US EPA, ASARCO Mission Complex Fact Sheet: EPA PERMIT NO. AZ0024635, September 22, 2008.
[55] US Department of Interior, Bureau of Reclamation, San Xavier District Arroyos Recharge Project, Final Environmental Assessment, May 2009. p. 16.
[56] Nevada Department of Environmental Protection, NDEP Fact Sheet, Robinson Mine, Permit No. NEV0092105.
https://ndep.nv.gov/uploads/documents/NEV0092105_fsFY18.pdf
[57] Id.
[58] Id. p. 88
[59] US EPA, Damage Cases and Environmental Releases from Mines and Mineral Processing Sites, 1997, p. 170. The Robinson Mine was formerly owned by BHP Copper, Magma Nevada Mining Company.
[60] United States and State of New Mexico v. Freeport McMoran Corporations, et. al, Consent Decree, Case 1:11-cv-01140. December 2011.
[61] Stratus Consulting, Preassessment Screen for the Chino, Tyrone, and Morenci Mine Sites, Grant County, New Mexico, and Morenci, Arizona, Prepared for US Fish and Wildlife Service, June 18, 2003.
[62] New Mexico Office of Natural Resources Trustee, "Final Groundwater Restoration Plan for the Chino, Cobre and Tyrone Mine Facilities, January 4, 2012. Table 2.1. p. 2-14.
[63] U.S. Fish and Wildlife Service and State of New Mexico, Wildlife and and Wildlife Habitat Restoration Plan and Environmental Assessment for the Chino, Cobre and Tyrone Mine Facilities, October 2013: https://onrt.env.nm.gov/wp-content/uploads/FMIWildlifeRPEAOctober2013.pdf
[64] Stratus Consulting, Preassessment Screen for the Chino, Tyrone, and Morenci Mine Sites, Grant County, New Mexico, and Morenci, Arizona, Prepared for US Fish and Wildlife Service, June 18, 2003. Table 2.3. p. 2-11.
[65] Stratus Consulting, Preassessment Screen for the Chino, Tyrone, and Morenci Mine Sites, Grant County, New Mexico, and Morenci, Arizona, Prepared for US Fish and Wildlife Service, June 18, 2003.
[66] Maest, Ann S. and John Metesch, Butte Groundwater Injury Assessment Report, Clark Fork River Basin NPL Sites, Prepared for the State of Montana Natural Resources Damage Program, April 1993. p. 2-1.
[67] https://www.itrcweb.org/miningwaste-guidance/References/2079-ZickPA.pdf
[68] US Department of Interior, Bureau of Land Management, Greater Phoenix Project, Draft Environmental Impact Statement, Volume 1, September 2017, p. 3-22.
[69] Arizona Department of Environmental Quality, Website: Pinal Creek Site Overview. http://static.azdeq.gov/wqarf/pnlck_rr.pdf
[70] USGS, Hydrogeology and Geochemistry of Aquifer and Stream Contaminated Related to Acidic Water in Pinal Creek Basin Near Globe Arizona, 1996.
[71] Arizona Department of Environmental Quality, Website: Pinal Creek Site Overview. http://static.azdeq.gov/wqarf/pnlck_rr.pdf
[72] http://static.azdeq.gov/wqarf/pnlck_rr.pdf
[73] Arizona Daily Star, "Asarco Unit to pay $110,000 to settle mine spill charges," January 9, 2013
https://tucson.com/business/local/asarco-unit-to-pay-k-to-settle-mine-spill-charges/article_0dc1c34e-6a53-11e2-a438-0019bb2963f4.html
[74] ADEQ, Press Release: Silver Bell Mining to Pay $170,000 in civil penalties for water quality violations in Pima County. April 7, 2009

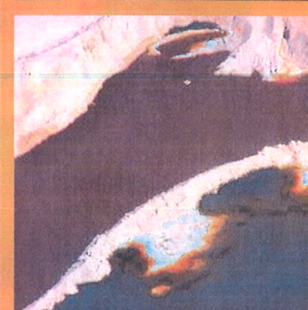
Appendix F

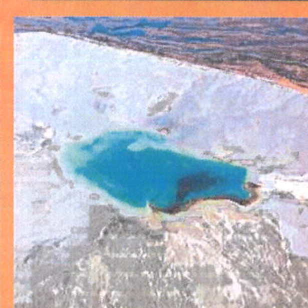
U.S. Copper Porphyry Mines

Report

THE TRACK RECORD OF WATER QUALITY IMPACTS RESULTING FROM PIPELINE SPILLS, TAILINGS FAILURES AND WATER COLLECTION AND TREATMENT FAILURES.

JULY 2012





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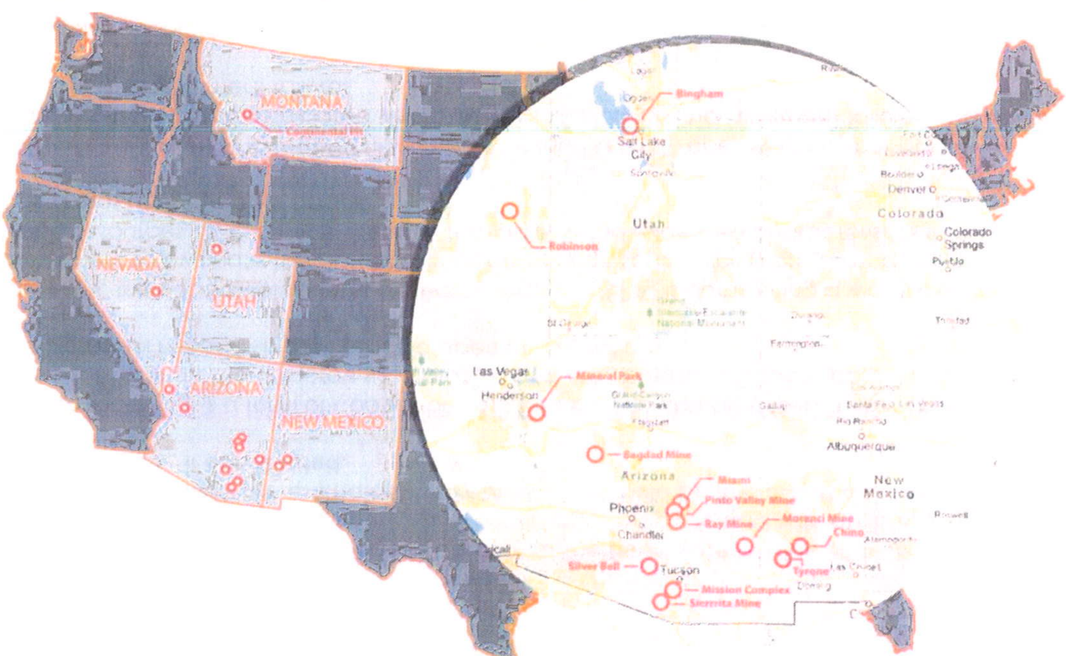

Map Data 2012 © Google

The Bingham Canyon Mine, the largest copper porphyry mine currently operating in the United States, will also generate water pollution in perpetuity from the mine's waste rock piles. Mine operations have resulted in a plume of contaminated groundwater extending over 70 square miles, and the State of Utah filed a natural resource damage claim against the mine in 2008 for impacts to water and wildlife resources.

Tailings spills have occurred at nine operations, and a partial failure of the tailings impoundment occurred at four out of fourteen mines (28%). These included a 1997 partial failure of the tailings impoundment at the Pinto Valley Mine, where the creek bed and surrounding upland were buried under material as deep as 42 feet. In 1993, heavy precipitation caused the Gila River to flood and breach the tailings impoundment at the Ray Mine, carrying pollutants 11 miles downriver. And in 1980, 2.6 million cubic yards of tailings were released at the Tyrone mine, and flowed 8 kilometers downstream.

Many of the currently operating copper porphyry mines are located in the arid southwest, where precipitation is limited, and communication between surface and groundwater resources is limited. **More significant impacts could be expected at mines in wetter climates, with abundant surface water and shallow groundwater, such as is the case in the Bristol Bay region.** Research shows that mines with high acid generating potential and in close proximity to surface and groundwater are at highest risk for water quality impacts.[2]

Additional impacts at these mines, particularly water collection and treatment failures, are likely to occur after mining operations cease and groundwater pumps are no longer keeping the mine area dewatered.

A review of the track record of water quality impacts from copper porphyry mines found severe impacts to drinking water aquifers, contamination of farmland, contamination and loss of fish and wildlife and their habitat, and risks to public health. In some cases, water quality impacts are so severe that acid mine drainage will generate water pollution in perpetuity.

Table 2

Synopsis of pipeline spills, tailings spills and impoundment failures, and water capture and treatment failures for 14 copper porphyry mines (1986-2012).

Mine	Number of reported pipeline spills and other accidental releases*	Water collection and treatment failures	Tailings dam failures	Affected surface and/or ground water
Morenci	21	Yes		San Francisco River, Gila River, Chase Creek, groundwater aquifer
Bingham Canyon	28	Yes		72 square mile plume of contaminated groundwater; fish and wildlife habitat in the Great Salt lake ecosystem
Ray	54	Yes	Partial	Mineral Creek, Gila River, groundwater aquifer
Chino	10	Yes		Hanover/Whitewater Creek, contaminated groundwater will require water treatment in perpetuity
Bagdad	7	Yes		Boulder Creek, Burro Creek, Butte Creek, Bridle Creek
Sierrita	18	Yes		Demetrie Wash and its tributaries; groundwater aquifer including drinking water wells in Green Valley
Pinto Valley	3	Yes	Partial	Pinto Creek
Mission	3	Yes	Partial	Tributaries of the Santa Cruz River, groundwater aquifer
Robinson	8	Unknown		2.3 miles of downstream drainage bed
Tyrone	7	Yes	Partial	Mangas Creek, groundwater contamination will require water treatment in perpetuity
Mineral Park	3	Yes		Groundwater aquifer and surface water
Miami	8	Yes		Pinal Creek alluvial aquifer
Silver Bell	3	Yes		Cocio Wash
Continental Pit	2	Yes		Silver Bow Creek, groundwater aquifer

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

	resources at and in the vicinity of the site including surface water, sediments, soils, terrestrial habitats and terrestrial receptors."[37] A financial settlement followed an investigation of natural resource injuries related to the release of hazardous substances into the environment from acid mine drainage and process solution, among other sources. The investigation found that the main ore minerals are sulfide minerals, which have resulted in the development of acid mine drainage. According to the report, "Surface water has been, and most likely continues to be, exposed to hazardous substances released from the Morenci Mine through a variety of pathways."[38] Concentrations of hazardous substances measured in groundwater at the Morenci Mine and measured in the San Francisco and Gila Rivers downstream of the mine provide further indications that hazardous substances present in the source materials at the Morenci Mine have been released to the environment. The report found that "Concentrations of total and dissolved zinc have exceeded 1,000 ug/l in the Gila River and concentration of dissolved copper have exceeded 100 ug/l in the San Francisco River."[39] Contaminated groundwater is also released to surface water via seeps and springs.[40]
Tailings spills and impoundment failures	No impoundment failures.
Impacts to water, fish and wildlife	In 2012, the US Department of Justice and Department of Interior have jointly announced that Freeport McMoRan has agreed to pay $6.8 million to settle federal and state natural resource damages related to the Morenci Mine. According to the complaint, the hazardous substance release, which included sulfuric acid and metals, injured, destroyed or led to the loss of "surface waters, terrestrial habitat and wildlife, and migratory birds."[41] As described above, metals contamination occurred in the San Francisco and Gila Rivers downstream of the mine, and to groundwater supplies.

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

	1998: Report of copper sulfate released into a canal. 1998: Report of clogged piping system causing pipe to back up and overflow releasing acid rock drainage into water. 1997: Report of settling pond overflow due to clogged outlet valve. Release of copper sulfate into water. 1997: Report of pipeline rupture releasing process water (pH 2.5-4.0) into water. 1993: Report of 45,000 gallons of wastewater spilled due to a rupture of the transfer line.[63] 1991: Report of 30,000 gallons of industrial wastewater spilled at the wastewater treatment plant due to line break.[64]
Water collection & treatment failure	2011: Noncompliance in April-June 2011 for discharges of copper, zinc and total suspended solids at copper smelter.[65] Wastewater from the mine has escaped the site's collection system, contaminating groundwater with acid, metals and sulfates. The groundwater plume extends towards the nearby Jordan River and covers more than 72 square miles – rendering water for thousands of Salt Lake City residents undrinkable.[66] There have been multiple tailings spills.[67] Drainage from the waste rock piles will require water treatment in perpetuity to prevent additional groundwater pollution.[68] In February 2008, the United States Fish and Wildlife Service took legal action against Kennecott for the release of hazardous substances from the mine's facilities, including selenium, copper, arsenic, lead, zinc and cadmium.[69] Groundwater contaminated by mine operations has been released from the mine site through artesian springs into areas that serve as fish and wildlife habitats. According to the federal biologists, the release of these hazardous pollutants has harmed natural resources, including migratory birds and their support ecosystems, which includes wetlands, marshes, freshwater wildlife habitats, playas and riparian areas and freshwater ponds.[70]
Impacts to water, fish and wildlife.	In February 2008, the United States Fish and Wildlife Service took legal action against Kennecott for the release of hazardous substances from the mine's facilities, including selenium, copper, arsenic, lead, zinc and cadmium.[71] Groundwater contaminated by mine operations has been released from the mine site through artesian springs into areas that serve as fish and wildlife habitats. According to the federal biologists, the release of these hazardous pollutants has harmed natural resources, including migratory birds and their support ecosystems, which includes wetlands, marshes, freshwater wildlife habitats, playas and riparian areas and freshwater ponds.

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

	electrowinning plant and the electrowinning dam were continuously pumping PLS.[87] Multiple groundwater wells were found to be highly contaminated by a common leachate solution which was attributed to releases by ASARCO into shallow groundwater along Mineral Creek. It concluded that it is likely that the hazardous substance present in shallow groundwater will represent an ongoing source of chronic contamination to Mineral Creek (Lipton 2009).[88]
Tailings spills and impoundment failures	2012: Seepage from the tailings impoundment was released into two catch basins and into a tributary of the Gila River.[89] At the time of the report, seepage into the tributary was estimated at 75 gpm. 2011: A report of 6,000-8,000 tons of copper ore tailings released from one of the tailings pond due to a breach in the dike.[90] In 1993, heavy precipitation caused the Gila River to flood, and breach the AB-BC tailings impoundment containment dike.[91] According to a report by the U.S. EPA, "Continued flooding over the next several days resulted in a total of 13 separate breaches of the dike, three of which eroded through the dike and into the toe of the tailings pile. The total discharge was approximately 292,000 tons of tailings, which was about 216,000 cubic yards of material."[92] It also found that sampling of the river showed that elevated concentrations of pollutants occurred at least 11 miles downstream of the spill. The tailings formed bank and bottom deposits in the river, impairing both recreational uses and the quality of habitat for plants and animals.[93]
Impacts to water, fish and wildlife	In April 2009, the Department of the Interior and the State of Arizona, acting as natural resource trustees (Trustees) received a monetary settlement and three parcels of land from ASARCO, L.L.C. through the Natural Resource Damage Assessment and Restoration (NRDAR) program to account for injuries to trust resources incurred through multiple releases of hazardous substances by ASARCO L.L.C. into Mineral Creek and the Gila River in Pinal County, Arizona.[94] According to a 2012 ecological risk assessment by the State of Arizona, "The site of injury stretches from the Ray Mine and the Hayden Facility, to the Gila River from the Ashurst-Hayden Diversion Dam, upstream past the confluence of the San Pedro and Gila Rivers, and for a distance of 5 miles up each of those rivers beyond the confluence and to Mineral Creek from its confluence with the Gila River upstream to a point one mile above the Big Box Canyon Dam." The most substantial injuries occurred in the reach of Mineral Creek that extends from the tunnel outlet to the Gila River. The report finds that, "Dissolved copper concentrations in the surface water of this reach have been recorded up to 130 times surface water quality standards that will sustain aquatic life, and sediment copper concentrations have been recorded to exceed up to 22 times the level beyond which injury is inflicted on sediment-dwelling organisms (MacDonald et al. 2000)." These concentrations of copper caused a complete loss of aquatic life in this reach.[95] Overall, the report found that, "ecosystem services lost in the 117 acres that include Mineral Creek and its associated riparian habitat were estimated to be 100% from 1981-2005, and up to 50% from 2005 to the present (Lipton 2009). Hazardous releases also affected the aquatic and riparian portions of the Gila River near the Ray Mine/Hayden Smelter Complex, including approximately 2,930 acres upstream of Mineral Creek to the confluence with the San Pedro River, and approximately 1,620 acres downstream of Mineral Creek to the Ashurst-Hayden Dam. The most substantial loss of ecosystem services in these areas occurred during the three years following the release of 300,000 tons of tailings in 1993, when ecosystem service losses were estimated at 10-25% (Lipton 2009)."[96]

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

and impoundment failures	
Impacts to water, fish and wildlife	The 2003 ecological risk assessment reported elevated concentrations of the hazardous substances copper and zinc in surface water from five different drainages at the Chino Mine, including Hanover/Whitewater Creek, Bayard Canyon, Bolton Draw, the unnamed drainage between Bolton Draw and Lampbright Draw and Lambright Draw.[105] The areal extent of injured alluvial and regional groundwater at the Chino Mine is 13,935 acres.[106] According to the closure plan for the Chino Mine, contaminated groundwater will require water treatment in perpetuity.[107]

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

SIERRITA MINE, AZ (Freeport McMoRan) The Sierrita Mine is an open pit copper and molybdenum mining complex 20 miles southwest of Tucson, Arizona.	
Reports of pipeline failures and other accidental releases*	2011: Report of 849 gallons of sulfuric acid spills from a pipeline leak.[120] 2008: Report of 1,100 gallons of sodium hypochlorite spilled due to loose pipe.[121] 2005: Report of 1,000 pounds of sulfuric acid from broken pipeline.[122] 2005: Report of 8,058 pounds of sulfuric acid released from broken pipeline.[123] 2002: Report of 39,375 pounds of sulfuric acid spilled from pipeline from separated flange.[124] 2001: Report of 1,209 pounds of sulfuric acid spilled from pipeline.[125] 2000: Report of 5,350 gallons of leach solution spilled from pipe.[126] 1998: Report of 160,000 gallons of mill tailings spilled into water due to overflow resulting from power failure.[127] 1998: Report of 40,000 gallons leach solution spilled from pipeline.[128] 1998: Report of 120,000 gallons of leach solution spilled from pipeline.[129] 1997: Report of 2,798 pounds of sulfuric acid spilled due to pipeline rupture.[130] 1997: Report of release of 8,000 pounds of sulfuric acid due to pipe joint failure.[131] 1996: Report of release of 3,000 gallons of sulfuric acid due to pipeline failure.[132] 1994: Report of another pipeline break allowed a discharge into Demetrie Wash of approximately 120,000 gallons of reclaim water.[133] 1994: Report of approximately 5,000 gallons of reclaim water were released as a result of a pipeline break.[134] 1993: Report of a leak in a pipeline transporting process water discharged approximately 200,000 gallons of a mixture of process wastewater and storm water run-off to an unnamed tributary of Demetrie Wash.[135] 1993: Report of Cyprus Sierrita discharging approximately 2,700,000 gallons into the same wash as a result of another pipeline break.[136] 1993: Report of approximately 450,000 gallons released to the wash in October 1993 by a broken pipeline.[137]
Water collection and treatment failures	From the summer of 1992 until December 1994, Sierrita discharged contaminated process water and storm water run-off to Demetrie Wash and its tributaries from various overflows, seepages, and pipeline leaks and breaks.[138] On March 25, 1996, the U.S. Department of Justice issued a civil claim against Cyprus Sierrita on behalf of the State of Arizona and the United States pursuant to the Clean Water Act.[139] Cyprus Sierrita entered into a binding Consent Decree to pay a total civil penalty of $88,000 for numerous violations. According to a 2011 report, seepage from an unlined tailings pond at Phelps Dodge's Sierrita mine has sent a plume of contaminated groundwater toward the city of Green Valley, causing drinking water wells to record high levels of sulfates.[140] In 2006, the company signed a mitigation order on consent with the State of Arizona to address sulfate in drinking water. It requires the company to develop a mitigation plan to be submitted in 2009.

PINTO VALLEY MINE, AZ (BHP Billiton) The Pinto Valley Mine is an open pit copper and gold mine located about 126 km east of Phoenix, AZ. Formerly owned by Magma Copper Company.	
Reports of pipeline failures and other accidental releases	2010: Report of a storm event, which caused 5,362 tons of tailings to spill onto soil and Pinto Creek, including 214 pounds of arsenic and 11 pounds of lead.[141] 500 cubic yards were released into water. Pinto Creek is a tributary to Roosevelt Lake. 2010: Report of an unknown amount of mine tailings released onto land, with a potential release to water, due to heavy rains.[142] 2001: Report of 1,725 pounds of sulfuric acid released due to pipeline break.[143]
Water collection and treatment failures	According to a 2001 EPA report, a portion of Pinto Creek from its headwaters to Spring Creek was first listed as water quality limited in 1992 based on elevated copper concentrations and pH values that were related to discharges from the Pinto Valley and another mine. The remaining portions of the stream were added to the 303(d) list in 1994.[144] The report further states that, "Since 1989, extreme storm events caused releases of copper bearing sediments and liquids to Pinto Creek from Pinto Valley operations. These releases resulted from partial tailings dam failures, pipeline breaks, seepage flows, conveyance blockages, and storm water overflows. Recent significant release events occurred in August 1989, July 1990, January 1991, August to September 1991, January to February 1993, and October 1997. In each of these events, materials were released in quantities sufficient to impact Pinto Creek or its tributaries."[145] Based on EPA's review of discharge monitoring reports between January 1990 and September 1991, Magma (now Pinto Valley) reportedly discharged effluent to Pinto Creek or its tributaries in excess of allowable effluent limitations on numerous occasions, and/or did not collect and analyze samples, in violation of permit conditions.[146] According to the report, during the first episode, approximately 3,000 gallons of effluent containing total suspended solids and copper of unknown concentrations was discharged from the ditch. A similar discharge of 24,000 gallons occurred on September 5, 1991. An estimated 39,000 gallons of effluent in exceedance of Arizona Surface Water Quality Standards and Aquifer Water Quality Standards for copper, zinc, and lead were discharged from the ditch on September 23, 1991.[147]
Tailings spills or failures	In 1997, a partial tailings failure deposited an estimated 276,000 cubic yards of tailings in Pinto Creek.[148] It buried 8.1 acres of creek bed and surrounding upland with material as deep as 42 feet.[149] Another incident occurred in 1993, when heavy rainfall overwhelmed the mine's water management capabilities. During the rainfall event, a reservoir overflowed the tailings pile, tore out a levee, and carried tailings to Pinto Creek.[150] In addition, a retention pond that held storm water and mineral wastes discharged material into the creek after its dam was breached. According to an EPA report of the incident, "Critical water containment structures in place at the mine in 1992 were reportedly designed to hold a 100-year, 24-hour storm event. Nonetheless, the mine discharged hundreds of tons of tailings and millions of gallons of contaminated water into Pinto Creek."[151] Water quality sampling during January and February 1993 indicated 286 exceedances of daily and monthly water quality parameters. Fish surveys collected before and after the discharges showed a marked decline in populations of the desert sucker (*Pantosteus clarki*) following the discharges. Although they were abundant in 1992, a summer survey in 1993 found only one adult in Pinto Creek.[152] In January 1991, the face of Tailings Dam No. 3 failed, releasing 150 - 250 tons of tailings

MISSION COMPLEX MINE, AZ (ASARCO) The Mission Mine complex is an open pit copper mine and underground copper mine located near Sahuarita, Arizona (18 miles south of Tucson). The Mine covers approximately 29.7 square miles, and a portion of the mine occupies tribal lands.	
Reports of pipeline failures and other accidental releases*	2011: Report of a backup of a tailing line resulting in release of tailings into a dry wash.[155] 2002: A violation involving the discharge of primarily copper laden stormwater runoff and process water discharge to ephemeral tributaries of the Santa Cruz river near Tucson in violation of the facilities Multi Sector General Permit Case # 09-2002-0064. 2001: Report of a 36-inch distribution tailings line releasing 200 tons of tailings into a dry stream channel.[156]
Water collection and treatment failures	According to EPA fact sheet released in 2008, discharges from mine (outfall 001A) contain significant levels of copper and lead, and TSS, which have been out of compliance since October, 2003.[157] Outfalls from the Mission complex discharge to ephemeral streams that are tributaries to the Santa Cruz River. Three large tailings ponds and several mine dumps are located on land leased from the Indian landowners approximately 1 mile south of the Arroyos project area. According to a report by the Bureau of Reclamation, leachate from these tailings has contributed to elevated levels of sulfate, TDS, and hardness in the aquifer below and adjacent to the ponds.[158]
Tailings spills or impoundment failures	The Bureau of Reclamation Report also states that, "Surface drainage from a break in a tailings pond dike in 1990 released large volumes of material into wash complexes that drain toward the SCR."[159]
Impacts to water, fish and wildlife	Ground and surface water pollution.

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

TYRONE MINE, NM (Freeport McMoRan) The Tyrone Mine is located approximately 10 miles southwest of Silver City, New Mexico. The mine straddles the Continental Divide.	
Reports of pipeline failures and other accidental releases*	2006: Report of a spill occurring when a CTI tanker truck loaded with about 3,000 gallons of acid collided with a pickup truck, spilling about 500 gallons of the acid on the highway and adjacent property.[162] (non pipeline) 2003: Report of approximately 2,600 gallons of 16% sulfuric acid solution spilled at the Tyrone mine during maintenance activity on a pipeline system.[163] 2001: Report of 500-1000 gallons of solution leaked from the pipeline.[164] 2001: Report of 300 gallon spill of raffinate and organic solution from pipeline. 2001: Report of 150 gallon spill from the Seep 5# pond, which overflowed with 75 gallons entering Deadman Canyon. Seepage had a pH of 4 and Deadman Canyon was flowing at approximately 50 gpm at the time.[165] 1997: Report of 65,000 gallons of raffinate leaked from a ruptured weld in a raffinate pipeline.[166] 1997: Report of a transfer line rupture due to cold weather. 1994: Report of No. 2 diesel fuel oil from two broken pipes detected in groundwater.[167] 2012 report identifies diesel fuel contaminant concentrations in groundwater from a leak in distribution pipeline at diesel tank farm, which migrated to regional aquifer.[168]
Water collection and treatment failures	In 2011, the U.S. Department of Justice and State of New Mexico issued a consent decree for damages to natural resources from hazardous substances from the Tyrone, Chino, and Cobre mines.[169] The settlement followed an investigation of natural resource injuries related to the release of hazardous substances into the environment from acid mine drainage and process solution, among other sources.[170] According to the investigation, "groundwater in both the regional aquifer and the perched groundwater aquifers at the site have been exposed to hazardous substances through a variety of pathways."[171] The assessment at the Tyrone Mine identified 14 different mine area sources that have affected water quality, including seepage from tailings impoundments, leach stockpiles and waste rock stockpiles. A 2012 groundwater assessment concluded that contaminated seepage from the mine will require water treatment in perpetuity. [172]
Tailings spills and impoundment failures	There have been multiple spills of tailings, releasing hazardous substances. The largest event occurred at the No. 3 tailings dam in 1980, spilling 2.6 million cubic yards of tailings into the Mangas Valley.[173] Tailings flowed 8 kilometers downstream and inundated farmland.[174] The failure occurred due to a dam wall breach. 2001: 5 tons of tailings spilled into the Mangas Wash from the stormwater containment dike at the tailings dam.[175] 1990: Minor tailings spills from the No. 1 tailings pond in January 1990, and similar minor spills from the No. 2 tailings pond during 1990.[176]
Impacts to water, fish and wildlife	Streams and washes in the vicinity of the Tyrone Mine facility are ephemeral – they flow only after significant precipitation events. According to the 2003 preliminary assessment, "Surface water is exposed to hazardous substances released from the Tyrone Mine through a variety of pathways. Mangas Creek,

MIAMI MINE, AZ (Freeport McMoRan; formerly owned by Phelps Dodge and Cyprus Amax Minerals) The Miami Mine is an open pit mine located 90 miles east of Phoenix, Arizona.	
Reports of pipeline failures and other accidental releases*	2011: Report of 1,600 pounds of sulfuric acid spilled from pipeline due to faulty weld.[179] 2009: Report of 1,000 pounds of sulfuric acid spilled due to pipeline break.[180] 2007: Report of a release of 9,450 pounds of sulfuric acid from pipeline.[181] 2001: Report of a release of 153 pounds and 6.4 pounds respectively of lead/arsenic from pipeline.[182] 2001: Report of a release of 2,070 pounds of acid plant blowdown from pipeline.[183] 1997: Report of 10,000 gallons of copper sulfate due to overflow of tank.[184] 1996: Report of 50,000 gallons of sulfuric acid due to tank failure.[185] 1996: Report of 8,995 pounds of sulfuric acid due to leaky pipe.[186]
Water collection and treatment failures	The Pinal Creek drainage was designated a Water Quality Assurance Revolving Fund (WQARF) site by the Arizona Department of Environmental Quality in 1989 due to acidity and metals contamination in the alluvial aquifer. The WQARF program is the state equivalent of the Federal "superfund" program. The Miami Mine, inherited from the Cyprus Miami Mine (formerly the Inspiration Mine) is a member of the Pinal Creek Water Quality Assurance Revolving Fund (WQARF) Site.[187] The Pinal Creek site was listed under the Arizona Water Quality Assurance Revolving Fund program in 1989 for contamination in the shallow alluvial aquifers within the Pinal Creek drainage near Miami, Arizona.[188]
Impacts to water, fish and wildlife	The Water Quality Assurance Revolving Fund (WQARF) program is the state equivalent of the Federal "superfund" program. The Miami Mine, inherited from the Cyprus Miami Mine (formerly the Inspiration Mine) is a member of the Pinal Creek Water Quality Assurance Revolving Fund (WQARF) Site.[189] The Pinal Creek drainage was designated a WQARF site by ADEQ in 1989 due to acidity and metals contamination in the alluvial aquifer.[190]

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

MINERAL PARK MINE, AZ (Mercator) Mineral Park is an open pit copper mine in the Cerbat Mountains near Kingman, AZ.	
Reports of pipeline spills and other accidental releases*	1996: Report of 150 - 200 gallons of sulfuric acid released from acid storage tank due to equipment failure.[197] 1996: Report of 200 gallons of sulfuric acid released.[198] 1996: Report of 1,100 gallons of sulfuric acid spilled.[199]
Water collection and treatment failures	According to a 1995 report by the Arizona Geological Survey, water quality samples were taken of streamflow just below the Mineral Park mine and of mine water seeping through a dam at the southwest end of the tailings.[200] Both samples showed extremely low pH values (3.2, 2.6), extremely high TDS values (5,549 and 6,625 mg/L) and extremely high sulfate contents (4,500 and 6,000 mg/L). According to the report, "the cadmium concentration of the stream flow just downstream of the Cyprus Mineral Park Mine place is 75.4 times higher than the standard, copper exceeds the standard 51 times and zinc 17.2 times." It further states that, "The discharge from the tailings ran down the washes until about two years ago, when the dam around the tailings was built. In years with very heavy rains the water could eventually reach the Sacramento Wash."[201] According to a 1999 EPA report, the Mineral Park Mine collected surface water samples from seven drainages and analyzed them for metals and radio-chemicals.[202] All of these drainages, except for Golden Eagle Spring, exceeded either the federal Maximum Contaminant Levels (MCLs) and or state guidelines for gross alpha or gross beta. According to the report, "ADEQ observed that surface water runoff emanating from the drainages in the mine area were affecting the water quality of the alluvial pediment." Data showed that the plume contained high levels of beryllium, cadmium, fluoride and nickel. The report further stated that, "the data show that TENORM is discharging from abandoned mine adits and is impacting surface water and that mining operations have impacted groundwater."[203] A 2006 technical feasibility report commissioned by the company also describes a plume of contaminated groundwater migrating down-gradient from the mine.[204]
Impacts to water, fish and wildlife	See above.

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

	Blacktail Creek and the Metro Storm Drain at the base of the Butte Hill.[211] Surface water flow above the tailings pond is intercepted by the tailings pond and used as makeup water in the milling process. From the tailings pond to the MR Concentrator, the original Silver Bow Creek channel no longer exists. Surface water in the active mining area is controlled by a series of ditches and ponds which convey runoff and mine process water to various locations, including the Berkeley Pit, leach pads, and concentrator area (Figure 2). From the MR Concentrator to the confluence with Blacktail Creek, the former creek has been reconfigured and is known as the Metro Storm Drain.[212]

*Limitations in the data for pipeline spills and other accidental releases make it difficult to determine, in some cases, whether water quality impacts resulted from the spill.

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Appendix G

4500-year-old mining pollution in Southwestern Spain: Long-Term implications for modern mining pollution

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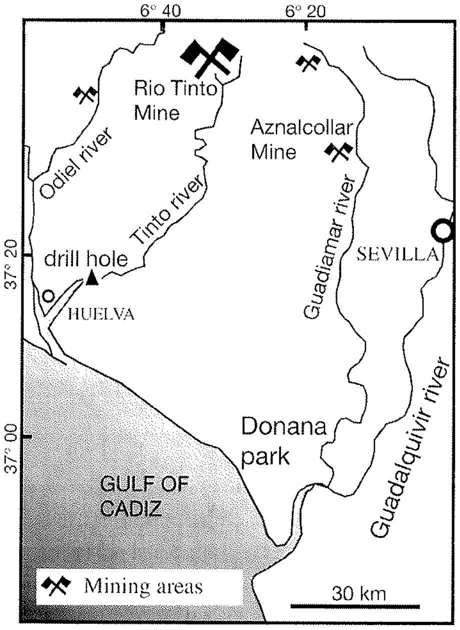

FIG. 1. Sketch map (southwest Spain) showing the location of the Rio Tinto and of the Aznalcollar mining areas and the location of the core drilled in the upper estuary of the Tinto river (Huelva ria).

drainage waters. The name of the Tinto river ("tinto " means "red wine" in Spanish) clearly refers to the uncommon brown-red color of its waters.

The Tinto river, which is 90 km long, remains strongly acidic (pH, 1.5–2.5) from its source zone, about 400 m elev, down to its estuary in the Ria of Huelva (Fig. 1). Its red-colored waters contain high sulfate and dissolved metal contents (Nelson and Lamothe, 1993; Elbaz-Poulichet et al., 1999). The mean discharge is relatively small—about 15 m^3/s, ranging from 1 to 100 m^3/s depending on seasonal variations, including dry periods and rainy periods with floods. The Tinto river sediments are gray sands, including quartz and slate elements and abundant detrital pyrite grains that are weakly weathered and slightly rounded.

Methods and Materials

A core was drilled (lat. 37°18'16", long. 6°48'10"), down to the bedrock, through the Holocene sediments of the upper part of the Rio Tinto estuary (Fig. 1). This zone corresponds today to a flood plain that is usually dry, being 1.15 m above the mean high-water level. The core, 7 cm diameter, is about 15 m in length. Core recovery was relatively good (92%) and the core material was only moderately disturbed and fragmented; consequently, there is no uncertainty in depth control. Core material was protected in a PVC sheath. It was sawed longitudinally in four parts for lithological, geochemical, and dating studies, and the last part was kept as reference. Lithology was studied both using optical microscopy and scanning electronic microscopy to investigate the sulfide phases. Twenty samples of core material (30–50 g dry material) were selected for major and trace elements analysis (Fig. 2).

Present sediments from the Tinto river were collected randomly within the uppermost 5 cm. They were dried before examination by SEM, then analyzed (30–50 g) for major and trace elements. The sulfide sludge from Aznalcollar was collected along the banks of the Guadiamar river one day after the spill.

The geochemical analyses for major (including S, CO_2,and organic C) and trace elements (including Cl and Hg) were done by X-RAL laboratories (Don Mills, Ontario, Canada) and at the Montpellier University, using XRF (X-ray fluorescence), NAA (neutron activation analysis), ICP-MS (inductively coupled plasma-mass spectrometry) and AA (Atomic Absorption) spectrophotometry.

The SEM investigations were performed with a Hitachi S-4500 instrument coupled with an energy-dispersive X-ray spectrometer (EDS); detection limits were about 0.1 percent, with a precision within 20 percent.

Activation mass spectrometry (AMS) radiocarbon dating was performed by Beta Analytic, Inc. (Miami). The analyzed sediment samples (35–75 g) contained enough organic carbon (0.5–1%) to ensure accurate analysis and all analytical steps went normally (graphitization and AMS radiocarbon counting); a charcoal fragment (4.3 g) was picked for complementary analysis. The conventional ^{14}C ages were calibrated to calendar years using the Pretoria Calibration Procedure based on tree-ring data as calibration curves (dendrocalibration); the calibrated ages are given BC ages with 95 percent probability.

The ^{210}Pb determinations were done on the uppermost 30 cm of the core in order to determine the chronology of pollu-

TABLE 1. Metal Contents of the Two Anomalous Horizons of the Core and Comparizon with the Normal Estuarian Sediments of the Core

	Zn	Cu	Pb	As	Cd	Sn	Ag	Tl	Hg	Au	Ba
Rio Tinto massive sulfide ore (avg)[1]	20,000	7,000	7,000	2,000	150	350	45	35	40	0.8	Unknown
Pyritic tailings of Aznalcollar (spill)	21,200	2,120	8,500	6,100	31	22	50	103	Unknown	0.06	70
Pyrite-rich sand from the Tinto river	3,200	950	1,200	3,900	57	20	14	24	12	0.07	2,900
Upper pyrite-rich sand horizon (core)	300	760	5,300	1,400	9	100	17	18	5.1	0.2	3,400
Lower pyrite-rich sand horizon (core)	240	400	2,500	900	6	45	10	12	3.0	0.1	1.600
Normal estuarian black mud (core)	67	24	7	12	<1	2	0.9	0.4	0.04	0.003	230

All values given in ppm

Metals concentrations in the sands from the upper part of the Tinto river, in Rio Tinto massive pyrite ore, and in pyrite sludge released from the Aznalcollar spill are given for comparizon with the anomalous horizons of the core

[1] Leistel et al. 1993

tion associated with modern mining (Davis et al., in press); analyses were conducted at Florida State University by W. Burnett and associates.

Results

Lithostratigraphy

From bottom to top, the following materials are present in the core (Fig. 2): (1) coarse detrital sediments (fluvial channel and fluvial bar); (2) shelly and sandy black muds, including shell-rich horizons with authigenic pyritic nodules (estuarine accretion bodies); (3) muddy sands with shell fragments (estuarine channel); (4) alternating yellow sands and dark green muds (channel margins); and (5) yellow sands of the flood plain at the top of the core. This uppermost horizon results from flood deposits that may be strongly erosional, as suggested by the lithologic break and the sharp discontinuity with the underlying muddy horizon. Almost every year there is a major flood from the Tinto river, eroding and/or depositing up to 50 cm of sandy material on the flood plain.

Presence of metal-rich horizons

The trace metal contents in the Holocene estuarine sediments (Fig. 2, Table 1) are similar to averaged continental sediments (Taylor and McLennan, 1985). The highest contents are in organic carbon-rich sediments containing diagenetic pyrite (Fig. 3D) overgrowing plant debris or shell fragments. Against this normal geochemical background two remarkable horizons (0–1.3 m and 3–4 m) are characterized by metal concentrations that are two orders of magnitude higher than those of the other layers (Fig. 2). These horizons contain 2,500 to 5,300 ppm Pb and 900 to 1,400 ppm As, respectively. In both cases the same metal association is present, composed of high Pb, Ba, As-Cu, Zn-Sn, Tl-Cd, Ag, Hg-Au, in decreasing order of importance.

SEM observations (Fig. 3)

The two anomalous horizons are also remarkable for their mineralogic composition. They consist mainly of light yellow sands and silts, including abundant clastic pyrite grains (2–12 wt %). The pyrite grains are small and well sorted (20–50 μm); they correspond to angular fragments of subhedral pyrite grains (Fig. 3A2) that have been only slightly rounded, and which exhibit only rare dissolution pits and cracks. The only oxidized material consists of ochre fragments in the silt layers. EDS-SEM investigations suggest that galena is present as small accessory grains (1–5 μm), partly included in pyrite; rare gold inclusions (0.5 μm) are also present in pyrite. The high barium content is clearly explained by the presence of lamellar fragments of barite in the pyrite-rich sands. Cassiterite is present as small, perfectly euhedral crystals (10 μm), explaining the high Sn contents (40–100 ppm Sn).

The lower horizon (0.5–1.2% organic carbon) contains black plant fragments that often display woody cellular textures (Fig. 3C). These charcoal fragments are very small and well sorted (0.1–1.2 mm). A few small globules (30–500 μm) of vesicular glass, with smooth surfaces, are also present in this horizon (Fig. 3B). EDS-SEM analysis suggests they consist either of a Fe-Si glass, with traces of sulfur, or of a carbon-iron material with small contents of copper and sulfur (0.1–1%). These compositions, which differ from those of natural vesicular glasses, such as lavas, are similar to those of scorias and slags from metallurgical furnaces.

Dating results

The four ^{14}C calibrated ages (BC) obtained are consistent with the relative stratigraphic position of the analyzed samples (Fig. 2) : 6,000 ±140 yr for the base of the estuarine accretion bodies (12.5 m); 3,600 ±100 yr for the base of the estuarine channel (7.5 m); 2,530 ±70 yr for the lower metal-contaminated horizon (4 m) and 1,930 ±–55 yr for the floor of the uppermost metal-contaminated horizon (1.3 m).

The ^{210}Pb concentrations along the uppermost 30 cm of the core (Davis et al., in press) are strikingly constant and relatively high (8 ± –2 Bq/kg).

Discussion

Evolution of the Holocene depositional environment

The lithostratigraphic sequence and the ^{14}C ages correspond fairly well to the Holocene transgression that started in the Huelva area about 8,000 BC, filled up the estuary, and ended with a stabilization of the sea level about 3,000 BC (Borrego et al., 1999). The transgression is connected with a deglacial sea-level rise (Mannion, 1997). From ^{14}C radiodating, it appears the sedimentation rates of the estuarine sediments were between 1 and 7 mm/yr.

The two metal-contaminated horizons correspond to well-sorted sandy flood deposits. The lower horizon results from input of fluvial sands during a progradation stage in the estuarine system; the overlying muddy and shelly horizon corresponds to tidal sediments along channel margins. The upper horizon results from discontinuous input of fluvial sands over the surface of the flood plain—which is usually dry—during seasonal floods.

Geochemical and mineralogical evidence for metal contaminations from the Rio Tinto mineralization

The metals present in these two anomalous horizons reflect fairly well those of the Rio Tinto sulfide ore, including base and trace metals (Table 1). For example, the relatively high Au content of the pyritic horizons (0.1–0.2 ppm) is in agreement with the presence of gold in the Rio Tinto mineralization (0.5–1.5 ppm); SEM observations reveal that gold inclusions are present in the detrital pyrite grains. The abundance of barium, and the presence of barite detrital grains, may be explained by the fact that barite is a common gangue mineral of the sulfide ores. The relatively high Sn concentrations and the presence of cassiterite grains are in agreement with the presence of cassiterite in the Rio Tinto ore. The arsenic concentrations in detrital pyrite grains, which have been picked up from the core, range from 1 to 2 percent As, explaining the high arsenic contents of the pyrite-rich horizons.

However, the order of abundance is not exactly the same. For example, Zn and Cd concentrations are low compared to the other base metals (Pb, Cu) in the pyrite-rich sands. This may be explained either by the fact that Zn and Cd are relatively more easily soluble in surface waters or that sphalerite was not abundant in the transported pyritic material.

The pyrite grains from the two metal-contaminated horizons are angular clastic pyrite grains (Fig. 3A2) that may be slightly rounded and corroded. They are clearly different in shape and size from the authigenic pyrite crystals and the spherulitic agregates of pyrite (Fig. 3D) that are present in the shelly black mud horizons of the core (Fig. 2). The only obvious source of pyrite in the catchment zone of the Tinto river is the Rio Tinto mining area. There are outcropping massive pyrite orebodies, with subhedral pyrite grains similar in shape and size to those of the anomalous horizons of the core, and huge stockpiles of pyrite-rich tailings and wastes from modern mining activity. The pyrite grains are very abundant in the present surface sands collected along the bed and the banks of of the Tinto river: in the immediate vicinity of the mine area, there are pyritic sands containing up to 60 wt percent pyrite, and downstream from the coring location, the estuarian sediments still contain 1 to 10 wt percent pyrite. The pyrite-rich sediments of the Tinto river display very high concentrations of toxic metals (0.5% As, 0.5% Pb, 0.3% Zn, 0.2% Cu; Table 1). These high metal contents can be ascribed to pyrite (this is the case for As) or to discrete Pb-Zn-Cu sulfide phases associated with or included in pyrite. The clastic pyrite grains from the surface sands along the Tinto river are similar in shape and size (Fig. 3A1) to those from the metal-contaminated horizons at depth in the core, providing evidence that pyrite grains may be transported by the Tinto river from the Rio Tinto mining zone to the estuarine zone. Considering the hydric flow during seasonal flood events and the average geometry of the Tinto river, the rate of sediment transport can be roughly calculated: the time for the transportation of the pyrite grains—from the source zone to the estuary—may be from 15 to 45 hours. Consequently, the pyrite grains may be deposited very quickly in the estuarine sediments without having suffered any weathering during their transportation. The same shape and size of pyrite grains characterize the pyritic sludge released within a few hours by the Aznalcollar tailings spill in the Donana national park, 40 km downsream (Fig. 1).

These geochemical and mineralogical observations are the first indication that the two anomalous horizons correspond to input of pyrite-bearing and metal-rich sands resulting from mining activity in the Rio Tinto source region.

Age of the upper metal-contaminated horizon

The impact of intensive modern mining activity that started 130 yr ago has been clearly recorded in shelf surface sediments of the Gulf of Cadiz (Van Geen et al., 1997). The upper metal-contaminated horizon of the core may correspond to this modern mining. The uppermost 30 cm of the core have high and constant ^{210}Pb concentrations; this means that the upper part of the upper contaminated horizon was deposited a short time ago, probably during recent flood events. However, considering the discontinuous sedimentary and/or erosional history of the flood plain of the upper estuary, we are not sure that this 1.3-m-thick pyrite-rich horizon corresponds in its entirety to the modern mining period. A ^{14}C AMS radiocarbon dating was performed on an ochre layer, just below the upper horizon (Fig. 2). The ochre has an age of 1930 ±50 BC (calibrated age). This is consistent with the chronostratigraphy of the core but indicates that the upper part of the Holocene sequence has been eroded before or during the deposition of the upper, metal-contaminated horizon.

Age of the lower metal-contaminated horizon

The lower horizon has been dated at 2530 ±70 BC (AMS ^{14}C calibrated age). The analyzed sample (pyrite-rich sand) contains 1 percent organic carbon. Tiny black fragments of charcoal are the only possible organic carbon source; there are no shell fragments or carbonate (<0.1%). Dating of a single charcoal material, picked up 10 cm below the first dated sample, has given a 500-yr older age (3015 ±70 yr BC), which could indicate derivation from a 500-yr-old tree ("old wood effect") or material derived from an older layer. Although the ancients may have been burning old wood in their furnaces, this is unlikely to have significantly affected the observed ^{14}C stratigraphy of the core. The logical progression of ^{14}C dates down the core suggests that resedimentation processes in the estuary have not resulted in major disturbances in in the chronostrtigraphy.

These ages correspond to the Copper Age in the western Mediterranean area and confirm that active mining started early in the Rio Tinto district.

The presence of small droplets and fragments of likely slags (vesicular glasses with Fe-Si or C-Fe compositions and up to 0.5% copper and sulfur) in the lower horizon (Fig. 3B), is compelling evidence for contemporaneous metallurgical activity. In the same way, the presence of tiny and well-sorted charcoal fragments may reflect the common use of small charcoal fragments during metallurgical treatments.

Copper Age mining and metallurgy in the Rio Tinto area

The oldest findings indicate that metallurgical activities in the region date from 2700 BC (Rothenberg and Blanco Freijero, 1980). Except for a few metal tools in some graves and scarce traces of mining excavations and ovens, there has been little evidence of important Copper Age mining activity in the Rio Tinto district. However, the Almerian Copper Age civilization (3000–2200 BC) is well known in eastern Andalusia, Spain, for the important development of copper mining and metallurgy (i.e., in the fortified site of Los Millares, Almeria). Similar activity was likely taking place in western Andalusia, notably in the Rio Tinto area (Briard, 1976). Unfortunately, the subsequent mining periods probably erased most of the Chalcolitic mining and metallurgical works. The Romans started their mining activity from the Tartessian-Phoenician works, and active mining today recovers gold (1–1.5 ppm) from the Roman mining wastes.

Conclusions

1. We show here a new record of watershed-scale impact of early mining, over a distance of about 100 km. A 4,500-yr-old (2530 BC) metal contamination, caused by Copper Age mining, has existed in southern Spain. Notwithstanding the recent accident at Aznalcollar, it is possible that long-term release of metals from ancient mining operations that have not received the benefit of modern remediation may be a more serious problem than the impact of much larger, modern-day operations.

2. Anthropogenic input of metals may remain immobilized for millennia in estuarine sediments. Most metals can be locked as sulfides in estuarine sediments where anoxic condi-

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