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TEMA 6.
AGUAS SUBTERRÉNEAS

1. Parámetros
2. Fuentes de contaminación
3. Transporte de contaminantes
4. Tecnologías de descontaminación

1. Parámetros

LEY DE DARCY

Controversias sobre su nombre

Flujo 1-D

$$q = -K\frac{dh}{L}$$

Flujo del agua en suelo diferente al de tuberías o canales abiertos

Empleo para el cálculo de velocidades de infiltración desde río o de filtración al mar

No aplicable para cálculo de velocidades de infiltración a corto plazo, debido al impacto de las turbulencias en el flujo

IMAGEN TOMADA DE:
http://biosystems.okstate.edu/darcy/.
11/09/2012

FLUJO LAMINAR

$$R = \frac{v \cdot d}{\upsilon} < 1$$

$$\upsilon = \text{viscosidad cinemática} = \frac{\mu}{\rho}$$

(m²/s) (kg/m·s) (kg/m³)

Otros

1. Parámetros

CONDUCTIVIDAD HIDRÁULICA (*K*) → Facilidad con que un líquido fluye y con la que el suelo permite el paso de ese líquido (m/s)

$$K = \frac{k \cdot g}{\upsilon}$$

Capacidad del suelo para transmitir un fluido (m^2) ← PERMEABILIDAD (*k*)

$$k = 760 D^2 e^{-1.31\sigma}$$

POROSIDAD (n) → Volumen de huecos dividido por el volumen total de suelo (%)

POROSIDAD DE DRENAJE → Volumen de agua confinado en un suelo saturado

POROSIDAD DE FLUJO → Porosidad efectiva, que permite que el flujo de agua circule por el suelo

2. Fuentes de contaminación

METALES PESADOS

IMAGEN TOMADA DE: http://www.faunatura.com/envenenamiento-natural-agua-subterranea-asia.html. 04/10/2012

As

As(III) >>>> As(V)

Mineralología y geología del terreno

Bangladesh e India

OMS → 1 mg/d → Lesiones en la piel

IMAGEN TOMADA DE: http://purificadoresdeaguapura.blogspot.com.es/2012/07/informe-tecnico-sobre-el-arsenico-en.html. 04/10/2012

Insípido e incoloro. Intoxicación crónica

Carcinógeno (IARC – USEPA)

Arsénico como fuente de energía para algunas bacterias (As^{5+} → As^{3+})

Pb

Pb(II) → Compuestos inorgánicos

Pb(IV) → Compuestos orgánicos

Formación de compuestos de organoplomo

Inclusión en gasolina → 1922

Síntesis → 1859

Tetraetil-plomo $(CH_3\text{-}CH_2\text{-})_4Pb$

2. Fuentes de contaminación

Speciation and chemistry of some heavy metals.

Heavy metal	Speciation and chemistry	Concentration limits	References
Lead	Pb occurs in 0 and +2 oxidation states. Pb(II) is the more common and reactive form of Pb. Low solubility compounds are formed by complexation with inorganic (Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids). The primary processes influencing the fate of Pb in soil include adsorption, ion exchange, precipitation and complexation with sorbed organic matter	Surface agricultural soil: 7–20 ppm Soil levels: up to 300 ppm USEPA, Maximum Contaminant Level (MCL) in drinking water: 0.015 ppm	(Bodek et al., 1988; Evanko and Dzombak, 1997; Hammer and Hammer, 2004; Smith et al., 1995; WHO, 2000)
Chromium	Cr occurs in 0, +6 and +3 oxidation states. Cr(VI) is the dominant and toxic form of Cr at shallow aquifers. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) (especially Ba^{2+}, Pb^{2+} and Ag^+). Cr (III) is the dominant form of Cr at low pH (<4). Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions. The leachability of Cr(VI) increases as soil pH increases	Normal groundwater concentration: < 0.001 ppm Lethal dose : 1–2 g MCL of USEPA in drinking water: 0.1 ppm	(Lenntech, 2004; Smith et al., 1995)
Zinc	Zn occurs in 0 and +2 oxidation states. It forms complexes with a anions, amino acids and organic acids. At high pH, Zn is bioavailable. Zn hydrolyzes at pH 7.0–7.5, forming $Zn(OH)_2$. It readily precipitates under reducing conditions and may coprecipitate with hydrous oxides of Fe or manganese	Natural concentration of Zn in soils: 30–150 ppm Concentration in plant: 10–150 ppm Plant toxicity: 400 ppm WHO limit in water: 5 ppm	(Evanko and Dzombak, 1997; Lenntech, 2004; Smith et al., 1995)
Cadmium	Cd occurs in 0 and +2 oxidation states. Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) dominate at high pH whereas Cd^{2+} and aqueous sulphate species dominate at lower pH (<8). It precipitates in the presence of phosphate, arsenate, chromate, sulphide, etc. Shows mobility at pH range 4.5–5.5	Soil natural conc: >1 ppm Plant conc: 0.005–0.02 ppm Plant toxicity level: 5–30 ppm USEPA MCL in water: 0.005 ppm	(Matthews and Davis, 1984; Smith et al., 1995)
Arsenic	As occurs in −3, 0, +3, +5 oxidation states. In aerobic environments, As(V) is dominant, usually in the form of arsenate $(AsO4)^{3-}$. It behaves as chelate and can coprecipitate with or adsorb into Fe oxyhydroxides under acidic conditions. Under reducing conditions, As(III) dominates, existing as arsenite $(AsO_3)^{3-}$ which is water soluble and can be adsorbed/coprecipitated with metal sulphides	MCL in drinking water- USEPA: 0.01 ppm WHO: 0.01 ppm	(Bodek et al., 1988; Smith et al., 1995)
Iron	Fe occurs in 0, +2, +3 and +6 oxidation states. Organometallic compounds contain oxidation states of +1, 0, −1 and −2. Fe(IV) is a common intermediate in many biochemical oxidation reactions. Many mixed valence compounds contain both Fe(II) and Fe(III) centers, e.g. magnetite and prussian blue	Tolerable upper intake level (UL) - Dietary Reference Intake (DRI): For adults: 45 mg per day For minors: 40 mg per day	(Holleman et al., 1985; Medscape)
Mercury	Hg occurs in 0, +1 and +2 oxidation states. It may occur in alkylated form (methyl/ethyl mercury) depending upon the Eh and pH of the system. Hg^{2+} and Hg_2^{2+} are more stable under oxidizing conditions. Sorption to soils, sediments and humic materials is pH-dependent and increases with pH	Groundwater natural conc: >0.0002 ppm USEPA regulatory limit in drinking water: 0.002 ppm	(Bodek et al., 1988; Smith et al., 1995)
Copper	Cu occurs in 0, +1 and +2 oxidation states. The cupric ion (Cu^{2+}) is the most toxic species of Cu e.g. $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$.In aerobic alkaline systems, $CuCO_3$ is the dominant soluble species. In anaerobic environments CuS(s) will form in presence of sulphur. Cu forms strong solution complexes with humic acids	Soil natural conc: 2–100 ppm Normal range in plants: 5–30 ppm Plant toxicity level: 30–100 ppm USEPA MCL in water: 1.3 ppm	(Dzombak and Morel, 1990; LaGrega et al., 1994)

IMAGEN TOMADA DE:

Hashim *et* al. (2011). Remediation technologies for heavy metal contaminated groundwater. Journal of Enviromental Management 92: 2355-2388.

2. Fuentes de contaminación

Table 1
Vulnerability of groundwater to pollution with regard to land-usage and environmental factors

Environmental categories			Ability to convey water and pollutants	Land-usage categories and intensities								
Categories	Components	Conditions		Conservation	Recreation		Agriculture		Residential		Industry and commercial	
					High	Low	Field crops	Orchards	High	Low	High	Low
				Potential pollution impact								
				L	h	L	H	l	h		H	h
Hydrology	Water table	Shallow	S	SL	Sh	SL	SH	Sl	Sh	SL	S	Sh
		Deep	w	wL	wh	wL	WH	wl	wh	wL	wH	Wh
	Recharge	High	S	SL	Sh	SL	SH	Sl	Sh	SL	SH	Sh
		Low	w	wL	wh	wL	wH	wl	wh	wL	wH	Wh
	Hydraulic conductivity	High	S	SL	Sh	SL	SH	Sl	Sh	SL	SH	Sh
		Low	w	wL	wh	wL	wH	wl	wh	wL	wH	Wh
Physiography	Slope	<20%	S	SL	Sh	SL	SH	Sl	Sh	SL	SH	Sh
		>20%	W	wL	wh	wL	wH	wl	wh	wL	wH	wh
Soils	Permeability	Permeable	S	SL	Sh	SL	SH	Sl	Sh	SL	SH	Sh
		Impermeable	W	WL	Wh	WL	WH	Wl	Wh	WL	WH	Wh
Tree and other vegetation cover		Low	S	SL	Sh	SL	SH	Sl	Sh	SL	SH	Sh
		High	W	wL	wh		w	Wl	wh	wL	wH	wh

Key symbols—land-use factors: H, high; h, moderately high; l, moderately low; L, low. Environmental factors: S, strong; s, moderately strong; w, moderately weak; W, weak.

IMAGEN TOMADA DE:
Collin *et* al. (2003). Assessing groundwater vulnerability to pollution to promote sustainable urban and rural development. Journal of Cleaner Production 11: 727-736.

COEs

2. Fuentes de contaminación

COMPUESTOS ORGÁNICOS EMERGENTES

Table 1
Summary statistics for maximum concentrations (ng/L) found in groundwater for EOCs and degradates that were detected in at least 4 separate studies, their major use and K_{ow}.

	n	Lowest	Average	Highest	Use[a]	log K_{ow}
Pharmaceuticals						
Carbamazepine	23	1.64	5312	99,194	Antiepileptic	1.51[e]
Sulfamethoxazole	15	5.7	252	1110	Antibiotic	0.9[f]
Ibuprofen[d]	14	0.6	1491	12,000	Anti-inflamatory[c]	2.48[e]
Diclofenac	11	2.5	121	590	Anti-inflamatory	1.9[e]
Clofibric acid[b,d]	8	4	1113	7300	Lipid regulator	2.88[e]
Paracetamol[d]	8	15	15,142	120,000	Analgesic	0.46[f]
Ketoprofen	6	3	611	2886	Anti-inflamatory	3.12[i]
Tridosan	6	7	509	2110	Antibiotic	4.76[k]
Iopamidol	5	130	760	2400	X-ray contrast media	−2.42[l]
Lincomycin	5	100	188	320	Antibiotic	0.56[m]
Propyphenazone	5	15	553	1250	Analgesic	2.02[e]
Sulfamethazine	5	120	298	616	Veterinary medicine	0.28[j]
DEET	4	454	2251	6500	Insect repellent	2[n]
Phenazone	4	25	1503	3950	Analgesic	2.32[o]
Primidone	4	110	3380	12,000	Barbiturate	0.91[o]
Salicylic acid[b,d]	4	43	418	1225	Analgesic	2.26[i]
Life-style compounds						
Caffeine	14	13	9774	110,000	Diuretic	−0.07[f]
Cotinine[b]	4	60	173	400	Stimulant	0.07[k]
Industrials						
Bisphenol A[d]	9	470	2527	9300	Plasticiser	3.18[g]
Nonylphenol[b,d]	6	1500	23088	84,000	Detergent	4.4[g]
Galoxalide[d]	5	6	4984	23,000	Fragrance	5.9[k]
TCEP	4	495	656	740	Fire retardant	1.78[p]
Hormones						
Estrone[b,d]	6	0.1	9	45	Estrogenic hormone	2.95[h]
17b-Estradiol[d]	4	0.79	31	120	Estrogenic hormone	3.86[h]

n = number of studies.
[a] Primary use.
[b] Degradate.
[c] Also an analgesic.
[d] Known or potential EDS, DEET = *N,N*-diethyl-meta-toluamide, TCEP = Tris(2-Chloroethyl) phosphate.
[e] K_{ow} reference: Scheytt et al. (2005).
[f] K_{ow} reference: Yargeau et al. (2007).
[g] K_{ow} reference: Shao et al. (2007).
[h] K_{ow} reference: de Mes et al. (2005).
[i] K_{ow} reference: Ni et al. (2002).
[j] K_{ow} reference: Sangster (1997).
[k] K_{ow} reference: SRC (2010).
[l] K_{ow} reference: Verliefde et al. (2007).
[m] K_{ow} reference: Kutcha and Cessna (2009).
[n] K_{ow} reference: Meinen and McKay (1987).
[o] K_{ow} reference: Hansch et al. (1995).
[p] K_{ow} reference: EC (2008).

IMAGEN TOMADA DE:
Lapworth *et* al. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environmental Pollution 163: 287-303.

↑ Tiempo de residencia en aguas subterráneas

3. Transporte de contaminantes

"El estado cuantitativo de una masa de agua subterránea puede tener repercusiones en la calidad ecológica de las aguas superficiales y de los ecosistemas terrestres asociados con dicha masa de agua subterránea"

DMA (2000)

«estado de las aguas subterráneas»: la expresión general del estado de una masa de agua subterránea,

«aguas subterráneas»: todas las aguas que se encuentran bajo la superficie del suelo en la zona de saturación y en contacto directo con el suelo o el subsuelo.

determinado por el peor valor de su estado cuantitativo y de su estado químico.

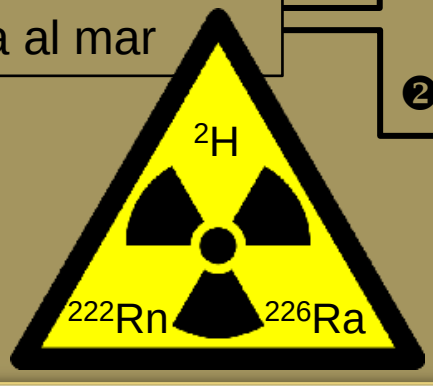
TRAZADORES NATURALES

Empleados para estimar las entradas de agua subterránea al mar

❶ Enriquecimiento en trazadores geoquímicos (agua subterránea / agua del mar)

❷ Empleo de perfiles verticales de la composición geoquímica en el sedimento

Empleados para estimar intercambios agua superficial y agua subterránea



4. Tecnologías de descontaminación

TECNOLOGÍAS DE TRATAMIENTO QUÍMICO

FORMACIÓN DE QUELATOS

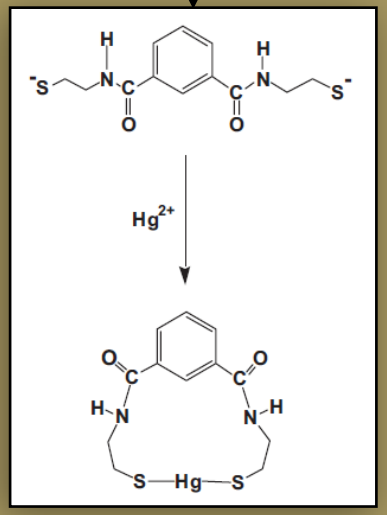


IMAGEN TOMADA DE:
Blue *et* al. (2008). Low-level mercury removal from groundwater using a synthetic chelating ligand. Water Research 42: 2025-2028.

REACCIONES DE REDUCCIÓN

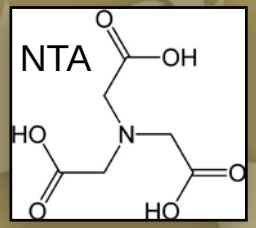
$Fe(III) \rightarrow Fe(II)$

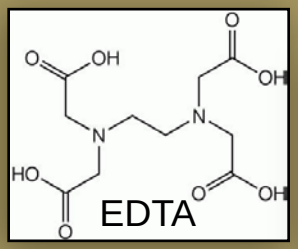
$Arcilla\text{-}Fe(III) + 4SO_2^- \rightarrow Arcilla\text{-}Fe(II) + 2S_2O_4^=$

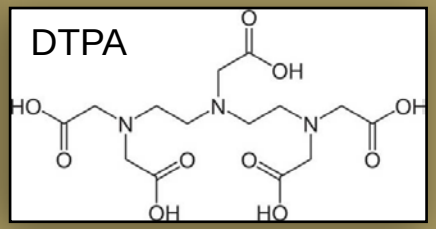
$N_2(g)$ ⇓ $Cr(VI) \rightarrow Cr(III)$

$8CrO_4^= + 3H_2S + 4\,H_2O \rightarrow 8Cr(OH)_3\downarrow + 3SO_4^=$

- No biodegradables (EDTA, DTPA)
- Otros cancerígenos (NTA)
- Caros







IMÁGENES TOMADAS DE:
http://chemistry.about.com/.
04/10/12

4. Tecnologías de descontaminación

TECNOLOGÍAS DE TRATAMIENTO BIOLÓGICO

BACTERIAS REDUCTORAS DEL SULFATO (SRB)

$SO_4^{=} \rightarrow S^{=} + Me^{2+} \rightarrow MeS\downarrow$

ELIMINACIÓN DE RADIONÚCLIDOS

U(VI) → U(IV)

Acetato → CO_2

ELIMINACIÓN DE ARSÉNICO ASOCIADA AL HIERRO

Fe(II) → Fe(III)

As(III) → As(V)

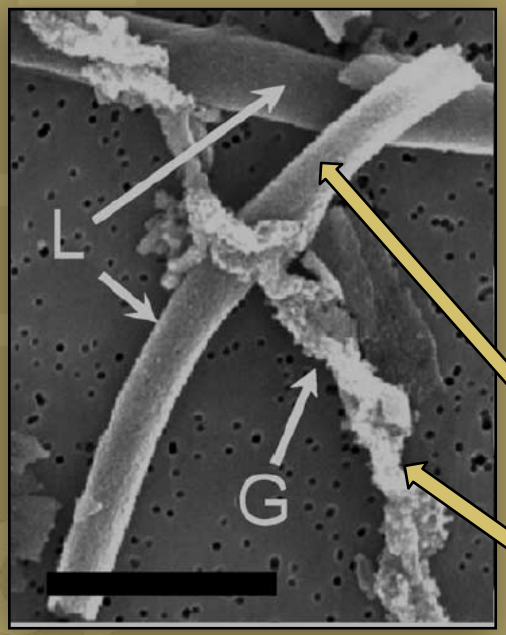


IMAGEN TOMADA DE: James and Ferris (2004). Evidence for microbial-mediated iron oxidation at a neutrophilic groundwater spring. Chemical Geology 212: 301-311.

Leptothrix ochracea

Gallionella ferruginea

FQ

4. Tecnologías de descontaminación

TECNOLOGÍAS DE TRATAMIENTO FÍSICO-QUÍMICO

BARRERAS REACTIVAS PERMEABLES (PRB)

Medio reactivo sub-superficial diseñado para interceptar una pluma de contaminante y transformarlo hasta formas medioambientalmente aceptables (USEPA, 1989)

PROCESOS DE ADSORCIÓN-PRECIPITACIÓN → Zeolitas

→ ZVI (Arsénico)

Reacción anaeróbica

$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$

Reacción aeróbica

$2Fe^0 + O_2 + 2H_2O \rightarrow Fe^{2+} + 4OH^-$

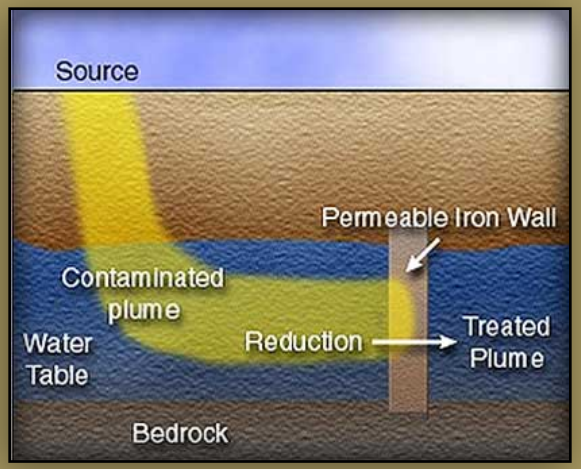


IMAGEN TOMADA DE:
http://www.st-ma.com/prb.html. 18/10/12

TRATAMIENTO ELECTROCINÉTICO

$H_2O \rightarrow 2H^+ + ½ O_2(g) + 2e^-$

$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$

SOME ENGLISH TERMS TO BE FAMILIAR WITH

- ✓ Agentes quelantes → Chelating agents
- ✓ Bacterias reductoras del sulfato → Sulphate-reducing bacteria
- ✓ Barreras reactivas permeables → Permeable reactive barriers (PRB)
- ✓ Compuestos orgánicos emergentes → Emerging organic compounds
- ✓ Estudio de viabilidad → Feasibility study
- ✓ Filtración de agua subterránea → Groundwater seepage
- ✓ Perfiles verticales → Vertical profiles
- ✓ Porosidad de drenaje → Specific yield
- ✓ Tratamiento electrocinético → Electrokinetic remediation
- ✓ Trazadores naturales → Natural tracers
- ✓ Zona de captación → Catchment area
- ✓ ZVI → Zero valent iron

One step beyond!

UNDERSTANDING GROUNDWATER (I)

UNDERSTANDING GROUNDWATER (II)

GROUNDWATER CONTAMINATION

THE HIDDEN SOURCE OF LIFE

LOSING OUR GROUNDWATER?

GROUNDWATER REPLENISHMENT

IMAGEN TOMADA DE: www.gifmania.com.es

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