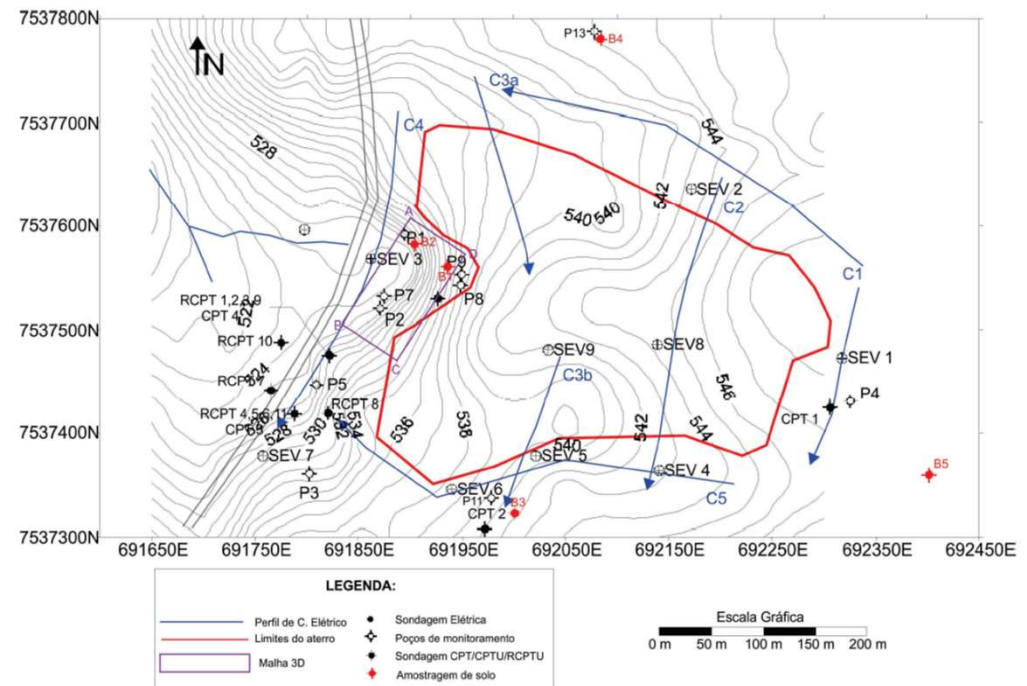


## Exercício individual 4 (entrega 08/12/22)

- (1) Avaliar as análises químicas de água subterrânea do Aterro Sanitário de Bauru, usando a ferramenta dos mapas de contorno das concentrações de Cl, Fe, K e Ca.
- (2) Avaliar as análises químicas de água subterrânea do Aterro Sanitário de Bauru, usando a ferramenta dos mapas de contorno da razão DBO/DQO.





# **Metais tóxicos no ambiente**

**Andréa Teixeira Ustra**

**AGG 0201 Geoquímica de Ambientes Superficiais**

# Metais no ambiente

- Fundações da civilização (Au, Cu, Ag, Pb, Sn, Fe e Hg)
- Era industrial – emissão e disposição de metais no ambiente
- Acúmulo em ambientes terrestres e aquáticos em altas concentrações – nocivo aos animais e humanos (ingestão via solo, alimento, água e ar)



Element	Natural source or metallic minerals	Anthropogenic sources	Common forms in wastes
Ag	Free metal (Ag), chlorargyrite (AgCl), acanthite (Ag <sub>2</sub> S), copper, lead, zinc ores	Mining, photographic industry	Ag metal, Ag–CN complexes, Ag halides, Ag thiosulfates
As	Metal arsenides and arsenates, sulfide ores (arsenopyrite), arsenolite (As <sub>2</sub> O <sub>3</sub> ), volcanic gases, geothermal springs	Pyrometallurgical industry, spoil heaps and tailings, smelting, wood preserving, fossil fuel combustion, poultry manure, pesticides, landfills	As oxides (oxyanions), organo-metallic forms, H <sub>2</sub> AsO <sub>3</sub> CH <sub>3</sub> (methylarsinic acid), (CH <sub>3</sub> ) <sub>2</sub> -AsO <sub>2</sub> H (dimethylarsinic acid)
Be	Beryl (Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> ), phenakite (Be <sub>2</sub> SiO <sub>4</sub> )	Nuclear industry, electronics industry	Be alloys, Be metal, Be(OH) <sub>2</sub>
Cd	Zinc carbonate and sulfide ores, copper carbonate and sulfide	Mining and smelting, metal finishing, plastic industry, microelectronics, battery manufacture, landfills and refuse disposal, phosphate fertilizer, sewage sludge, metal scrapheaps	Cd <sup>2+</sup> ions, Cd halides and oxides, Cd–CN complexes, Cd(OH) <sub>2</sub> sludge
Cr	Chromite (FeCr <sub>2</sub> O <sub>4</sub> ), eskolaite (Cr <sub>2</sub> O <sub>3</sub> )	Metal finishing, plastic industry, wood treatment refineries, pyrometallurgical industry, landfills, scrapheaps	Cr metal, Cr oxides (oxyanions), Cr <sup>3+</sup> complexes with organic/inorganic ligands
Cu	Native metal (Cu), chalcocite (Cu <sub>2</sub> S), chalcopyrite (CuFeS <sub>2</sub> ),	Mining and smelting, metal finishing, microelectronics, wood treatment, refuse disposal and landfills, pyrometallurgical industry, swine manure, pesticides, scrapheaps, mine drainage	Cu metal, Cu oxides, Cu humic complexes, alloys, Cu ions
Hg	Native metal (Hg), cinnabar (HgS), degassed from Earth's crust and oceans	Mining and smelting, electrolysis industry, plastic industry, refuse disposal/landfills, paper/pulp industry, fungicides	Organo-Hg complexes, Hg halides and oxides, Hg <sup>2+</sup> , (Hg <sub>2</sub> ) <sup>2+</sup> , Hg <sup>0</sup>

Element	Natural source or metallic minerals	Anthropogenic sources	Common forms in wastes
Ni	Ferromagnesian minerals, ferrous sulfide ores, pentlandite	Iron and steel industry, mining and smelting, metal finishing, microelectronics, battery manufacture	Ni metal, Ni <sup>2+</sup> ions, Ni amines, alloys
Pb	Galena (PbS)	Mining and smelting, iron and steel industry, refineries, paint industry, automobile exhaust, plumbing, battery manufacture, sewage sludge, refuse disposal and landfills, pesticides, scrapheaps	Pb metal, Pb oxides and carbonates, Pb-metal–oxyanion complexes
Sb	Stibnite (Sb <sub>2</sub> S <sub>3</sub> ), geothermal springs	Microelectronics, pyrometallurgical industry, smelting, mine drainage	Sb <sup>3+</sup> ions, Sb oxides and halides
Se	Free element (Se), ferroselite (FeSe <sub>2</sub> ), uranium deposits, black shales, chalcopyrite–pentlandite–pyrrhotite deposits	Smelting, fossil fuel combustion, irrigation waters	Se oxides (oxyanions), Se-organic complexes
Tl	Copper, lead, silver residues	Pyrometallurgical industry, microelectronics, cement industry	Tl halides, Tl–CN complexes
Zn	Sphalerite (ZnS), willemite (Zn <sub>2</sub> SiO <sub>4</sub> ), smithsonite (ZnCO <sub>3</sub> )	Mining and smelting, metal finishing, textile, microelectronics, refuse disposal and landfills, pyrometallurgical industry, sewage sludge, pesticides, scrapheaps	Zn metal, Zn <sup>2+</sup> ions, Zn oxides and carbonates, alloys

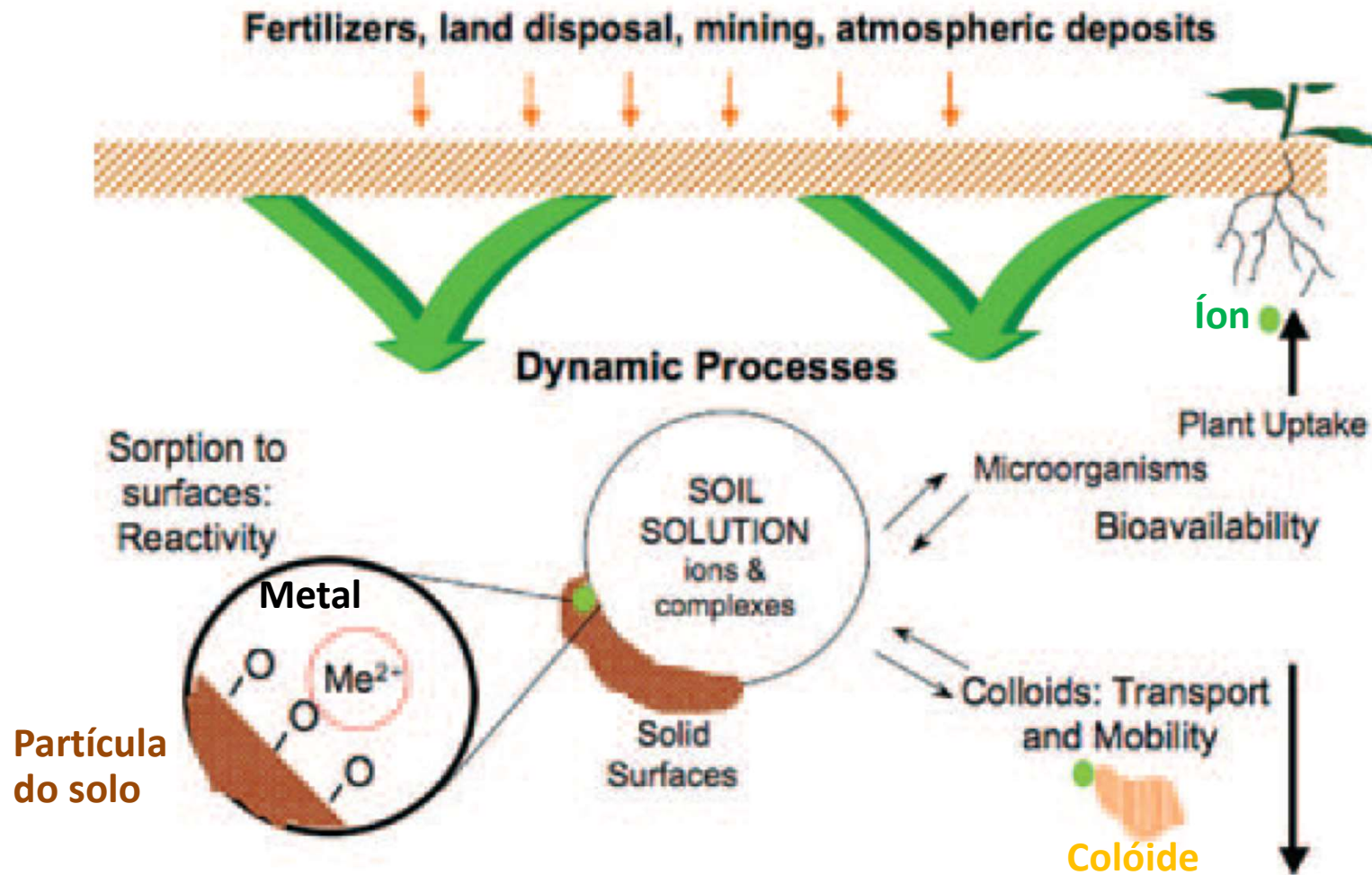
# Metais no ambiente

- Diversos processos biogeoquímicos envolvendo argilas, óxidos e hidróxidos metálicos, raízes, micróbios, substâncias húmicas
- Esses processos controlam sua solubilidade, mobilidade, biodisponibilidade e toxicidade no ambiente

# Metais nos sistemas biológicos

- Alguns metais são essenciais para plantas, animais e humanos
- Micronutrientes para plantas (B, Cu, Fe, Zn, Mn e Mo)
- Nutrição animal (As, Co, Cr, Ni, Se, Sn e V)
- Micronutrientes – pouca quantidade (diferentemente de N, P e K)
- Tóxicos em excesso
- Limitante em deficiência

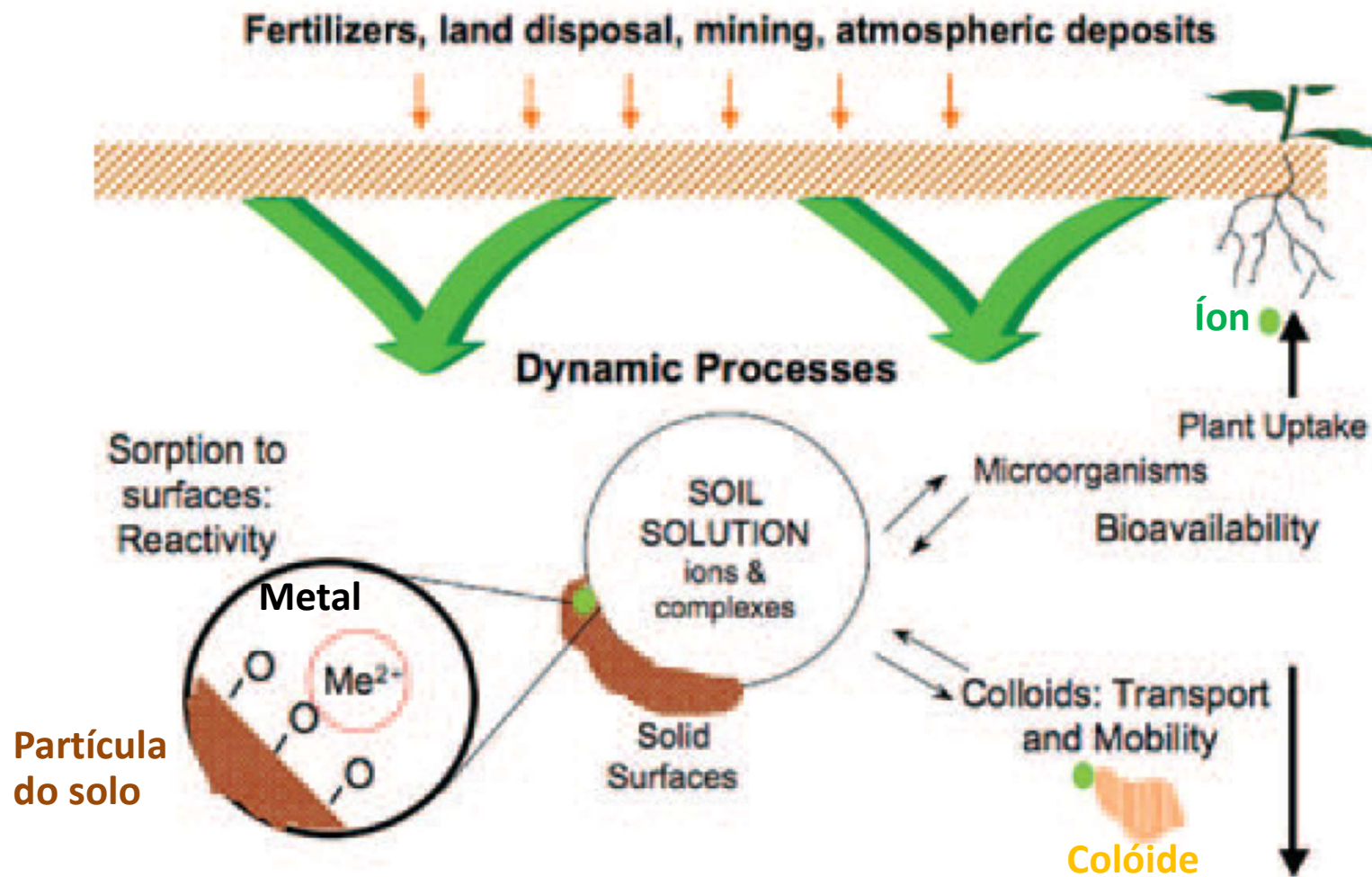
# Processos e caminhos biogeoquímicos dos metais nos solos



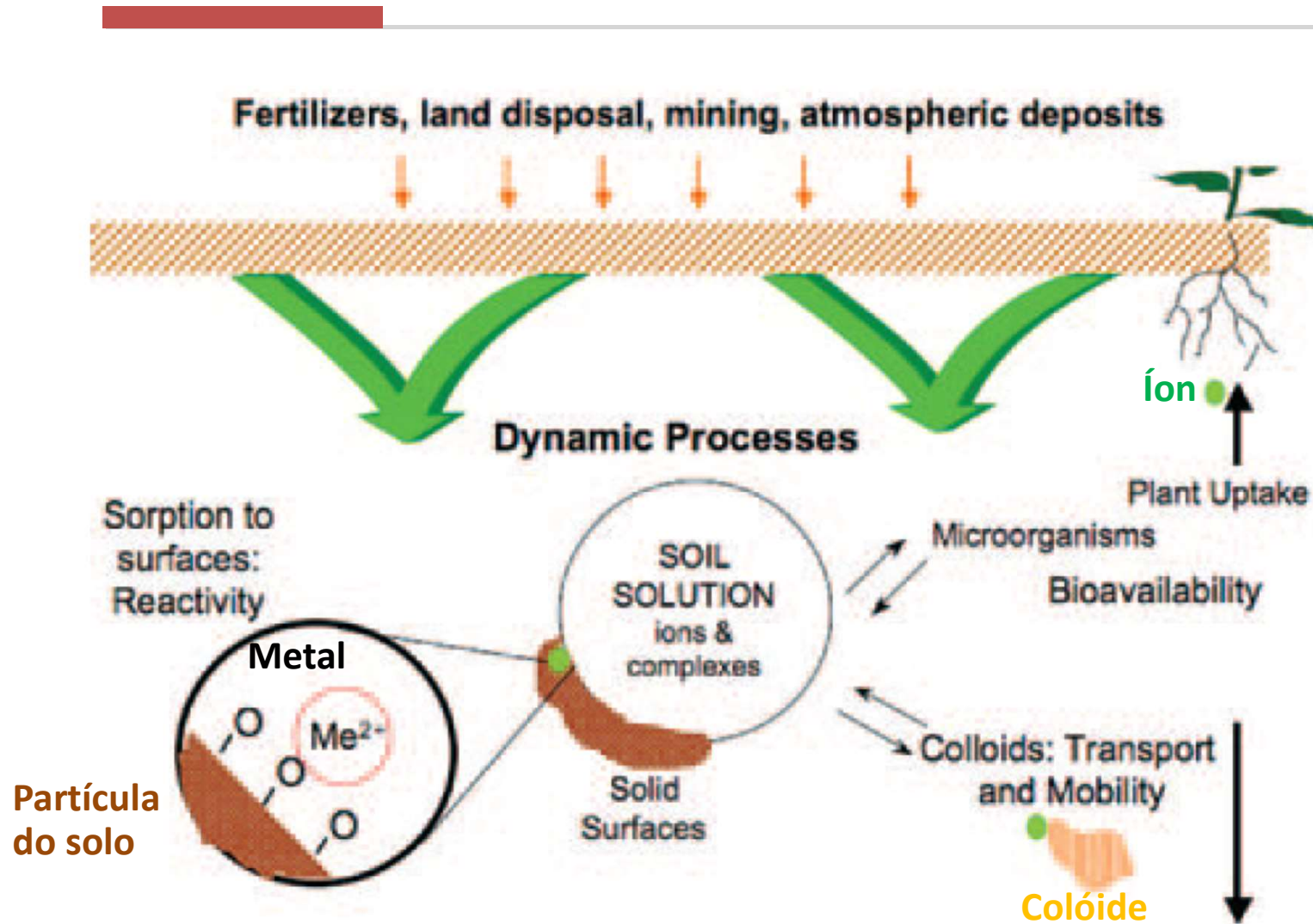


# Processos e caminhos biogeoquímicos dos metais nos solos

- Retenção por plantas

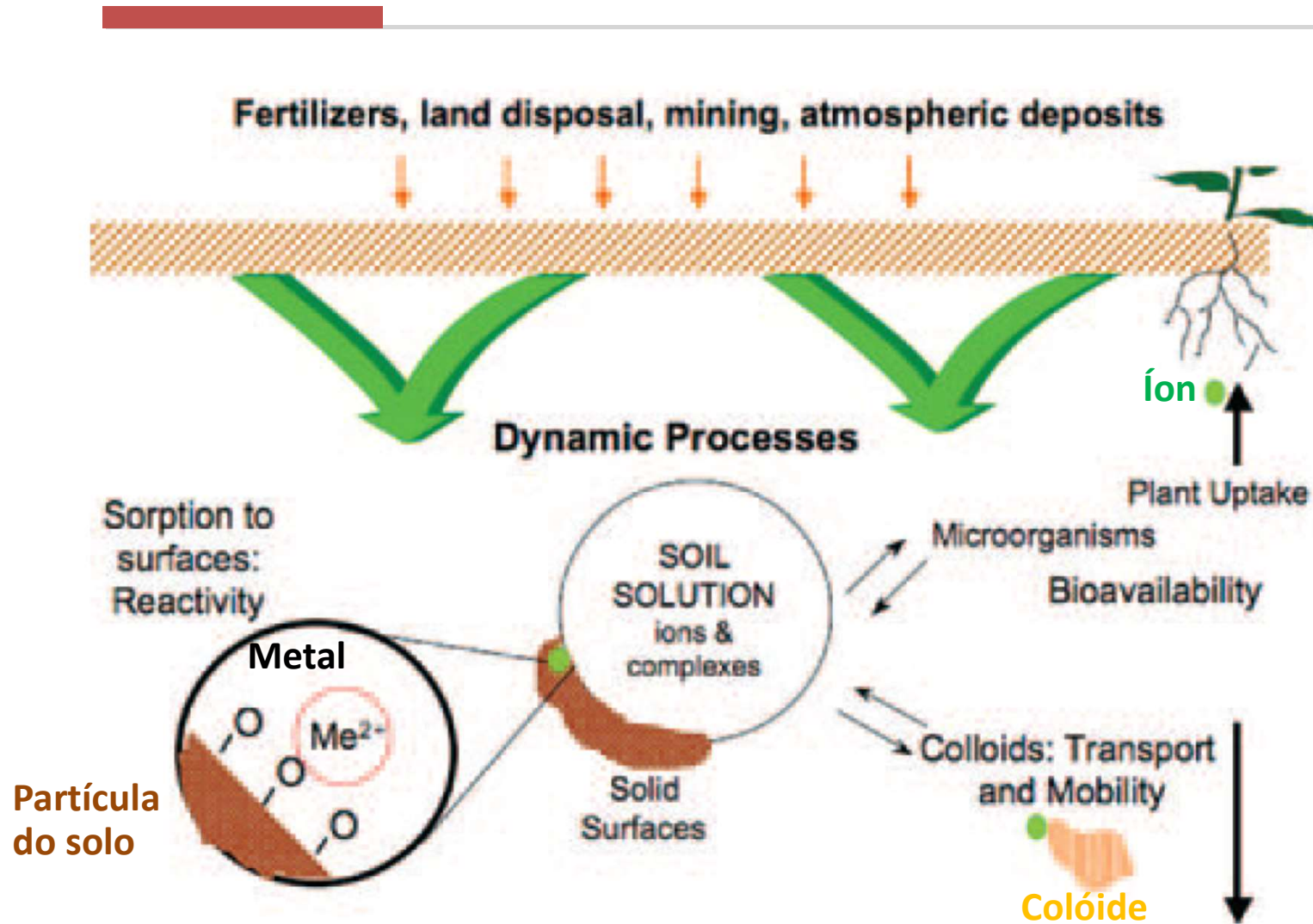


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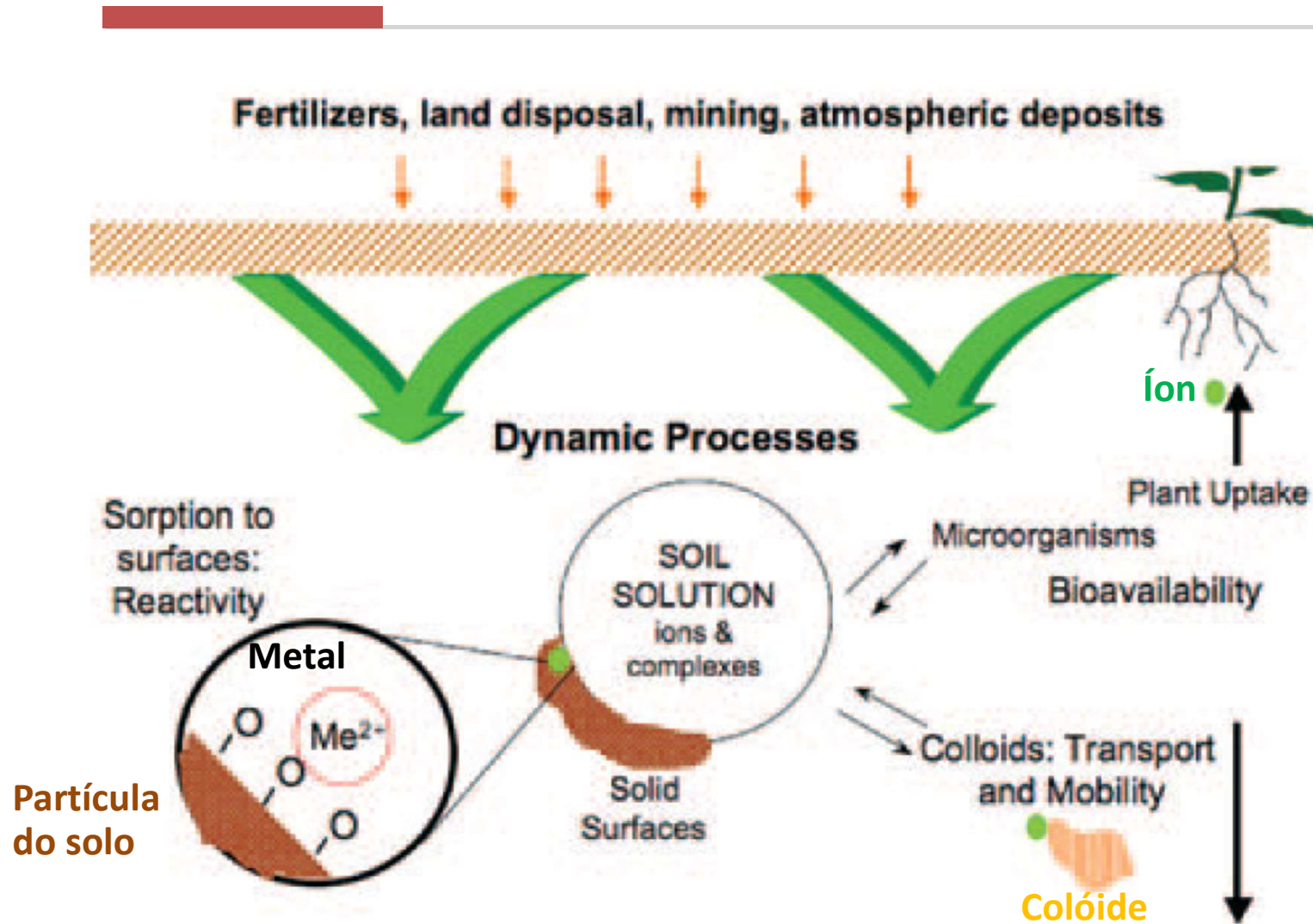
- Retenção por plantas
- Retenção por superfícies minerais, matéria orgânica e micróbios

# Processos e caminhos biogeoquímicos dos metais nos solos



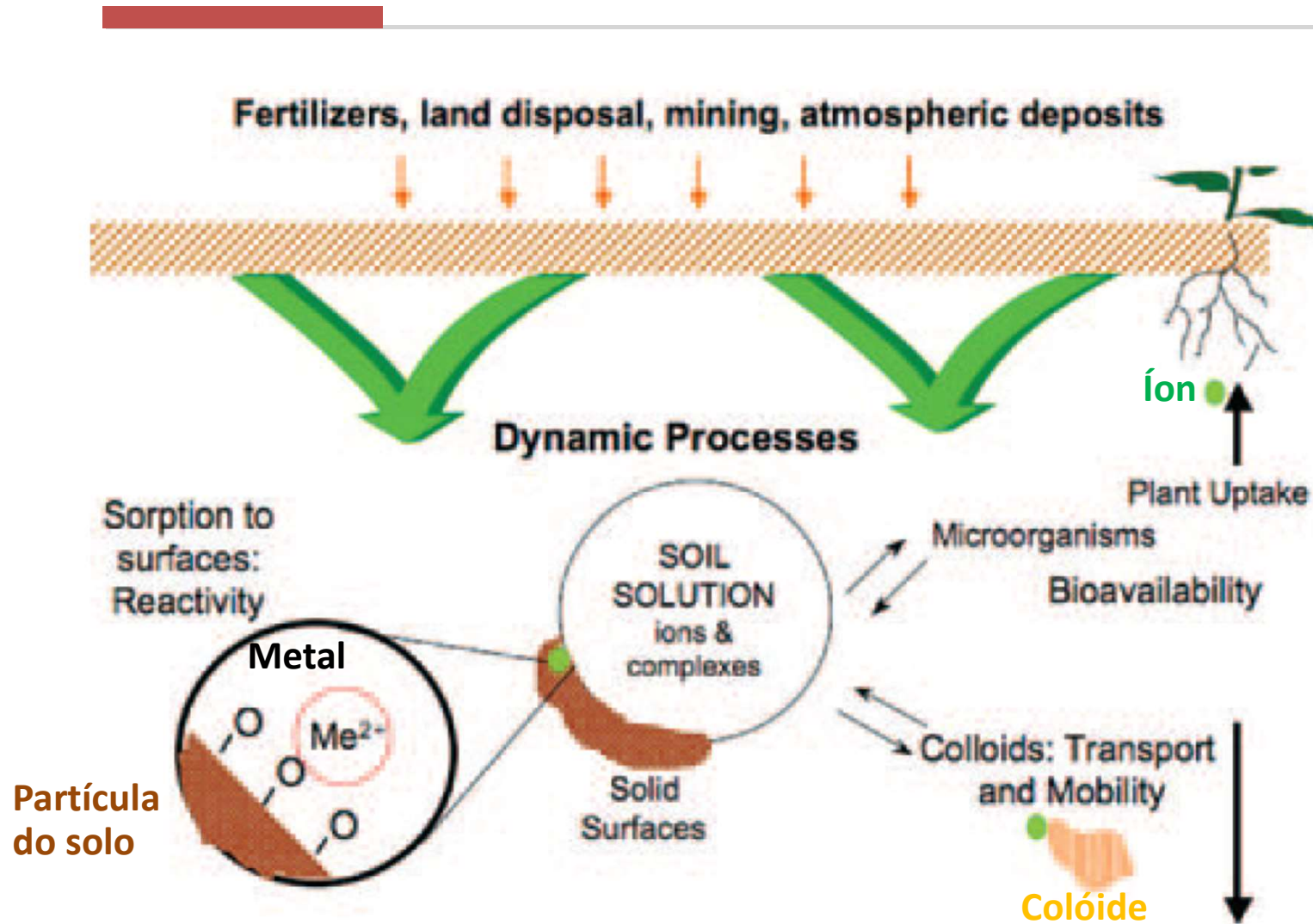
- Retenção por plantas
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- Transporte pelo solo para água subterrânea

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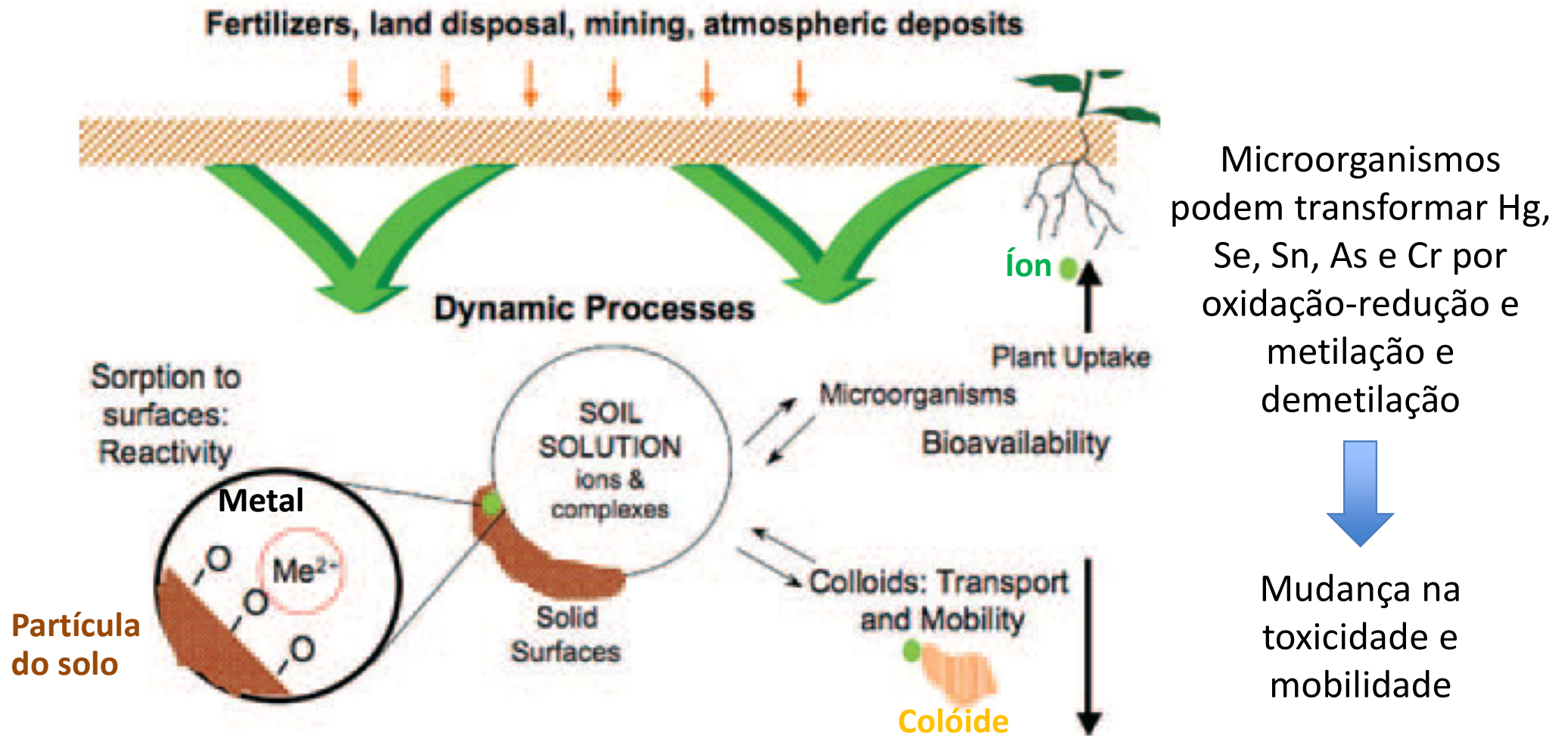
- Retenção por plantas
- Retenção por superfícies minerais, matéria orgânica e micróbios
- Transporte pelo solo para água subterrânea
- Precipitação como fases sólidas

# Processos e caminhos biogeoquímicos dos metais nos solos



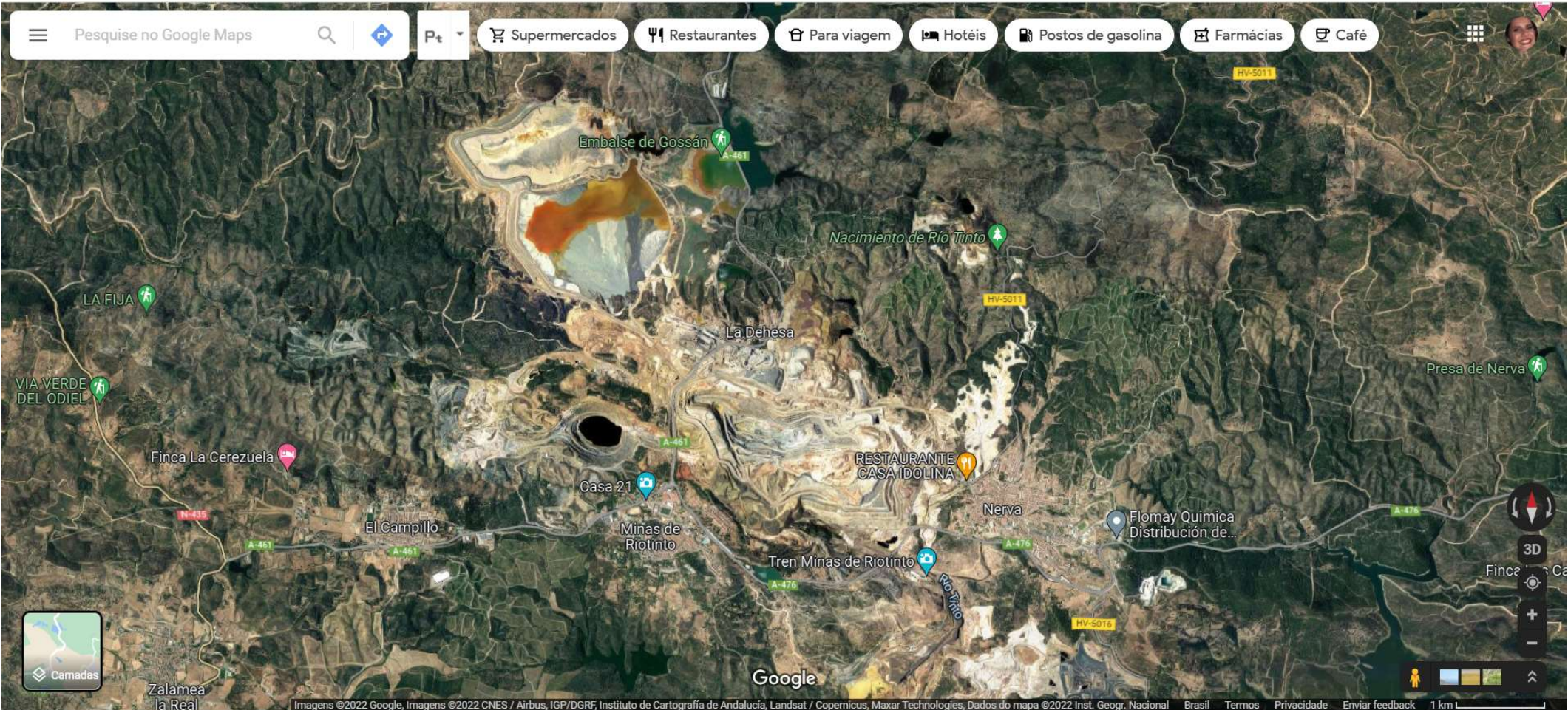
- Retenção por plantas
- Retenção por superfícies minerais, matéria orgânica e micróbios
- Transporte pelo solo para água subterrânea
- Precipitação como fases sólidas
- Difusão pelo meio poroso

# Processos e caminhos biogeoquímicos dos metais nos solos



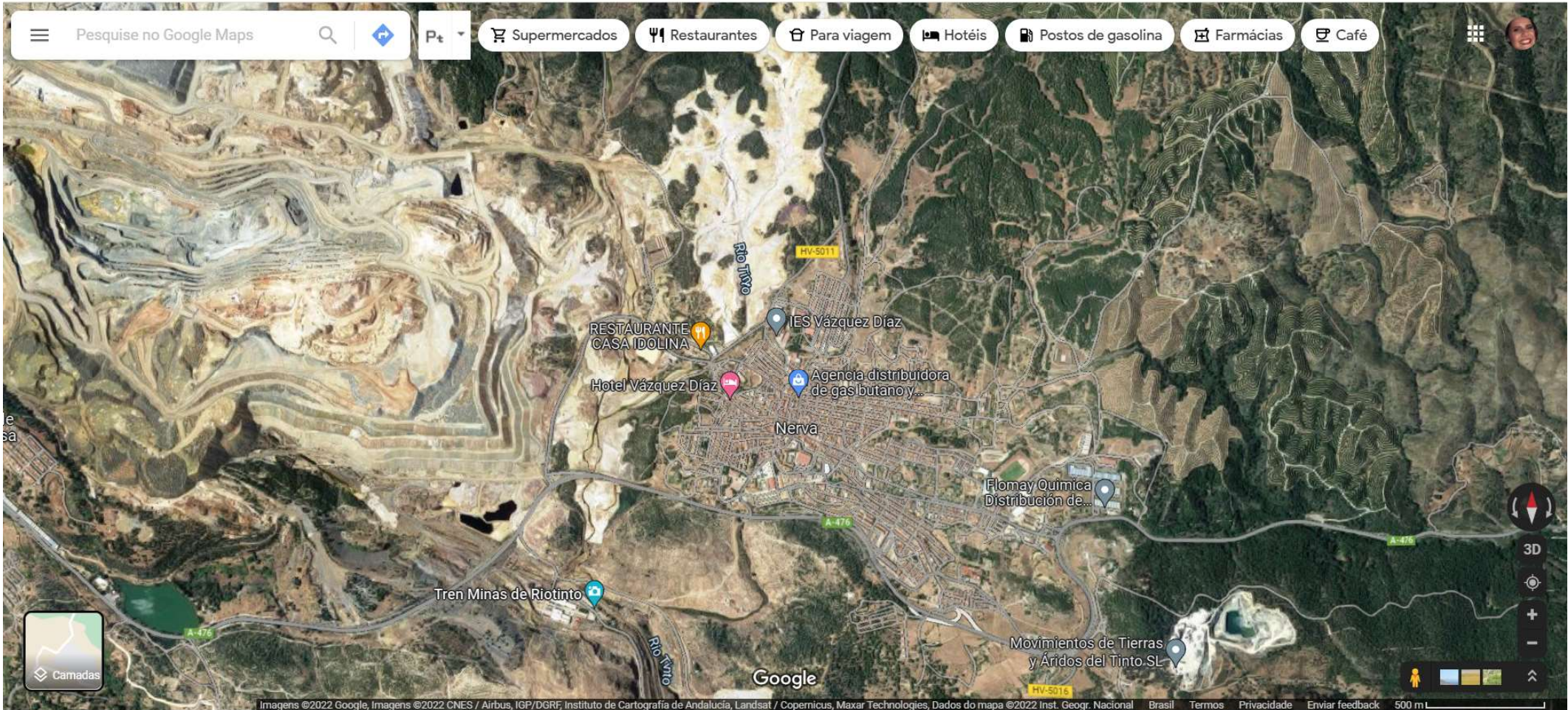
# E quanto as fontes de metais

- Exemplo: Minas Riotinto
- Intemperismo natural e pelo menos 5000 anos de mineração de depósitos de sulfetos → natural acid rock drainage (NARD) e AMD → rio vermelho e ácido (pH = ~1.7–2) → 60 km a jusante da área
- Input constante de rejeitos mantem o pH tão baixo, além de microrganismos oxidam a pirita (FeS) e dissolução de sulfatos

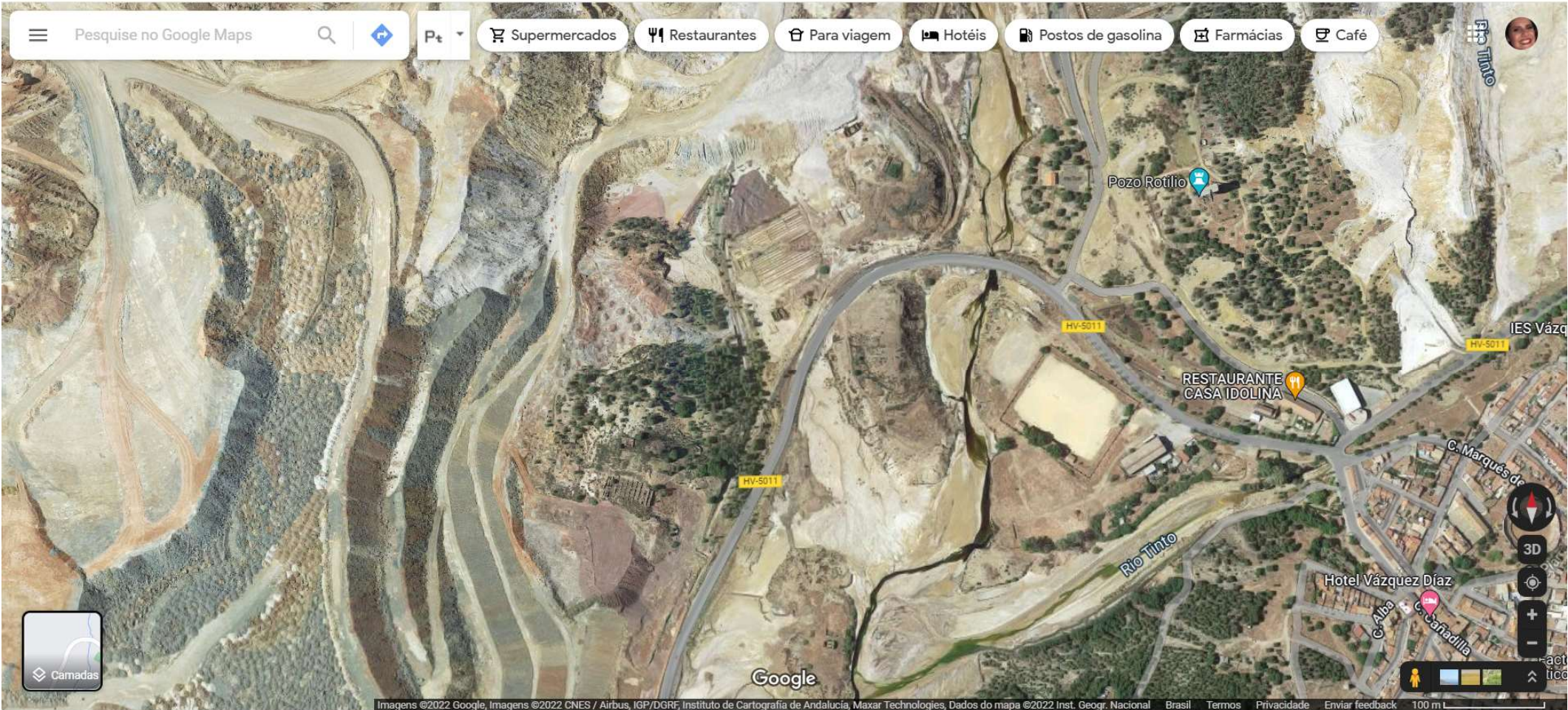


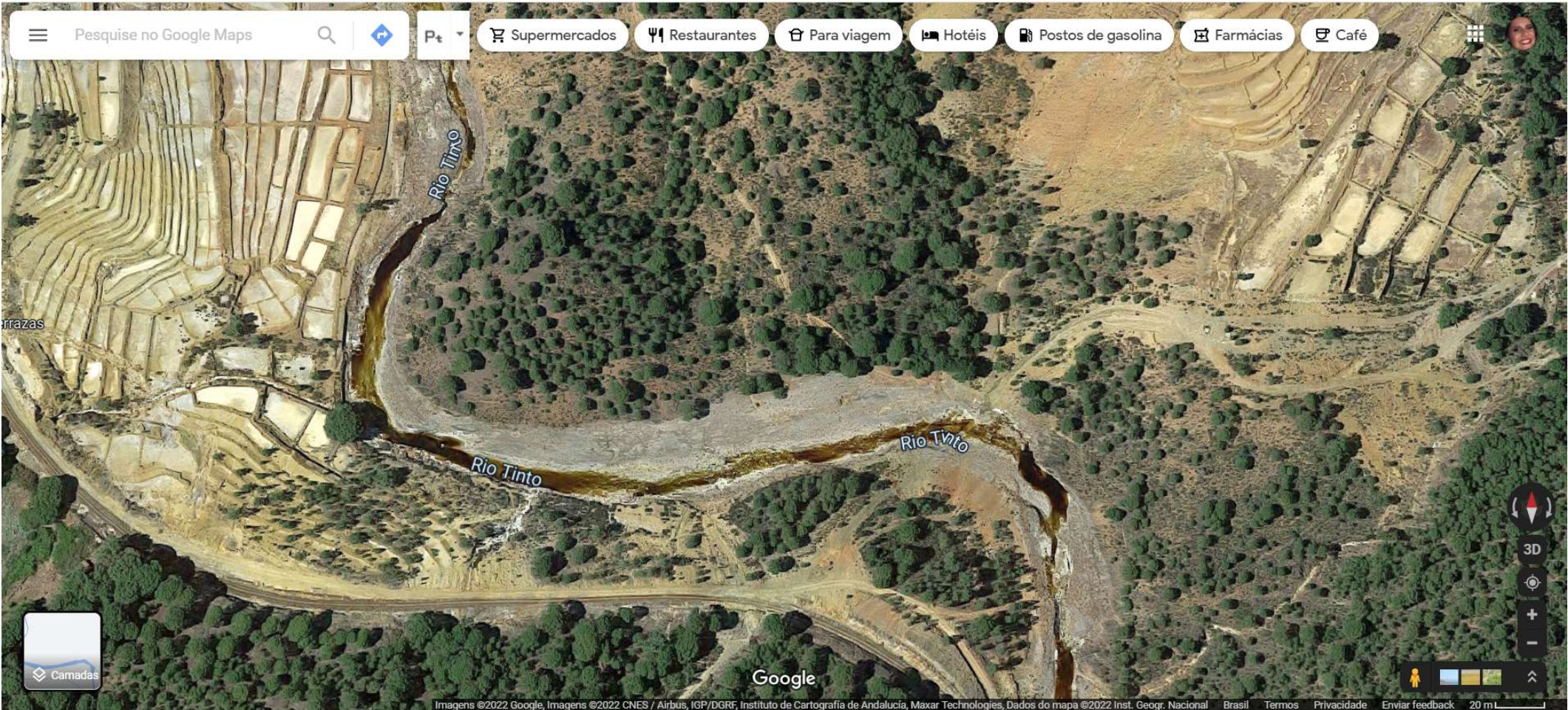


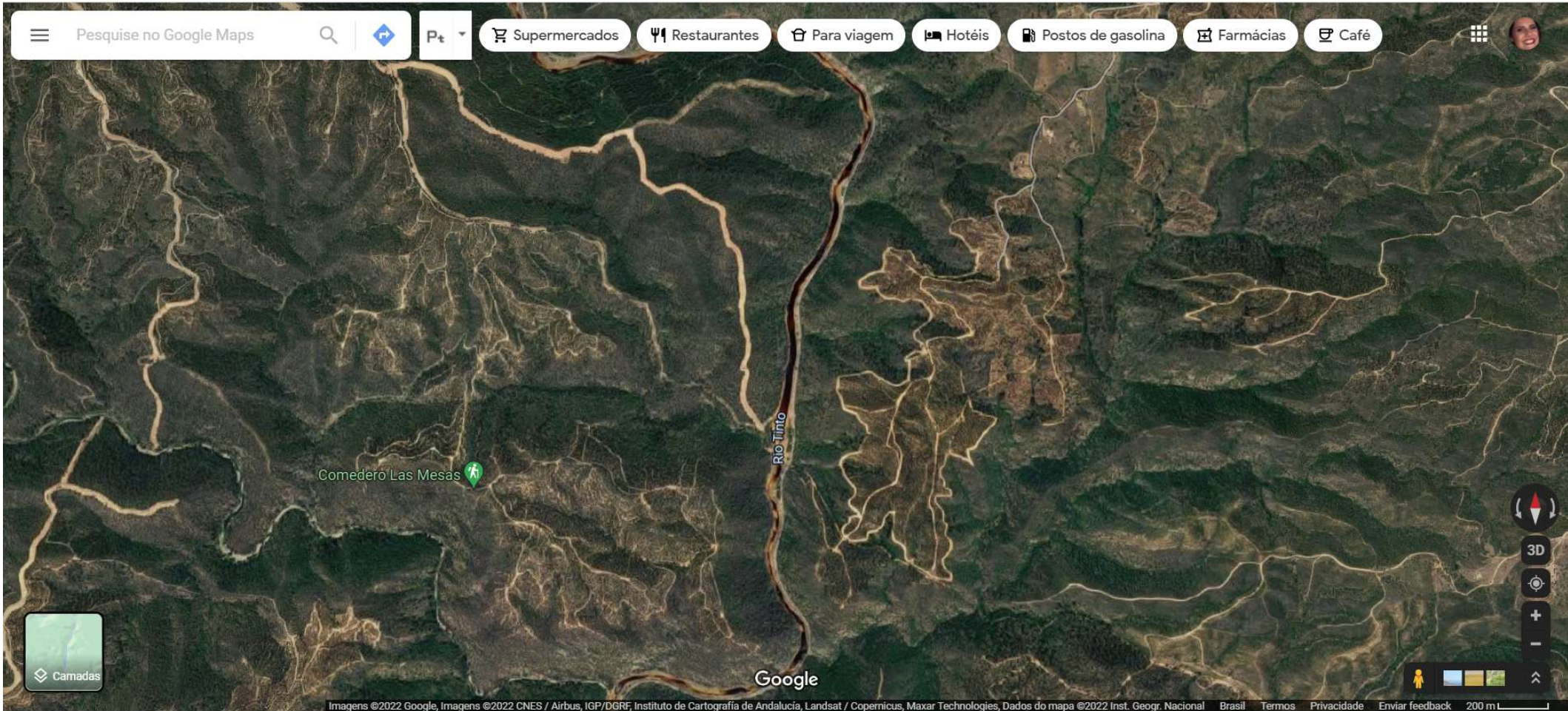


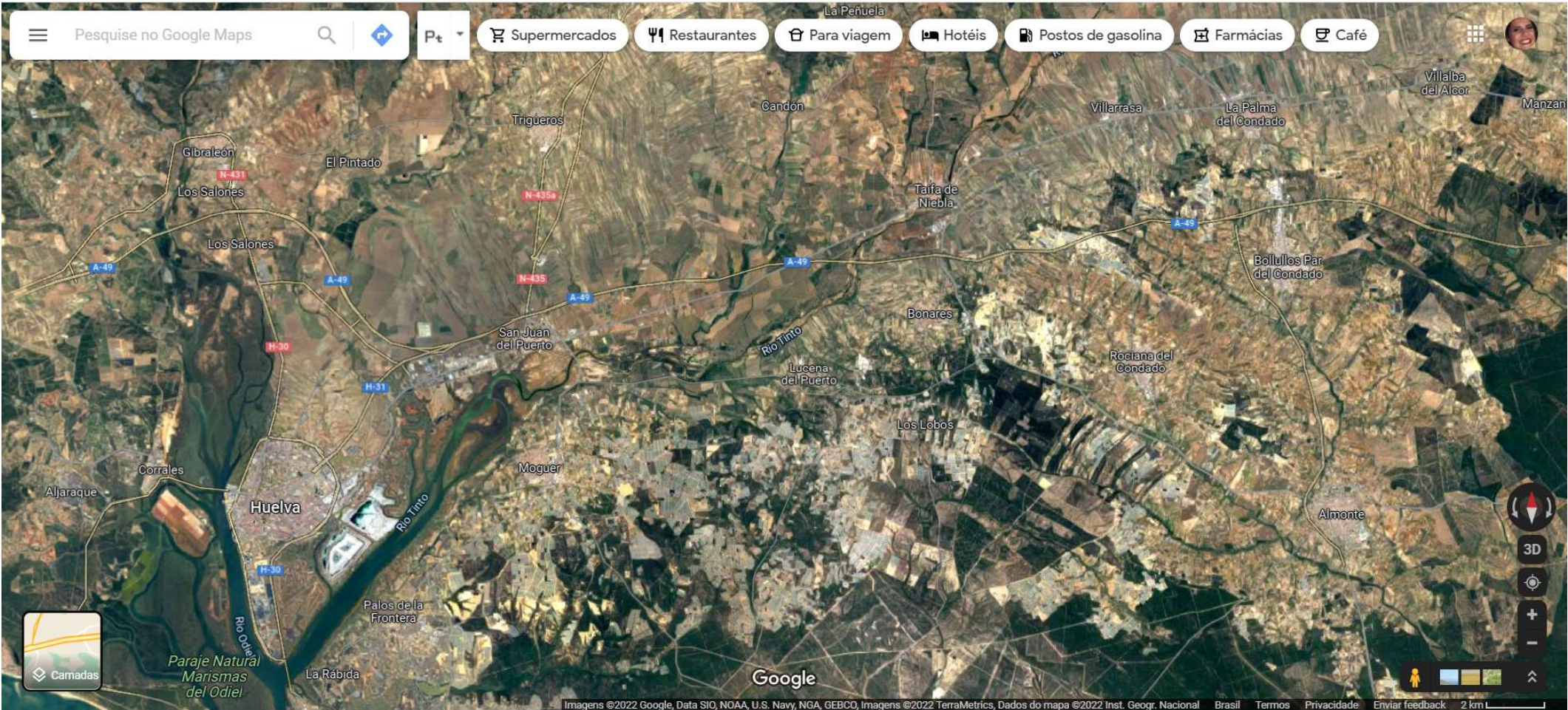












# Rejeitos de minas: Passado, presente e futuro

- Materias que não tem mais valor econômico
- Volumes grandes, frequentemente com alta concentração dos elementos e compostos nocivos ao meio ambiente



# Passado

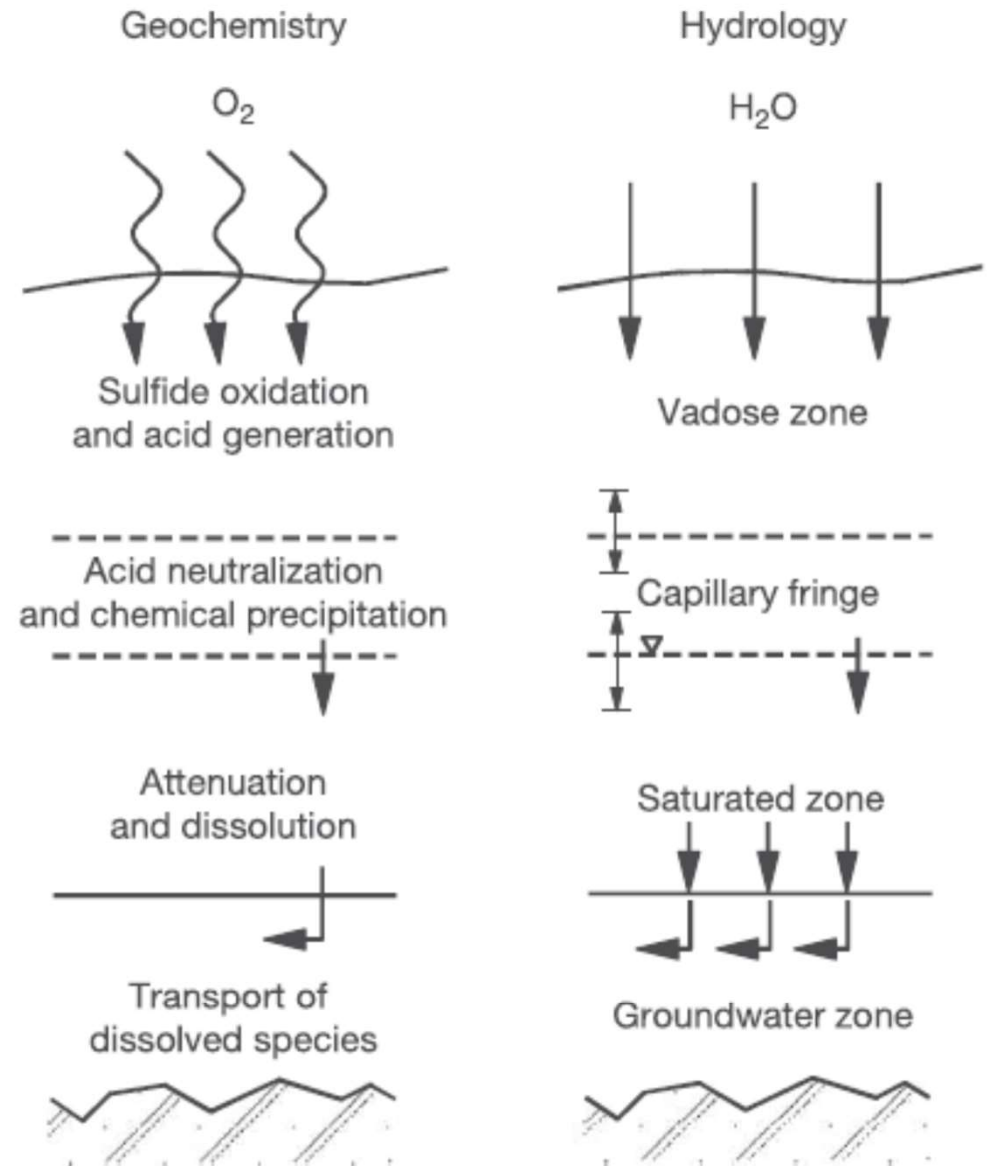
- Humanidade sempre explorou metais para uso, energia e construção
- Exploração de metais → riquezas . Ex “Idade do ouro” da Espanha nos séculos 16 e 17 foi construída pela extração de ouro e prata de minas nas Americas

## “Mining for Metal”



# Presente

- Exploração mineral → produção de grandes quantidades de resíduos sólidos e líquidos → legado ambiental global
- Resíduos podem conter As, Pb, Cn em concentrações de risco ambiental
- Acid mine drainage (AMD) = resíduos líquidos ácidos, tem grande impacto ambiental – um dos maiores desafios ambientais da indústria de mineração



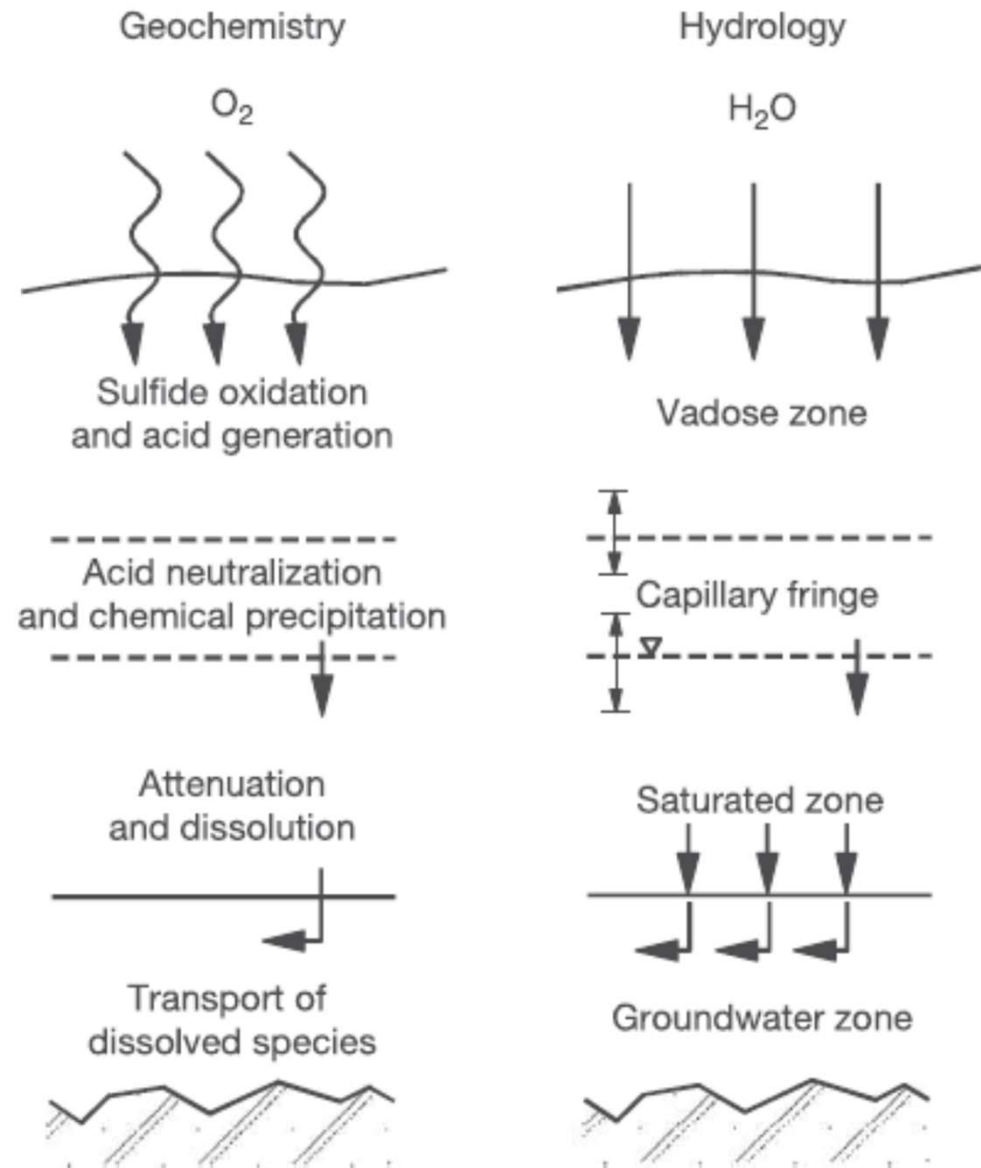
**Figure 9** Schematic diagram showing the hydrology and geochemistry of a decommissioned mine-tailings impoundment. Reproduced with permission from Blowes DW and Ptacek CJ (1994) Acid-neutralization mechanisms in inactive mine tailings. In: Blowes DW and Jambor JL (eds.) *The Environmental Geochemistry of Sulfide Mine-Wastes*, vol. 22, pp. 271–292. Nepean, ON: Mineralogical Association of Canada.

# Drenagem Ácida de Mina (DAM)

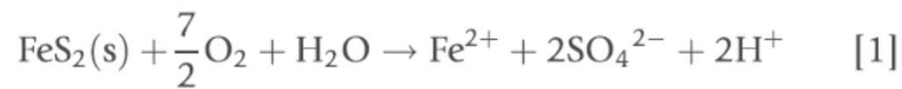
Solução ácida enriquecida em íons dissolvidos, especialmente em metais, cuja redução do pH ocorre em função da oxidação de minerais sulfetados e posterior formação de ácido sulfúrico

Processo natural - equilíbrio entre os sistemas hidrológico e geológico

Mineração – intensifica a oxidação dos sulfetos pela maior disponibilidade de oxigênio e infiltração de água em pilhas de rejeito



**Figure 9** Schematic diagram showing the hydrology and geochemistry of a decommissioned mine-tailings impoundment. Reproduced with permission from Blowes DW and Ptacek CJ (1994) Acid-neutralization mechanisms in inactive mine tailings. In: Blowes DW and Jambor JL (eds.) *The Environmental Geochemistry of Sulfide Mine-Wastes*, vol. 22, pp. 271–292. Nepean, ON: Mineralogical Association of Canada.

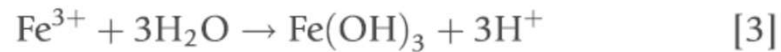


## Oxidação da pirita

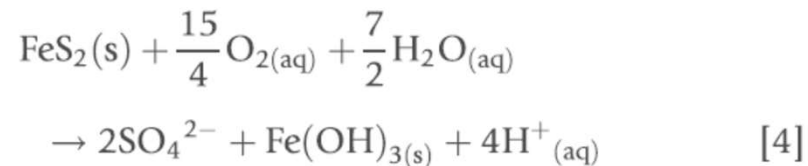
The Fe(II) thus released may be oxidized to Fe(III):



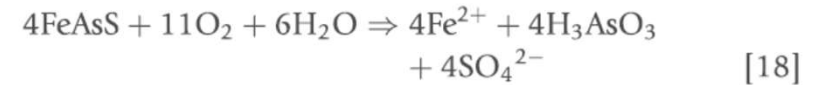
Fe(III) oxyhydroxides such as ferrihydrite (nominally  $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) may precipitate:



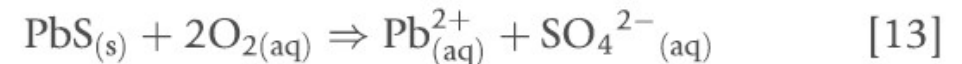
where  $\text{Fe}(\text{OH})_3$  is a surrogate for ferrihydrite. Adding eqns [1]-[3] yields the overall reaction:



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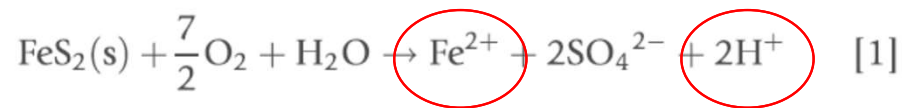


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Galena may also be oxidized by Fe(III) under acidic conditions (Rimstidt et al., 1994):

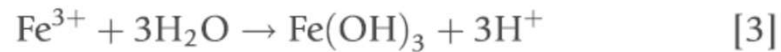




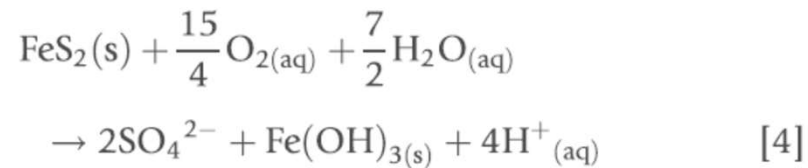
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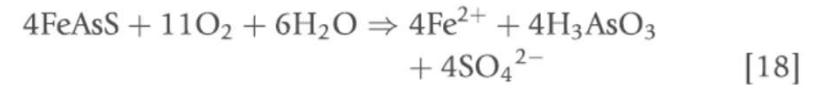
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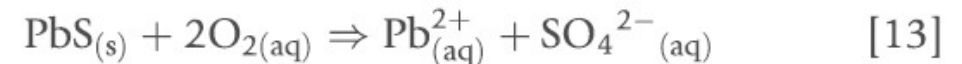
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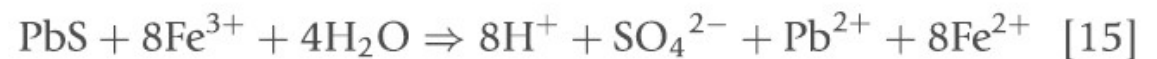
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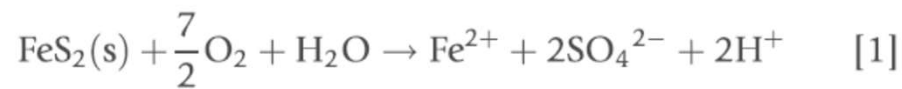


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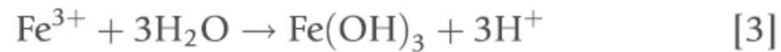




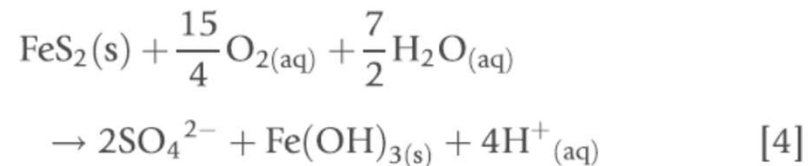
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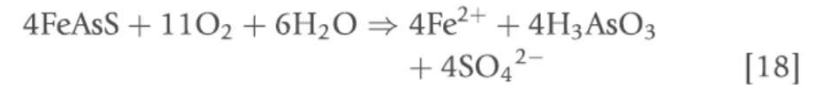


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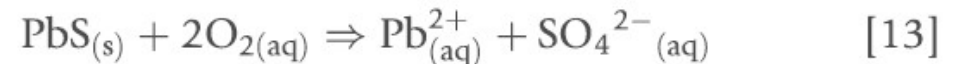


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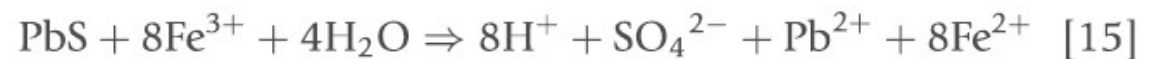
### Drenagem ácida

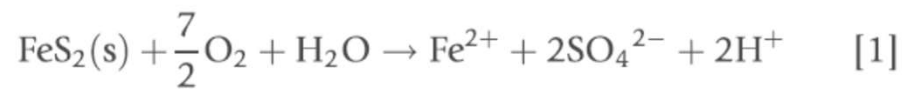


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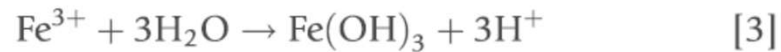


## Oxidação da pirita

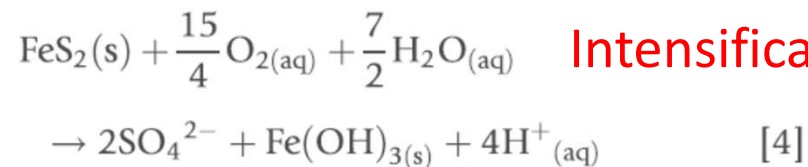
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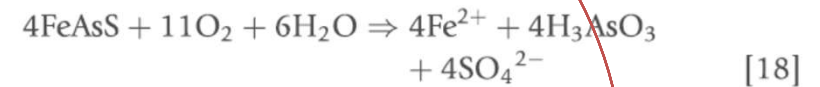
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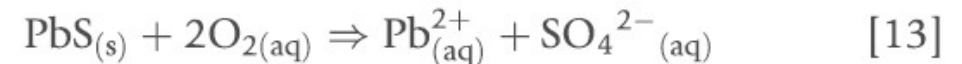


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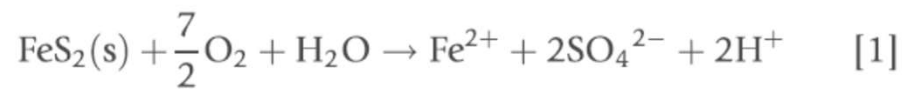
## Intensificação da

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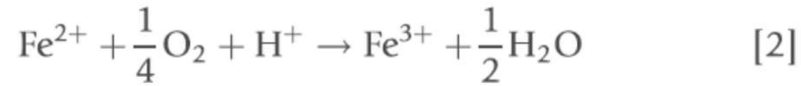


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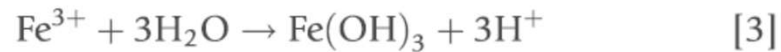




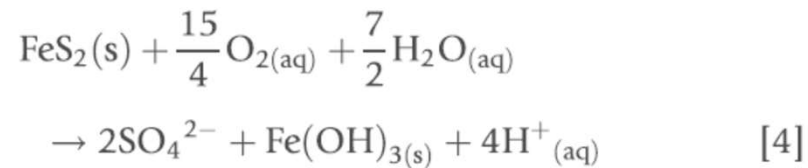
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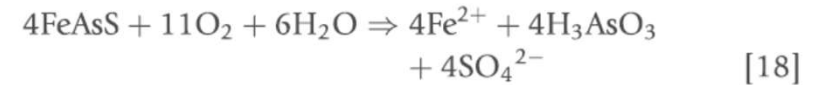


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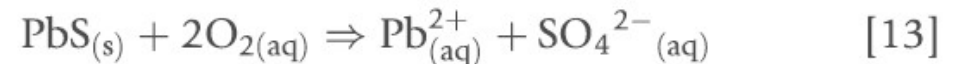
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## Arsênio acompanha

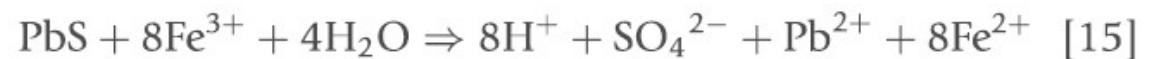


## Chumbo também

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# Associação dos elementos

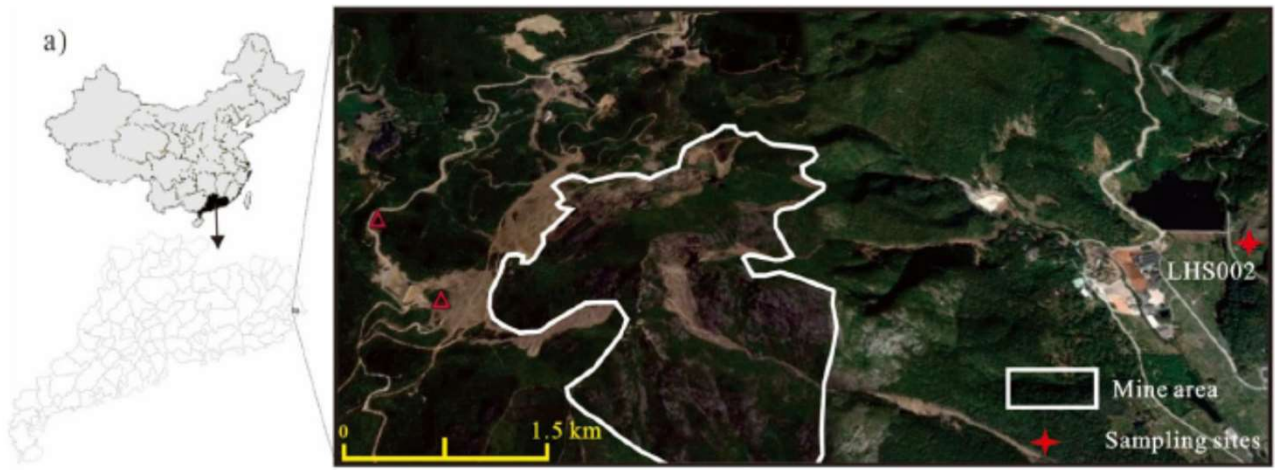
Licht, 1998. Prospecção geoquímica: Princípios, técnicas e métodos. CPRM

<b>Associações Plutônicas</b>	
Rochas ultramáficas	Cr, Co, Ni, Cu
Rochas máficas	Ti, V, Sc
Rochas alcalinas	Ti, Nb, Ta, Zr, ETR, F, P
Carbonatitos	ETR, Ti, Nb, Ta, P, F
Rochas graníticas	Ba, Li, W, Mn, Sn, Zr, Hf, U, Th, Ti
Pegmatitos	Li, Rb, Cs, Be, ETR, Nb, Ta, U, Th, Zr, Hf
<b>Mineralizações Hidrotermais</b>	
Depósitos de Cu-pórfiro	Cu, Mo, Re
Sulfetos complexos	Hg, As, Sb, Se, Ag, Zn, Cd, Pb
Sulfetos de baixa temperatura	Bi, Sb, As
Metais básicos	Pb, Zn, Cd, Ba
Metais preciosos	Au, Ag, Cu, Co, As
Metais preciosos (ultramáficas)	Ni, Cu, Pt, Co
<b>Metamorfismo de Contato</b>	
Scheelita-cassiterita	W, Sn, Mo
Fluorita-helvita	Be, F, B
<b>Associações Sedimentares</b>	
Folhelhos negros	U, Cu, Pb, Zn, Cd, Ag, Au, V, Mo, Ni, As
Fosforitas	U, V, Mo, Ni, Ag, Pb, F, ETR
Evaporitos	Li, Rb, Cs, Sr, Br, I, B
Lateritas	Ni, Cr, óxidos de Mn, Co, W, As, Ba, P, Nb, Ti, ETR
<i>Red beds</i> continentais	U, V, Se, As, Mo, Cu, Pb
<i>Red beds</i> vulcanogênicos	Cu, Pb, Zn, Ag, V, Se
Bauxita	Nb, Ti, Ga, Be, Zn

**OPEN**

# Magnetic response of Arsenic pollution in a slag covered soil profile close to an abandoned tungsten mine, southern China

Tingping Ouyang<sup>1,2\*</sup>, Mingkun Li<sup>1</sup>, Erwin Appel<sup>3</sup>, Zhihua Tang<sup>2,4</sup>, Shasha Peng<sup>2</sup>, Sang Li<sup>1</sup> & Zhaoyu Zhu<sup>2</sup>

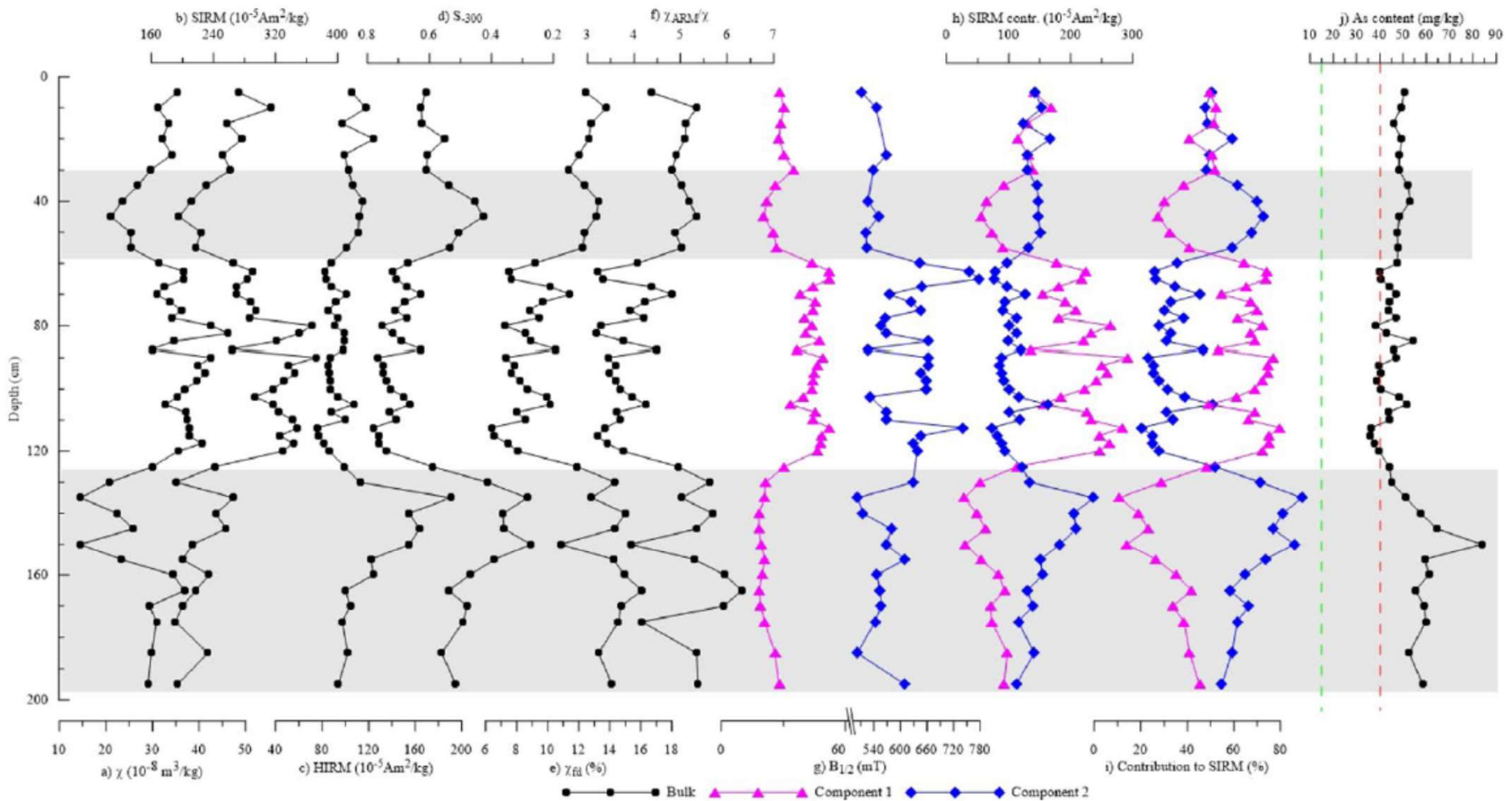


(a) Location of the study area and sampling site,

(b) picture of the soil profile under slags, and

(c) picture of collected soil samples.





**(a) Magnetic susceptibility;**

**(b) Saturation isothermal remanent magnetization;**

**(c) Hard isothermal remanent magnetization;**

**(d)  $S_{-300}$  ratio;**

**(e) Frequency dependent magnetic susceptibility coefficient;**

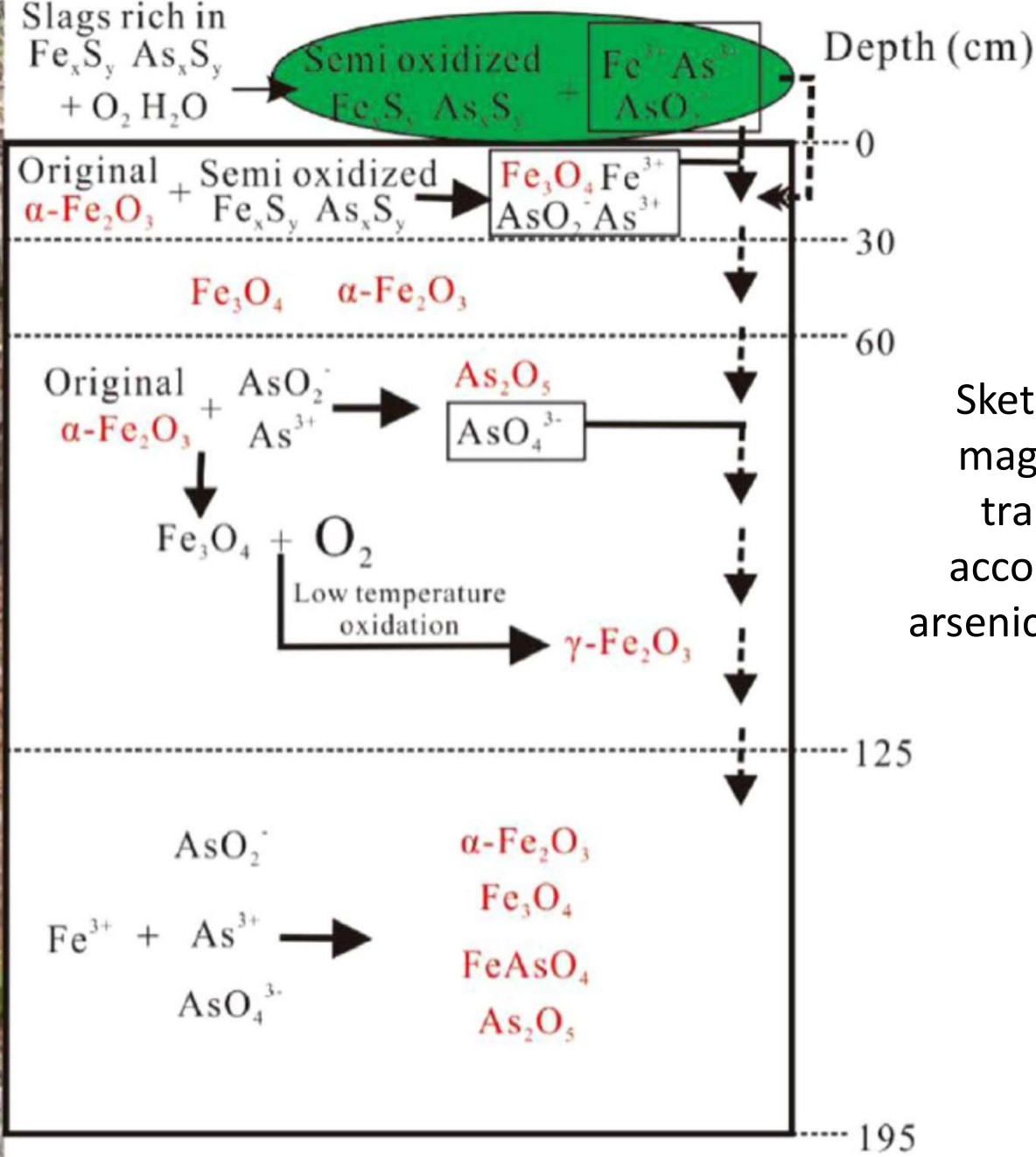
**(f) Ratio parameter susceptibility of anhysteretic remanent magnetization to magnetic susceptibility;**

**(g)  $B_{1/2}$  of different magnetic components;**

**(h) SIRM contribution of different magnetic components;**

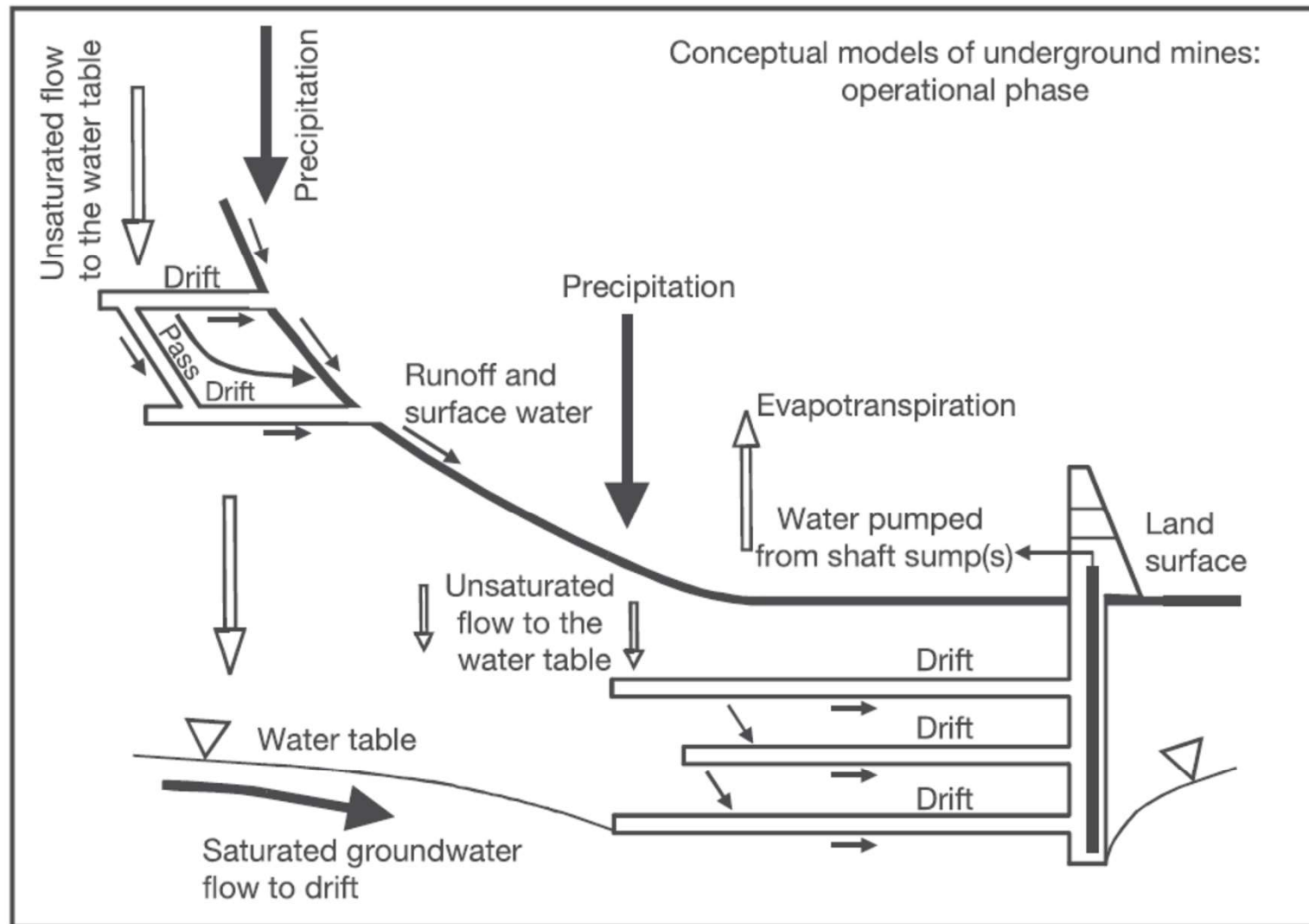
**(i) Contribution of different magnetic components to SIRM;**

**(j) Arsenic content**



Sketch illustrating magnetic mineral transformation accompanied with arsenic transportation.

# Minas subterrâneas



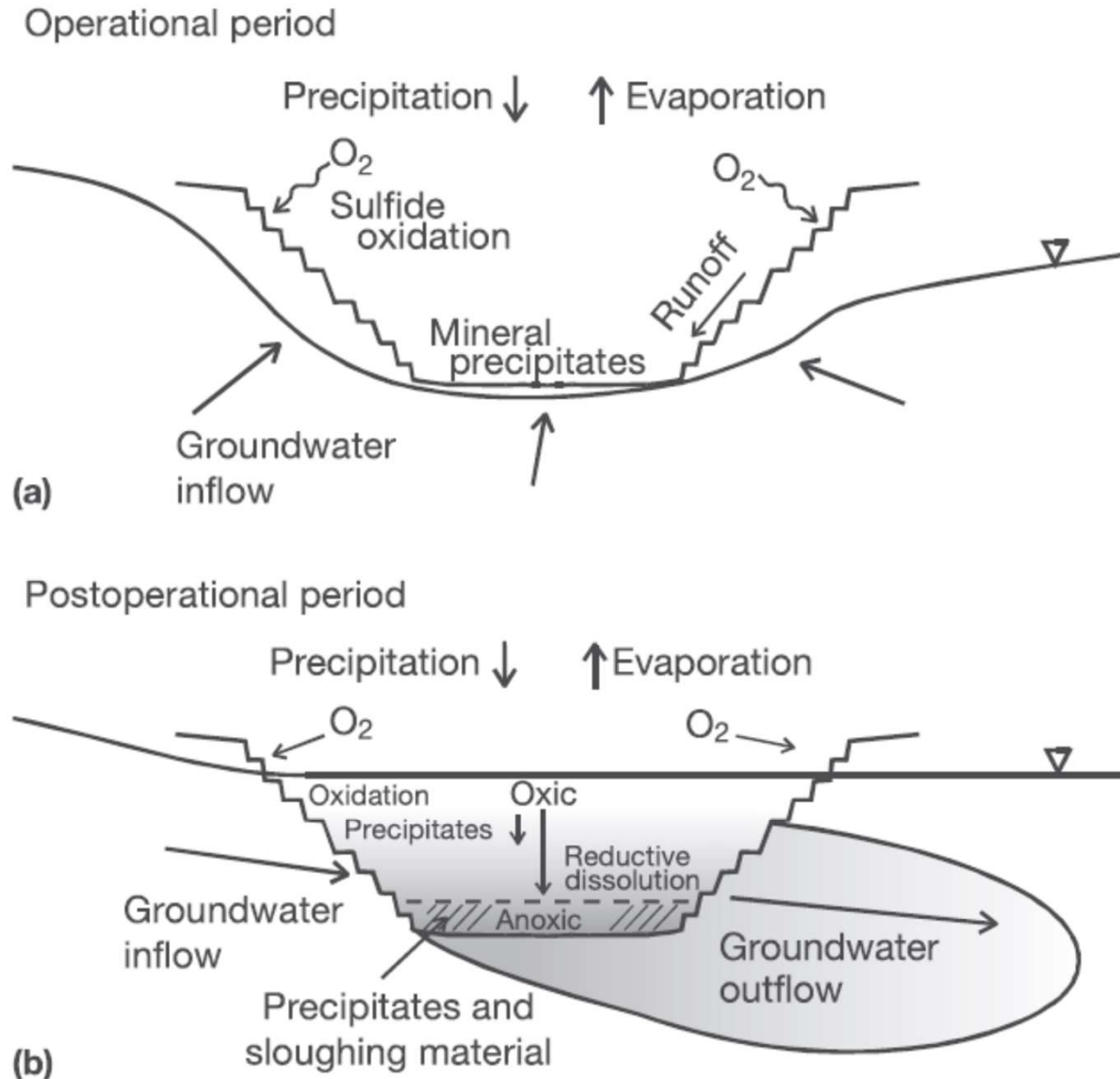
**Figure 4** Schematic diagram showing underground mine workings. Modified from [Morin KA and Hutt NM \(1997\) \*Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies\*](#). Vancouver, BC: MDAG Publishing.

# The Deepest Gold Mine in the World: Mponeng Mine



Mais de 4 Km de profundidade  
Temperatura atinge 65 oC

# Cavas abertas



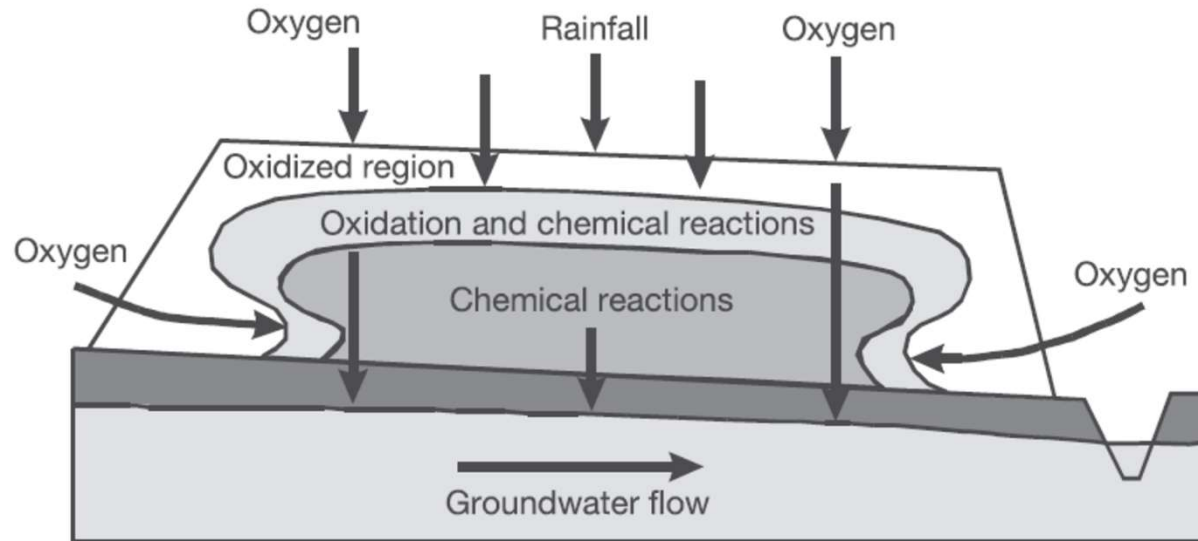
**Figure 5** Schematic diagram of an open-pit mine during and after operation. Modified from Eary and Castendyk (1999).



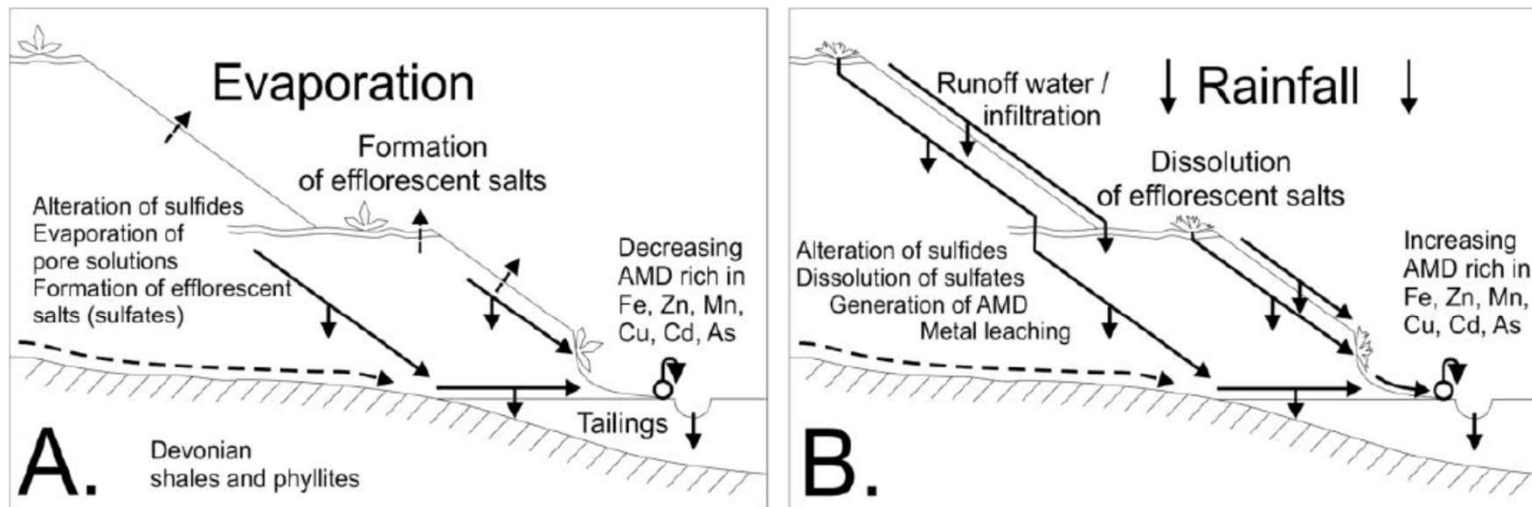
# Mina de Cobre - Chuquicamata, Chile



# Pilhas de rejeitos



**Figure 6** Schematic diagram of a waste-rock dump. Reproduced with permission from Ritchie AIM (1994) Sulfide oxidation mechanisms: Controls and rates of oxygen transport. In: Blowes DW and Jambor JL (eds.) *The Environmental Geochemistry of Sulfide Mine-Wastes*, vol. 22, pp. 201–246. Nepean, ON: Mineralogical Association of Canada.



**Figure 2:** Element transport at the Excelsior waste rock dump. A: during the dry season; B: during the wet season

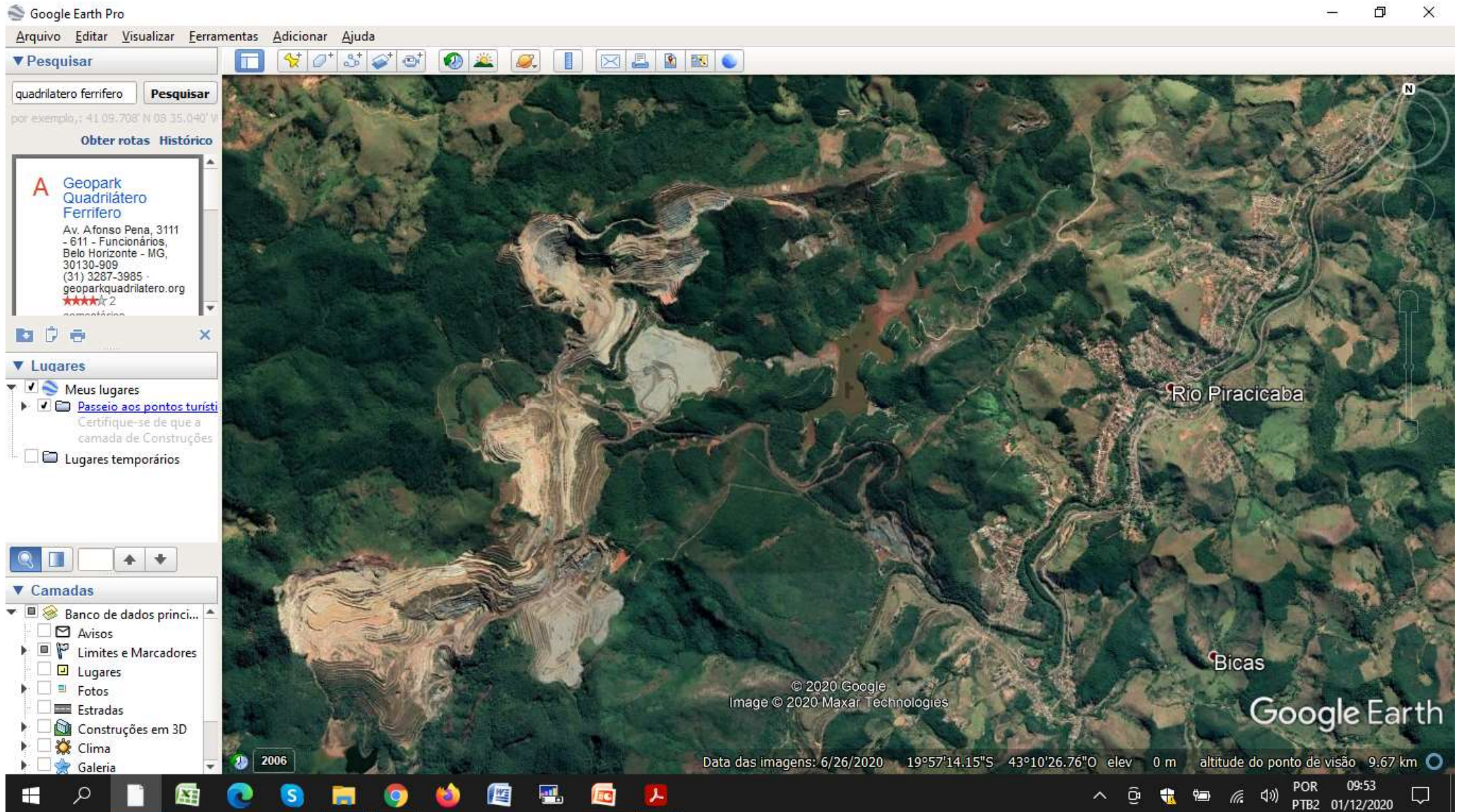
# Barragens

Quais são os riscos:

Contaminação do ar e solo, águas superficiais e subterrâneas

Rompimento (mais de 70 rompimentos de grande escala desde 1970)

# Brasil





## BARRAGEM I CÓRREGO DO FEIJÃO

RESOLUÇÃO CNRH Nº 143

CATEGORIA DE RISCO	DANO POTENCIAL ASSOCIADO		
	ALTO	MEDIO	BAIXO
ALTO	A	B	C
MEDIO	B	C	D
BAIXO	<b>E</b>	D	E

DN COPAM Nº 87

CLASSE III

**Finalidade:** Disposição de Rejeitos

**Localização:** Município de Brumadinho

**Empresa Projetista:** B. Inicial: ChristophErb; 1º e 2º Alteam.: Tecnosan; 3º Alteam.: Riad Chammas; 4º ao 6º Alteam. Tecnosolo; 9º e 10º Alteam. Geoconsultoria.

**Método Construtivo:** Alteamento Mortante (solo compactado e rejeito)

**Data da Construção:** 1976 (alteamentos de 1982 à 2013)

**Altura da Barragem:** 87 m

**Comprimento da Crista:** 694,0 m

**Área do reservatório:** 258.605,14 m<sup>2</sup>

**Volume do reservatório:** 12,7 Mm<sup>3</sup> ; **Volume Remanescente:** 735.554 m<sup>3</sup> (nov/2015)

**Vertedouro:** Operacional, TR 1.000 anos. Estrutura em torre, com galeria de fundo e canal a céu aberto

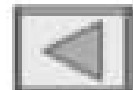


Tabela 8- Níveis de resposta por situação - PAE

NÍVEL DE RESPOSTA	SITUAÇÃO
<b>VERDE</b>	<p>Situações de incidente declarado ou previsível, com as seguintes características:</p> <ul style="list-style-type: none"> <li>i) serem estáveis ou que se desenvolvam muito lentamente no tempo;</li> <li>ii) poderem ser controladas pelo Empreendedor;</li> <li>iii) poderem ser ultrapassadas sem consequências nocivas no vale a jusante.</li> </ul>
<b>AMARELO</b>	<p>Situações que impõem um estado de atenção na barragem e/ou no vale a jusante, inclusive no caso em que a magnitude da vazão afluente ao reservatório exija a liberação de vazão efluente superior às condições de restrição a jusante (cotas ou vazões limites impostas para evitar inundação de habitações ou infraestruturas importantes). As características principais são:</p> <ul style="list-style-type: none"> <li>i) a situação tende a progredir lentamente, permitindo a realização de estudos para apoio à tomada de decisão;</li> <li>ii) existe a convicção de ser possível controlar a situação, embora o coordenador do PAE possa vir a necessitar de assistência especial de entidades externas;</li> <li>iii) existe a possibilidade de a situação se agravar e de se desenvolverem efeitos perigosos no vale a jusante sobre pessoas e bens.</li> </ul>
<b>LARANJA</b>	<p>Situações que impõem um estado de alerta geram na barragem. As características principais deste nível de resposta são as seguintes:</p> <ul style="list-style-type: none"> <li>i) a situação tende a progredir rapidamente, podendo não existir tempo disponível para a realização de estudos para apoio à tomada de decisão;</li> <li>ii) admite-se não ser possível controlar o acidente, tornando-se indispensável a intervenção de entidades externas;</li> <li>iii) existe a possibilidade de a situação se agravar com a ocorrência de consequências muito graves no vale a jusante.</li> </ul>
<b>VERMELHO</b>	<p>Situação de catástrofe inevitável, incluindo o início da ruptura da barragem.</p>

FONTE: Autor, 2018 (Adaptado do PNSB, 2018)

# Brumadinho



# Brumadinho





# MARIANA



# Futuro

- Volume de rejeitos apenas cresce
- Reciclagem, reuso e reabilitação de rejeitos
- Gordon et al. (2006) – na atual taxa de consumo, as reservas de Cu, Zn e Pb acabarão no futuro “imediatamente”

Discussão em grupos 5

Metais poluentes

# Geochemistry and Mineralogy of Solid Mine Waste: Essential Knowledge for Predicting Environmental Impact

Heather E. Jamieson\*

1811-5209/11/0007-0381\$2.50 DOI: 10.2113/gselements.7.6.381



Weathered Pb-Zn tailings from the Calumet Island mine, Québec

# Mine Waters: Acidic to Circumneutral

D. Kirk Nordstrom\*

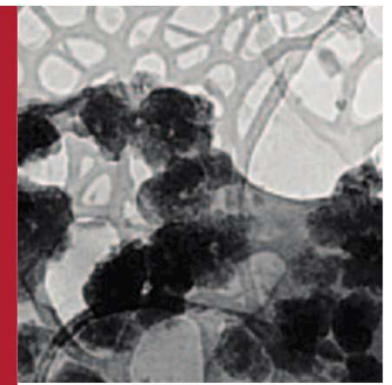
1811-5209/11/0007-0393\$2.50 DOI: 10.2113/gselements.7.6.393



Drainage water from the Zarshuran arsenic-gold mine in northern Iran.  
PHOTO BY SOROUSH MODABBERI

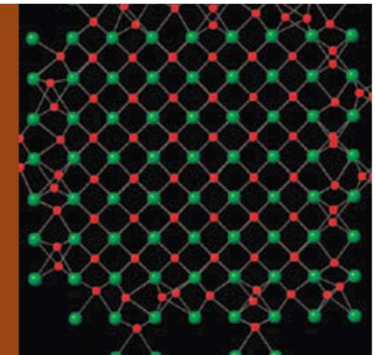
# Uranium Mill Tailings: Geochemistry, Mineralogy, and Environmental Impact

Abdesselam Abdelouas\*



# Biogenic Uraninite Nanoparticles and Their Importance for Uranium Remediation

John R. Bargar<sup>1</sup>, Rizlan Bernier-Latmani<sup>2</sup>, Daniel E. Giammar<sup>3</sup>, and Bradley M. Tebo<sup>4</sup>



Cross-section through a  
biogenic uraninite  
nanoparticle