מזהמי מים שונים – השפעתם ודרכי הטיפול בהם

ישי דרור

המחלקה למדעי כדור הארץ וכוכבי הלכת
הפקולטה לכימיה, מכון ויצמן למדע

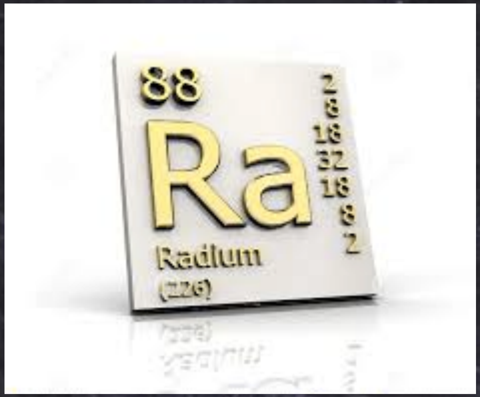
הרצאה מקוונת במסגרת אקדמיה ברשת
3. 1. 2018

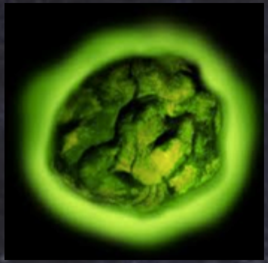
מבנה ההרצאה

1. הדברים שאנחנו לא יודעים - דוגמא אחת מהעבר הלא כל כך רחוק
2. הסיפור (בקצרה) של מזהמי מים שונים - או :
   מה היה הממתיק המלאכותי הראשון והאם הוא קשור לנפילה של האימפריה הגדולה וכמה זה רלוונטי לימינו?
   איזה דמות של דיסני מדגימה השפעות של חשיפה לזיהום?
   איפה סובלים מיליוני אנשים מזיהום כתוצאה מנסיון של גופים בינלאומיים גדולים לספק מים באיכות יותר טובה.
   ואיך קשורה התפתחות היכולת האנליטית ומכשור חדש לאיכות מקורות המים בעולם?
3. שיטות טיפול מקובלות – אתגרים ופתרונות לבעיות מורכבות
4. סיכום וכמה מילים על תחזיות לעתיד

הדברים שאנחנו לא יודעים - דוגמאות מהעבר הלא כל כך רחוק

רדיום





Radium was discovered by Marie Sklodowska and Pierre Curie (1898) in a uraninite sample. While studying the mineral earlier, the Curies removed uranium from it and found that the remaining material was still radioactive.

Radium is highly radioactive when ingested, 80% of the ingested radium leaves the body through the feces, while the other 20% goes into the bloodstream, mostly accumulating in the bones. Exposure to radium, internal or external, can cause cancer and other disorders, because radium and radon emit alpha and gamma rays upon their decay, which kill and mutate cells.

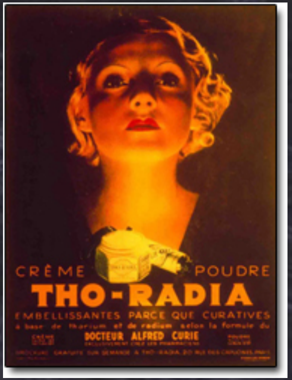

"Here's Health!"
TO keep that health you must keep Nature's laws. They are simple and easy to keep; but if they are broken Nature exacts a heavy penalty from each and every one. Get plenty of sleep, exercise and wholesome fun. Avoid overwork, all other excesses, eat fresh, natural foods, breathe fresh air, and drink plenty of fresh, invigorating, natural radioactive water from the Radium-Spa.


"STANDARD"
RADIUM PREPARATIONS
PERMANENT
PERMANENT
INDICATIONS
RADIUM CHEMICAL COMPANY
RADITHOR
CERTIFIED
Radioactive Water
Radium and Mesothorium
in Triple Distilled Water


Doramad
Radium-Strahlen
Radioaktive Zahncreme
Doramad
Radioaktive Zahncreme

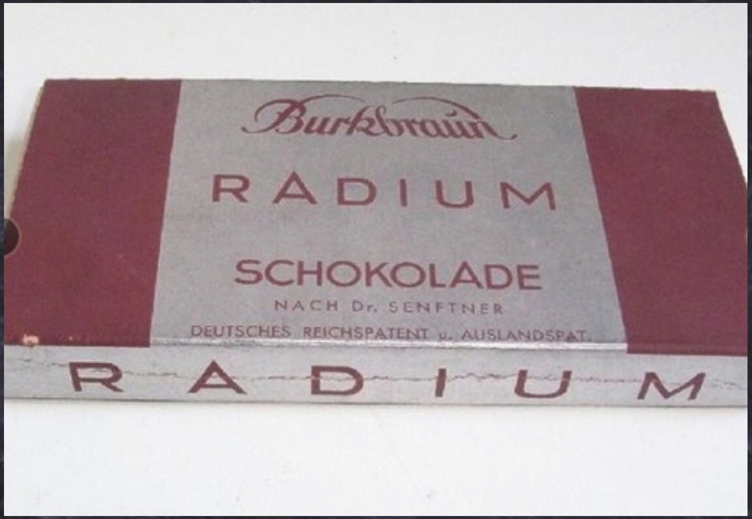
Nuclear Makeup

The product range, used to includ a cleansing milk, skin cream, powder, rouge, lipstick and toothpaste, was called Tho-Radia as it contained thorium chloride and radium bromide, both of which are radioactive.

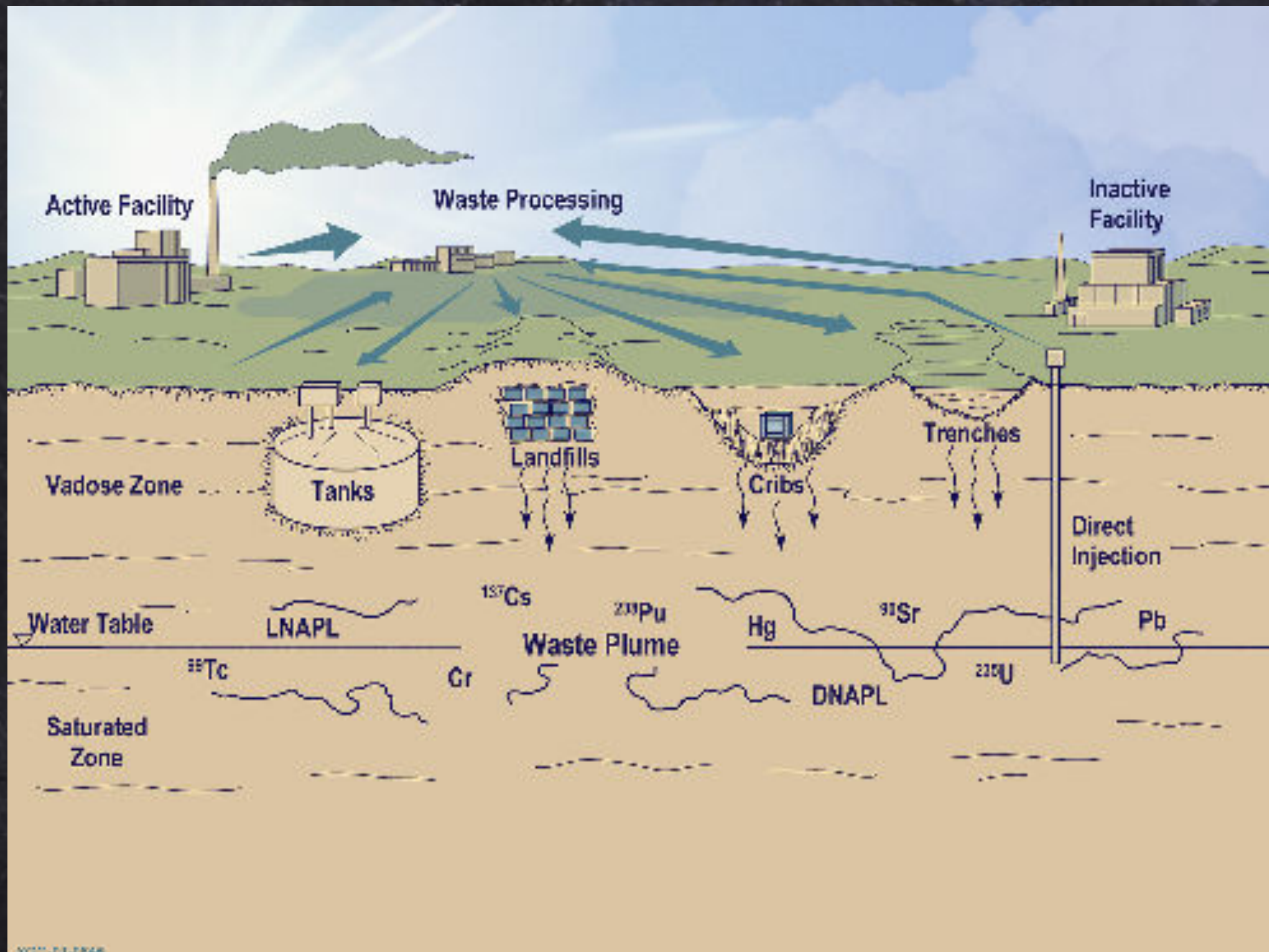


Fellas, there's a reason she's glowing, and it's not luminous beauty

Chockaholics aren't left out, Radium is everywhere. The ads claimed eating a block would make you look younger.



מקורות זיהום



מתכות כבדות

המושג מתכות כבדות מתייחס לכל יסוד כימי בעל צפיפות גבוהה (בד"כ מעל 5 גר/מל) שרעיל בריכוזים נמוכים. רשימה חלקית כוללת: ארסן As, קדמיום Cd, כרום Cr, כספית Hg, ועופרת Pb .

מתכות כבדות הן חומרים טבעיים שנמצאות בקליפת כדה"א באופן טבעי.

אי אפשר לפרק או להרוס מתכות כבדות.

החשיפה מתרחשת דרך אוכל, שתייה, ואויר אבל בד"כ כמויות משמעותיות נספגות כתוצאה מהתערבות אנושית בעיקר בגלל עיבוד וכריית מתכת.

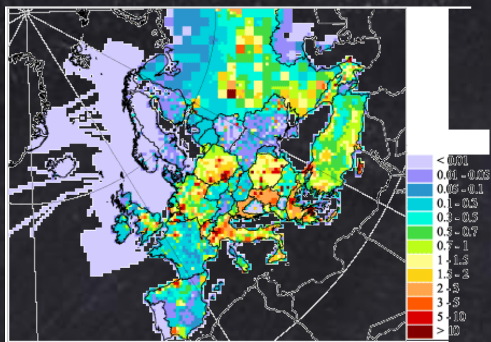
כבר לפני אלפי שנים ידעו על זיהום כתוצאה מחשיפה הקשורה לעיבוד והתכת מתכות.

ברמות של ריכוזי קורט חלק מהמתכות הכבדות דרושות לגוף (נחושת, ניקל, סלניום, אבץ).

תוצאות הזיהום: פגיעה בפעילות אנזימים, פגיעה במבנה התא (בעיקר ממברנות) שינויים ב DNA , הרעלות ברמות שונות , אלרגיות וסרטן.

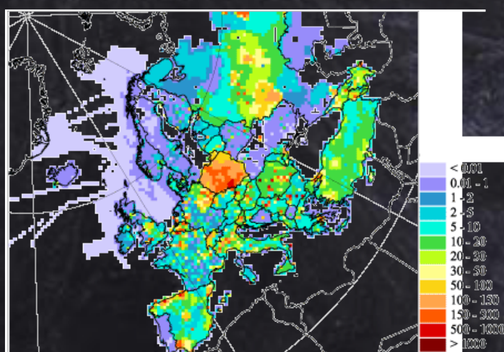
פליטת עופרת 2002

kg/km2/y



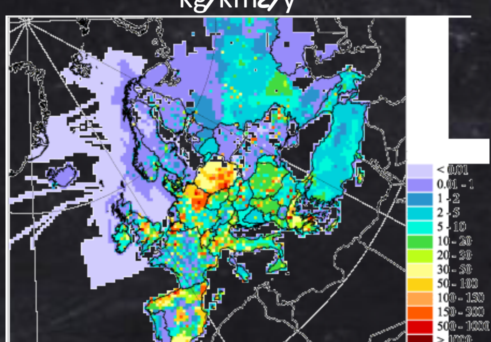
פליטת קדמיום 2002

kg/km2/y

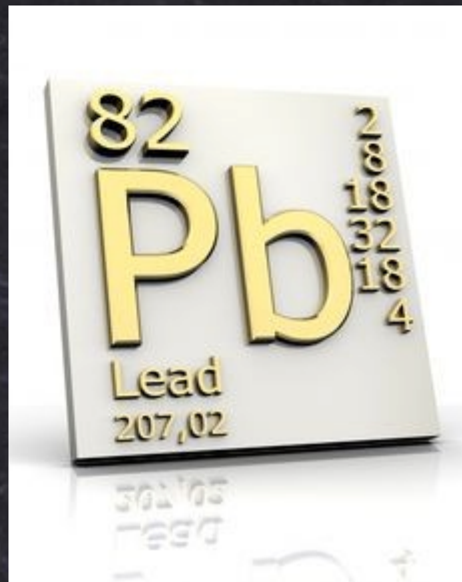


פליטת כספית 2002

kg/km2/y



עופרת



Lead is one of only a few elements known to ancient peoples.

Throughout history, Lead has been used to make water and sewer pipes; roofing; cable coverings; type metal and other alloys; paints; wrappings for food, tobacco, and other products; and as an additive in gasoline.

Lead is a moderately active metal. It dissolves slowly in water and in most cold acids. It reacts more rapidly with hot acids.

עופרת – הממתיק המלאכותי הראשון

Exposure

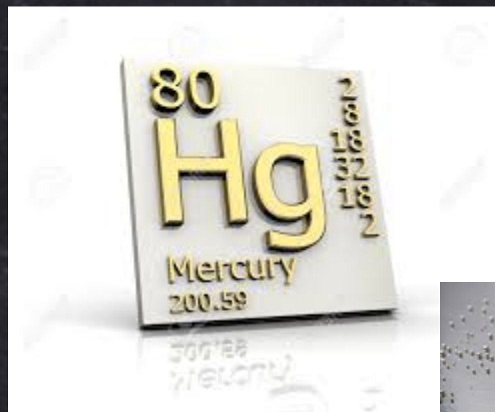
- Water system - plumbing (Pb) . Tap water from ancient Rome likely contained up to 100 times more lead than local spring water (Delile et al, PNAS 2014)
- Mining
- Processing
- Atmospheric release
- Tools (utensils and cooking pots)
- wine boiled down in lead pots
- Paints and cosmetics

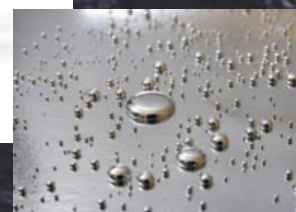
Sugar of Lead (Pb(II) Acetate)
The first artificial sweetener

Once inside the body, Pb interferes with the propagation of signals through the central nervous system, and it inveigles its way into enzymes, disrupting their role in processing the nutritious elements zinc, iron and calcium

The Romans were aware that lead could cause serious health problems, even madness and death. However, they were so fond of its diverse uses that they minimized the hazards it posed.

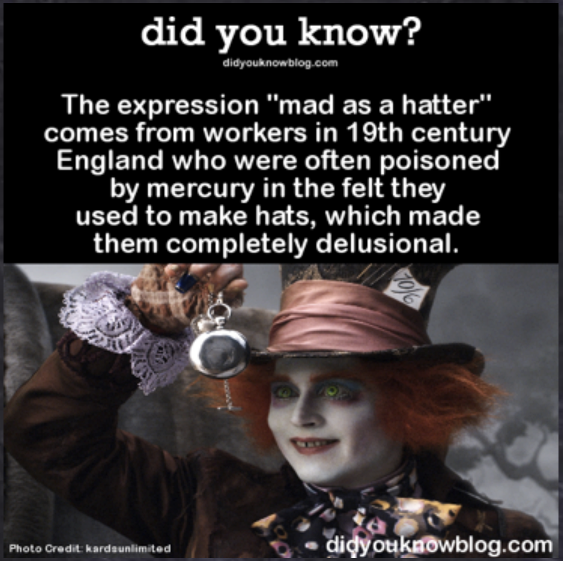
כספית





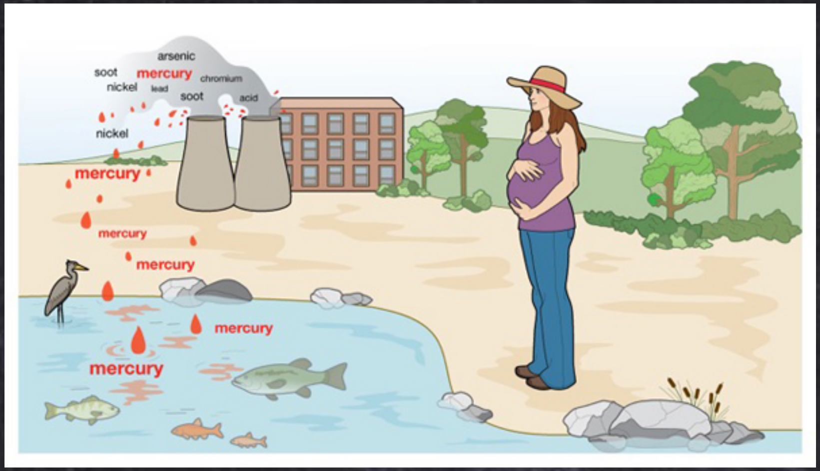
כספית הוא היסוד הלא רדיואקטיבי הרעיל ביותר שמוכר היום.

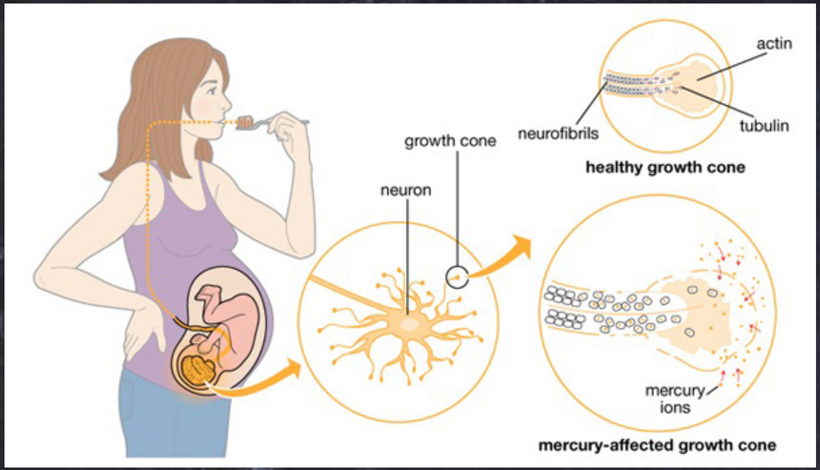
מספיק 2 ק"ג של כספית לזהם את כל הכנרת.

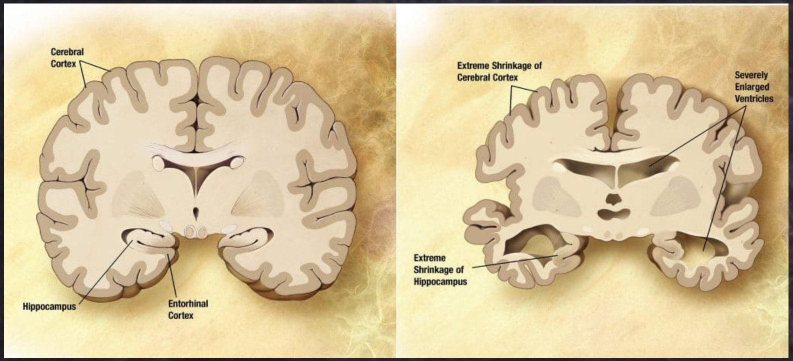


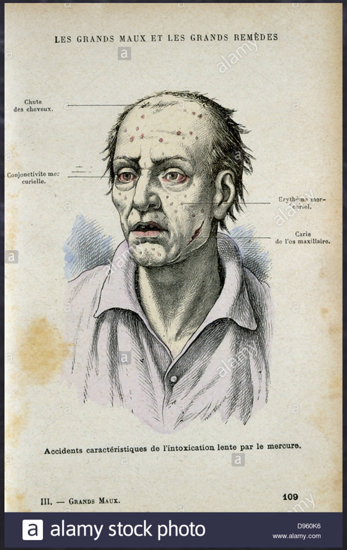
Some of the steps in the manufacture of felt hats are illustrated in this image from 1858.

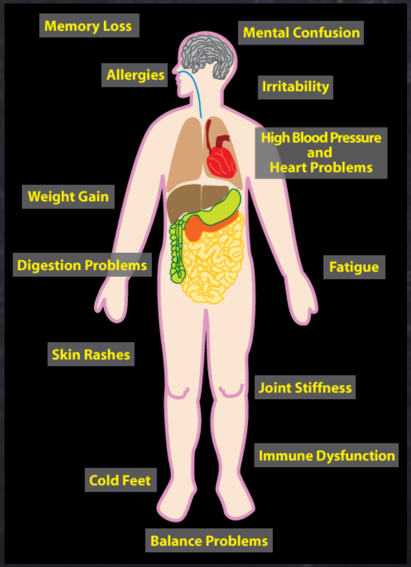
The true origin of the saying relates to a disease peculiar to the hat making industry in the 1800s. A mercury solution was commonly used during the process of turning fur into felt, which caused the hatters to breathe in Hg fumes. This led in turn to an accumulation of mercury in the workers' bodies, resulting in symptoms such as trembling (known as "hatters' shakes"), loss of coordination, slurred speech, loosening of teeth, memory loss, depression, irritability and anxiety -- "The Mad Hatter Syndrome."


arsenic
soot
mercury
chromium
nickel
lead
soot
acid
nickel
mercury
mercury
mercury
mercury
mercury


actin
neurofibrils
tubulin
growth cone
healthy growth cone
neuron
mercury ions
mercury-affected growth cone

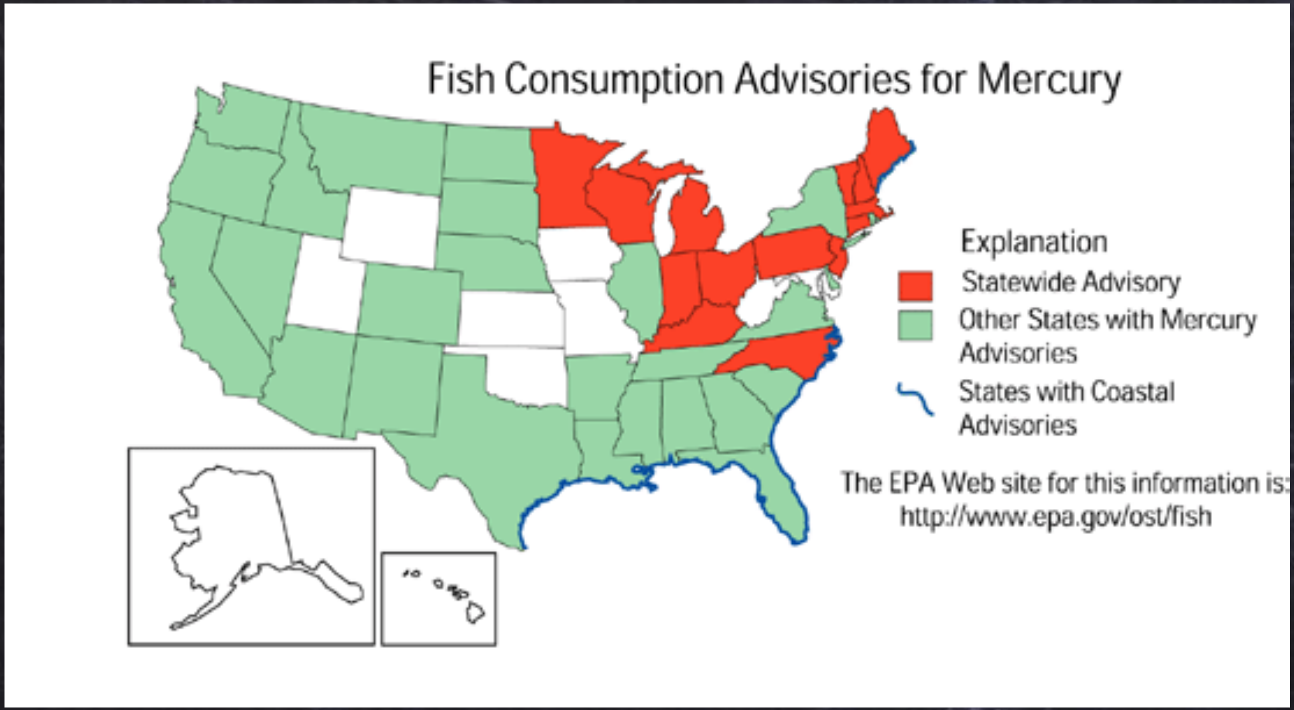

Cerebral Cortex
Hippocampus
Entorhinal Cortex
Extreme Shrinkage of Cerebral Cortex
Severely Enlarged Ventricles
Extreme Shrinkage of Hippocampus


LES GRANDS MAUX ET LES GRANDS REMÈDES
Chute des cheveux.
Carie de l'os maxillaire.
Accidents caractéristiques de l'intoxication lente par le mercure.
III. — Grands Maux.
109
alamy stock photo

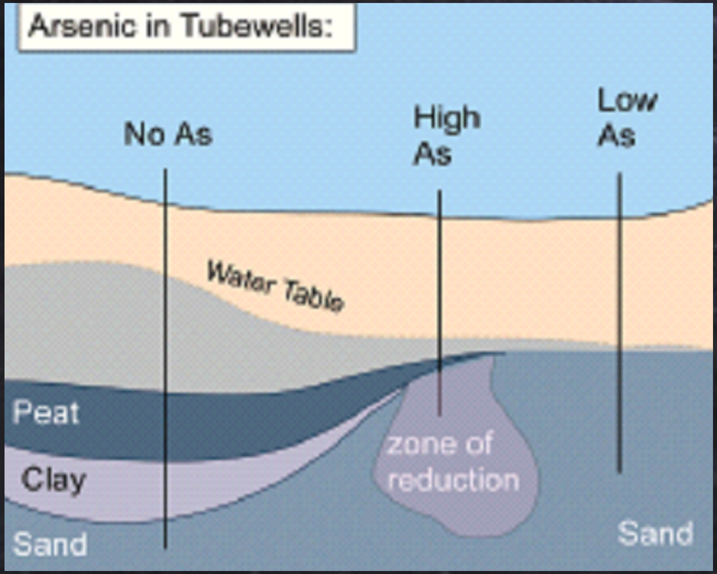

Memory Loss
Mental Confusion
Allergies
Irritability
High Blood Pressure and Heart Problems
Weight Gain
Digestion Problems
Fatigue
Skin Rashes
Joint Stiffness
Immune Dysfunction
Cold Feet
Balance Problems

Exposure to mercury, even in small amounts, is a great danger to humans and wildlife.

When mercury enters the body it acts as a neurotoxin, which means it harms our brain and nervous system. Mercury exposure is especially dangerous to pregnant women and young children, but all adults are at risk for serious medical problems.

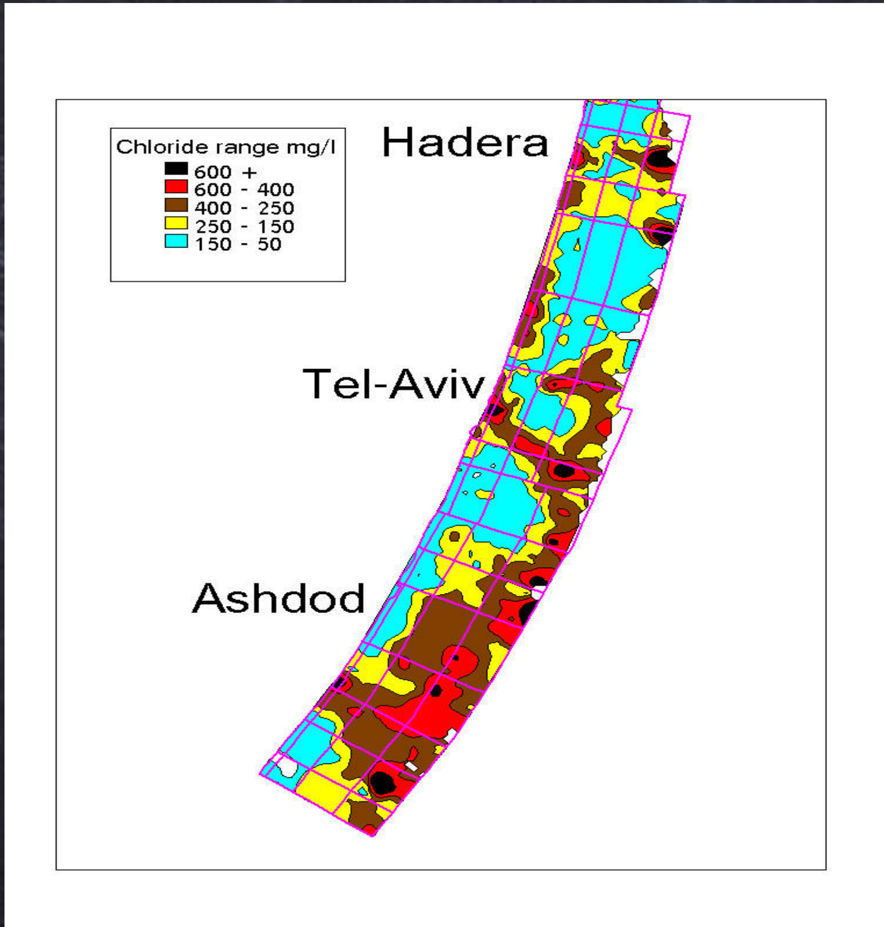


ארסן


Arsenic in Tubewells:
No As
High As
Low As
Water Table
Peat
Clay
Sand
zone of reduction
Sand

מלחים

מלחים היו תמיד בסביבה בכמויות גדולות. השימוש המוגבר במלחים שאיבה לא מבוקרת של מים מתוקים ושינויים בשימוש בקרקע מסיטים את המאוזן העדין וגורמים להמלחת קרקע ומים. התוצאות של המלחה כוללות הריסת נישות אקולוגיות, התדרדרות איכות המים עד רמה שהם הופכים לא ראויים לשתיה, פגיעה באיכות הקרקע שגורמת לאי פוריות ושינוי מבנה הקרקע.

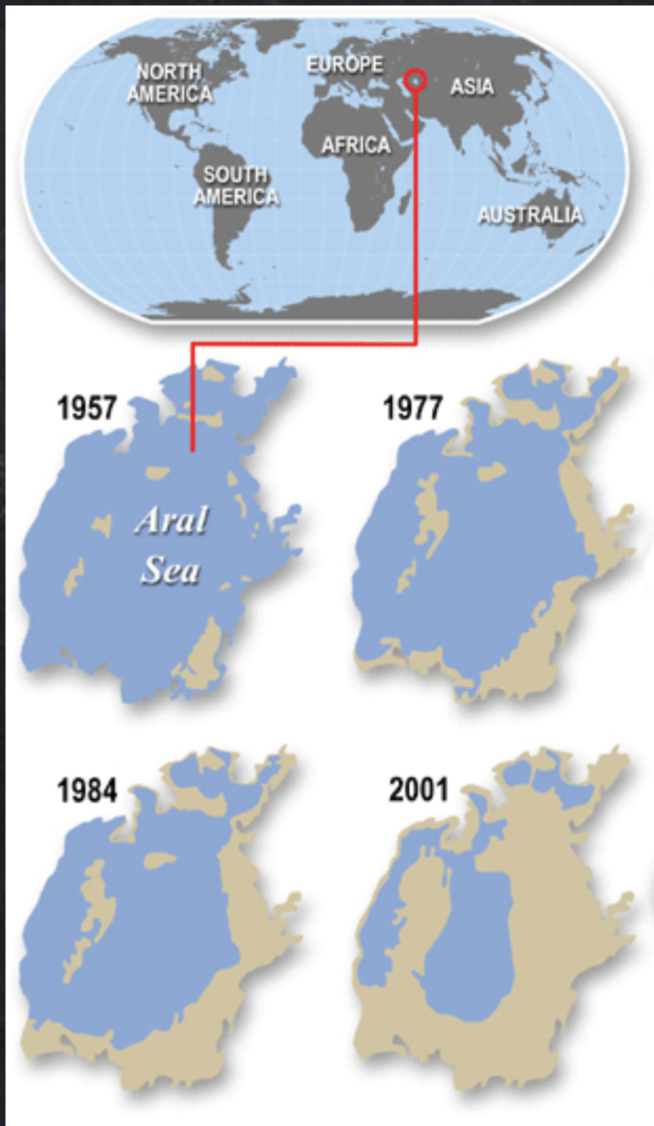


60% ממי ההשקיה נצרכים על ידי הצמחים אבל המלחים נשארים וגורמים להמלחת קרקעות ותשטיפים.

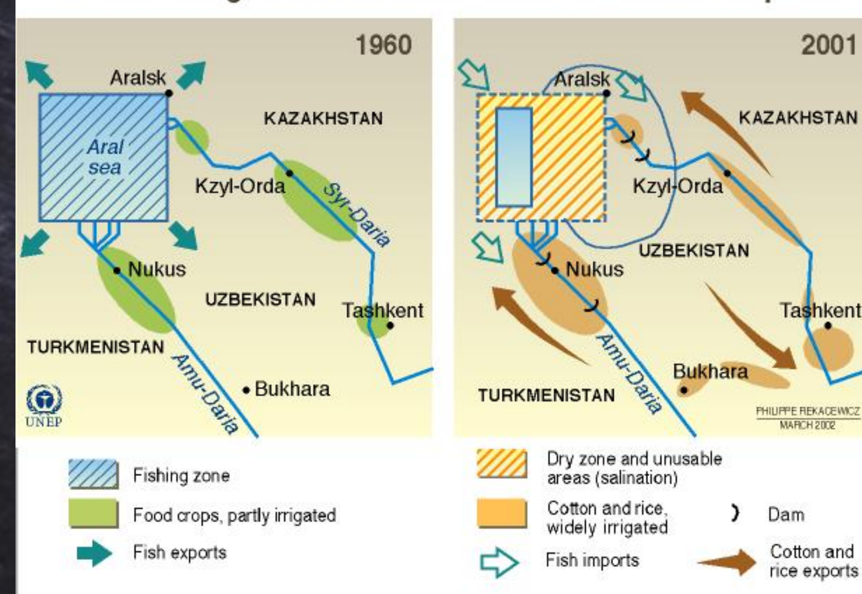
ריכוז מלחים גבוהה גורם להקטנת ההפרש האוסמוטי שמאפשר העברת מים מהקרקע לשורשים ולצמח.

המלחת הקרקע כתוצאה מהשקייה לא אופקטיבית משפיעה על 24% מהקרקע המושקת בעולם.

הדוגמא של ימת ארל

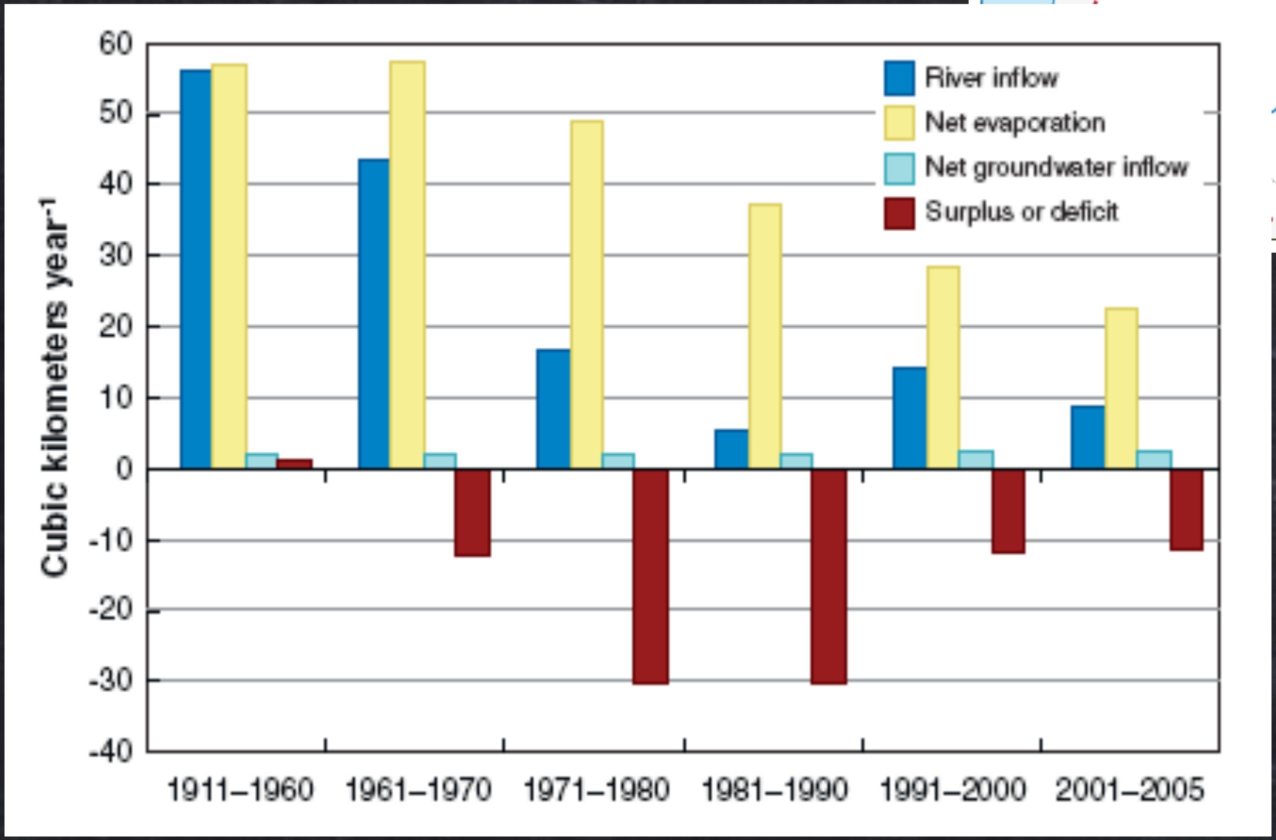


The Shrinking of the Aral Sea: Socio-Economic Impacts



Source: Philippe Rekacewicz, *An Assassinated Sea*, in Histoire-Géographie, initiation économique, page 333, Classe de Troisième, Hatier, Paris, 1993 (data updated in 2002); *L'état du Monde*, 1992 and 2001 editions, La Découverte, Paris.

הדוגמא של ימת ארל



חומרי הדברה

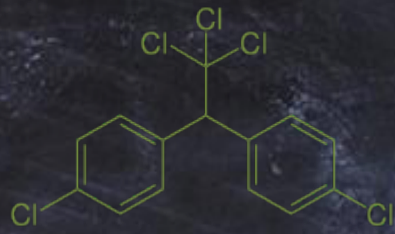
קבוצה גדולה מאוד, דוגמא קלאסית של זיהום על פני שטח גדול. בד"כ כמויות גדולות של חומרים מזיקים מפוזרות על פני שטחים נרחבים ונשטפות על פני הקרקע או בתוכה. (בשנת 2000 פוזרו ברחבי העולם 2,427 מיליארד ק"ג של חומרי הדברה).

חומרים רבים בקבוצה יציבים לתקופות ארוכות מאוד ולכן מזהמים את הסביבה לאורך שנים ארוכות.

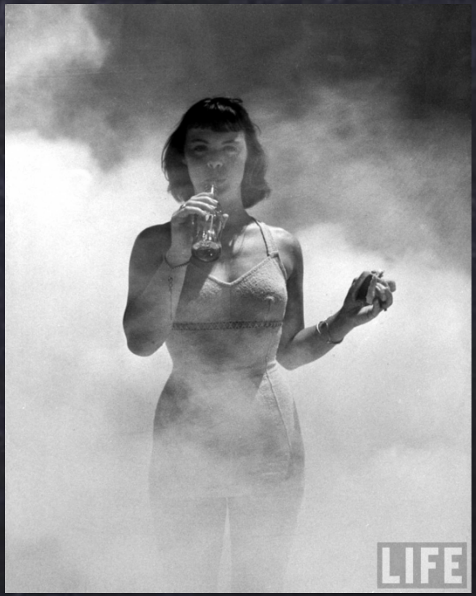
95-97% מהחומר המפוזר – לא מגיע למטרה אלא מפוזר בסביבה.

דו"ח של האו"מ מ 1990 מדווח על 3.5-5 מליון מקרים של הרעלה חמורה כתוצאה מחשיפה לחומרי הדברה.

DDT

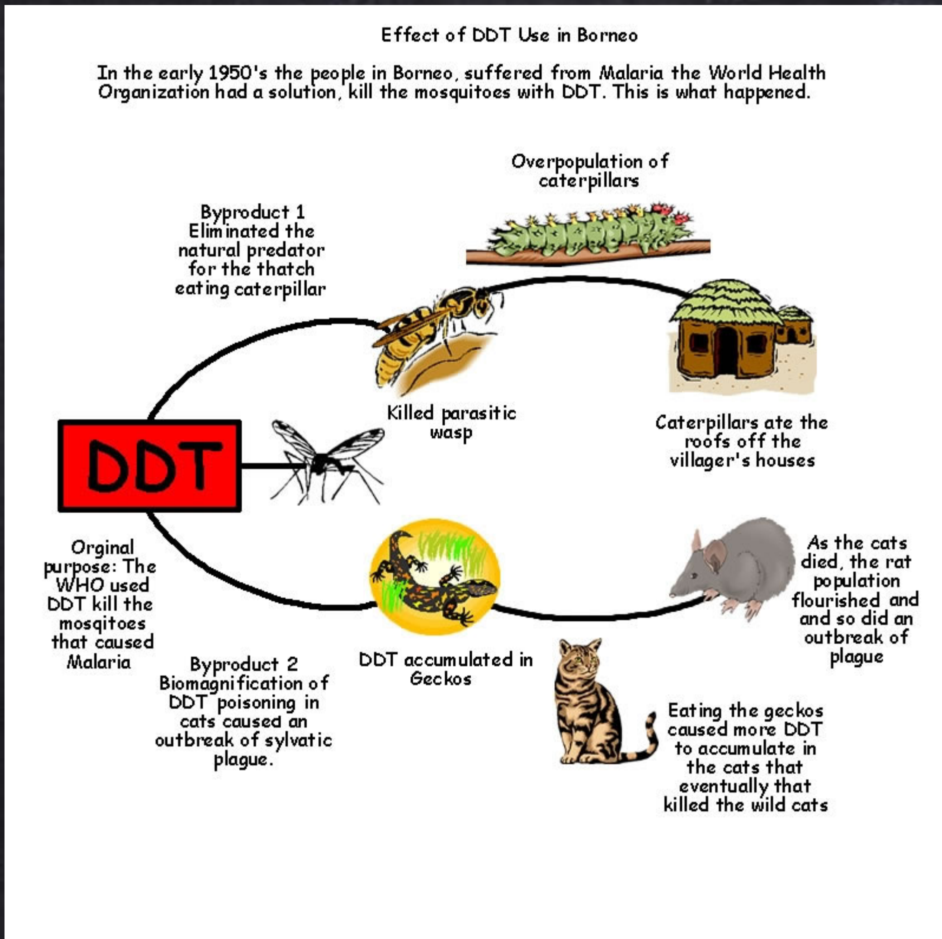


- DDT is an organochlorine insecticide that was first synthesized in 1874
- DDT's insecticidal action was discovered by the Swiss chemist Paul Hermann Müller in 1939.
- DDT was initially used by the military in WW II to control malaria, typhus, body lice, and bubonic plague. Cases of malaria fell from 400,000 in 1946 to virtually none in 1950.
- The reason why DDT was so widely used was because it is effective, relatively inexpensive to manufacture, and lasts a long time in the environment
- Müller was awarded the Nobel Prize in Physiology or Medicine "for his discovery of the high efficiency of DDT as a contact poison against several arthropods" in 1948.



DDT was banned for agricultural use worldwide by 2001 because it persists in the environment, accumulates in fatty tissues, and can cause adverse health effects on human and wildlife.

DDT is an endocrine disruptor. It is considered likely to be a human carcinogen although the majority of studies suggest it is not directly genotoxic. DDT is classified as "moderately hazardous" by the World Health Organization, based on the rat oral LD50.


Effect of DDT Use in Borneo
In the early 1950's the people in Borneo, suffered from Malaria the World Health Organization had a solution, kill the mosquitoes with DDT. This is what happened.
Overpopulation of caterpillars
Byproduct 1 Eliminated the natural predator for the thatch eating caterpillar
Killed parasitic wasp
Caterpillars ate the roofs off the villager's houses
DDT
Orginal purpose: The WHO used DDT kill the mosqitoes that caused Malaria
Byproduct 2 Biomagnification of DDT poisoning in cats caused an outbreak of sylvatic plague.
DDT accumulated in Geckos
Eating the geckos caused more DDT to accumulate in the cats that eventually that killed the wild cats
As the cats died, the rat population flourished and and so did an outbreak of plague


THE LADIES KNOW WHAT'S GOOD!
THE PROVEN, KILLING SPRAY
BISON
DIDIT
INSECT SPRAY
KILLS FLIES, MOTHS, FLEAS, ROACHES
MOSQUITOES, ANTS, BED BUGS

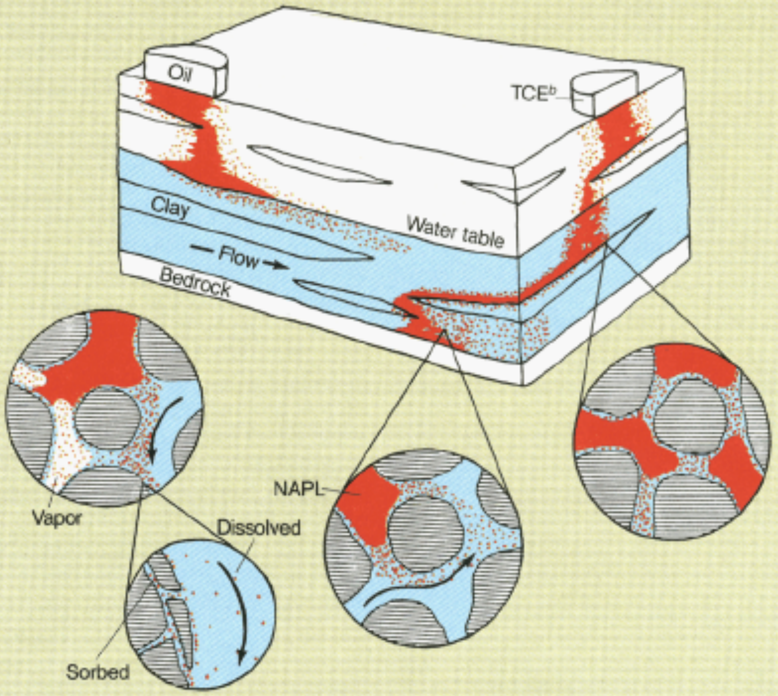

EFFECTS
DDT WAS LATER BANNED

דלקים ושמנים

מבחינה כמותית הקבוצה הגדולה ביותר שנובעת מהתערבות אדם
. כתוצאה מהכמויות האדירות של דלקים המשמשים למגוון יישומים
והפיזור שלהן בכל מקום בעולם ניתן למצוא מזהמים מסוג זה בכל
מקום ובכמויות גדולות.
70-90% מהמיכלים התת-קרקעיים לא עומדים במבחני אטימות.
תוספים שונים לדלקים יכולים להוות בעיה משמעותית.

הדלקים הם תערובות מורכבות של
עשרות/מאות פחמימנים והם יכולים
לנוע מתחת לפני השטח כפאזה
נפרדת כמומסים וכאדים בפאזה
הגזית.

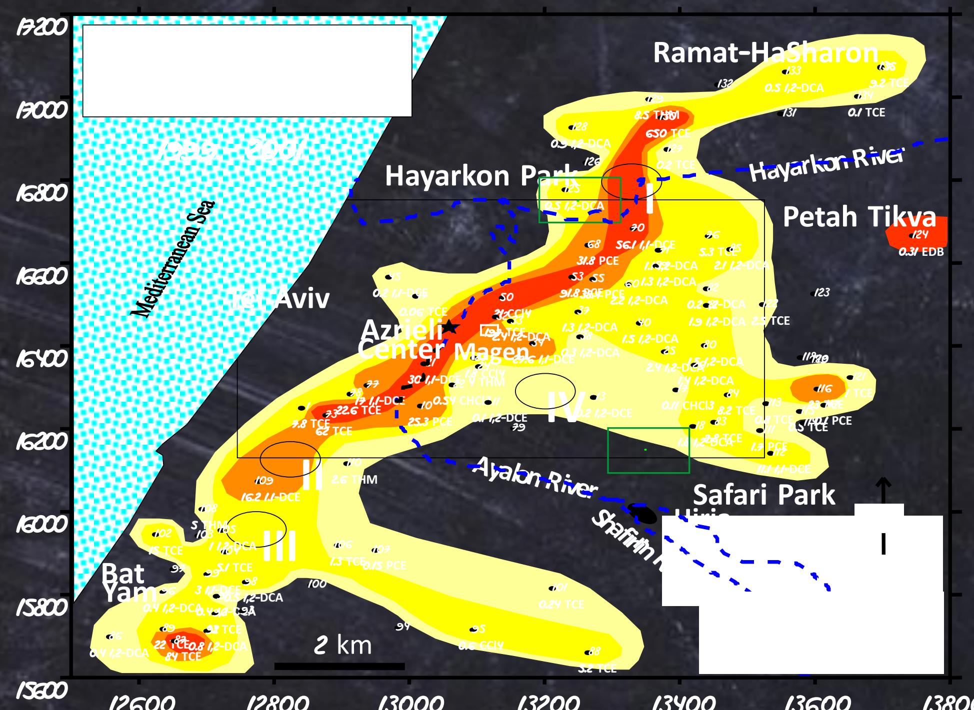
FIGURE 1
Schematic of granular subsurface environment[a]



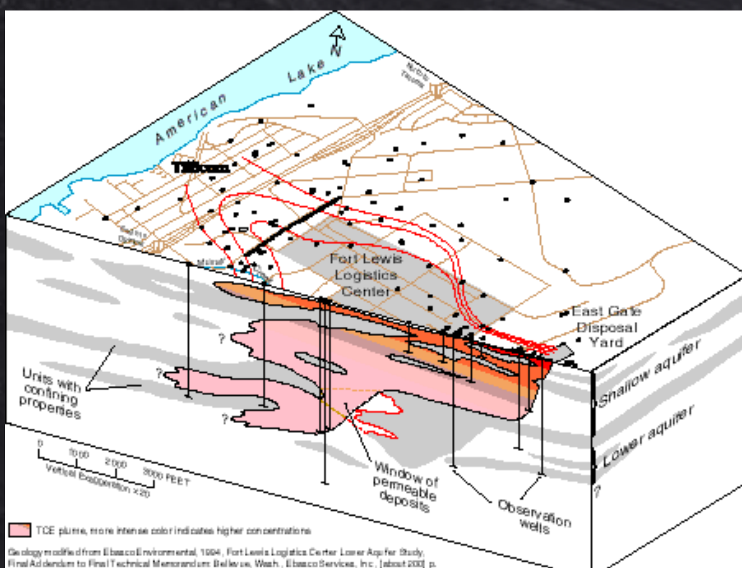
ממסים כלורואורגנים

- חומרים יציבים במיוחד בסביבה עמידים לרוב תהליכי הפירוק הטבעיים.
- ידועים כרעילים ומסרטנים גם בריכוזים נמוכים.
- חומרים מעשי ידי אדם כבדים ממים ובחלקם נדיפים למחצה.

הערכות מדברות שכמיליארד ממ"ק מי תהום מזוהמים באזור ת"א. חלק זה של האקוויפר מספק מידי שנה 8 מליון ממ"ק לתושבים ותעשיה.



Area I: >= 100% IDWS for one VOC or more (12.8% wells)
Area II 50% to <100% of IDWS " " " (12.8% wells)
Area III 10%-<50% of IDWS " " " (48.7% of wells)
Area IV 0<VOC<10% of IDWS " " " (25.7% of wells)
IDWS- Israel drinking water stand



USGS project 1998 Fort Lewis, Washington

(Graber, Ronen et al 2000\1)

Schematic of subsurface environment composed of fractured rock under the overburden[a]

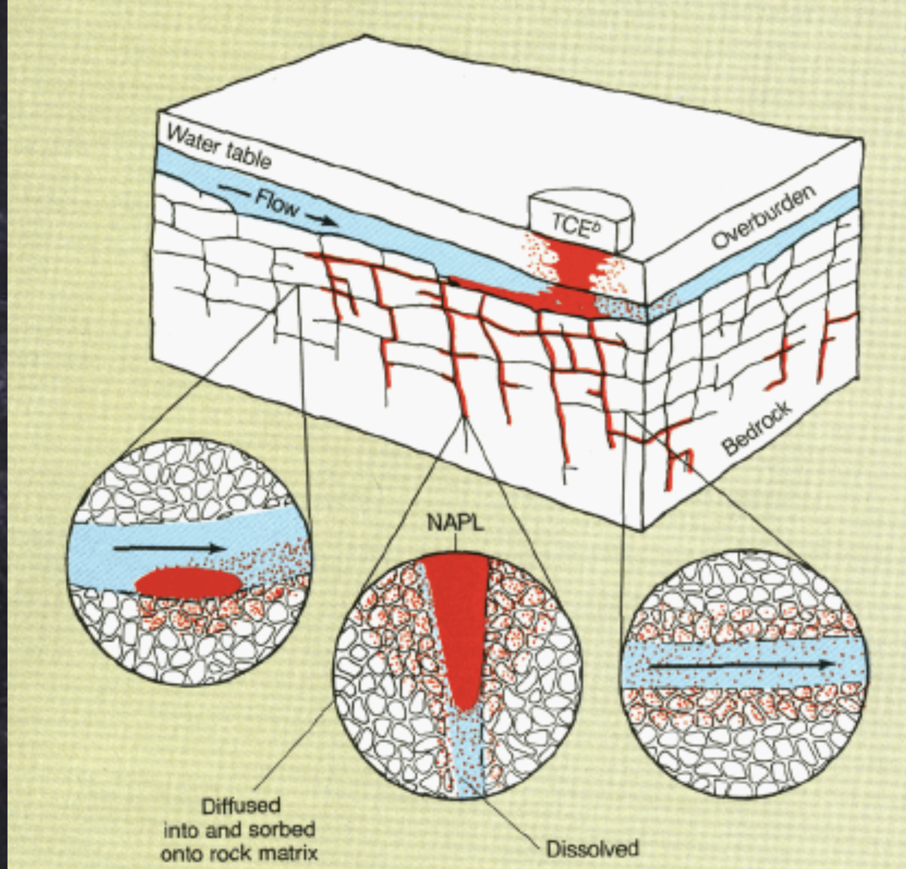
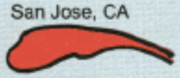


TABLE 1

Relatively well-documented organic contaminant plumes in sand–gravel aquifers[a]

Site location and plume map (0 — 5 km, Flow →)	Presumed sources	Predominant contaminants[b]	Plume volume (liters)[c]	Contaminant mass dissolved in plume (as equivalent NAPL volume in liters or 55-gal drums)[c]
Ocean City, NJ 	chemical plant	TCE TCA PER	5,700,000,000	15,000 (72 drums)
Mountain View, CA 	electronics plants	TCE TCA	6,000,000,000	9800 (47 drums)
Cape Cod, MA 	sewage infiltration beds	TCE PER Detergents	40,000,000,000	1500 (7 drums)[d]
Traverse City, MI 	aviation fuel storage	Toluene Xylene Benzene	400,000,000	1000 (5 drums)
Gloucester, ON Canada 	special waste landfill	1, 4 Dioxane Freon 113 DEE, THF	102,000,000	190 (0.9 drum)
San Jose, CA 	electronics plant	TCA Freon 113 1, 1 DCE	5,000,000,000	130 (0.6 drum)
Denver, CO 	trainyard, airport	TCE TCA DBCP	4,500,000,000	80 (0.4 drum)

[a] Readers aware of other well-documented cases for which reliable estimates of contaminant mass distribution and organic carbon content (f_{oc}) of the aquifer solids are available are encouraged to contact the authors, who plan to expand this compendium.

[b] TCE = trichloroethylene; TCA = 1, 1, 1 trichloroethane; PER = per-, i.e., tetrachloroethylene; 1, 1DCE = 1, 1 dichloroethylene; CHCL3 = chloroform; DEE = diethyl ether; THF = tetrahydrofuran; DBCP = dibromochloropropane.

[c] Approximate estimates derived from plume length, groundwater velocity, contaminant concentration distributions, etc., provided for illustrative purposes only. Estimated contaminant mass accounts only for the dissolved phase (i.e., does not account for contaminant sorbed to the aquifer media throughout the plume or for NAPL contaminant, if any, from the sources). Most of basic data is from unpublished sources; data on three plumes are published *(13, 27, 28, 29)*.

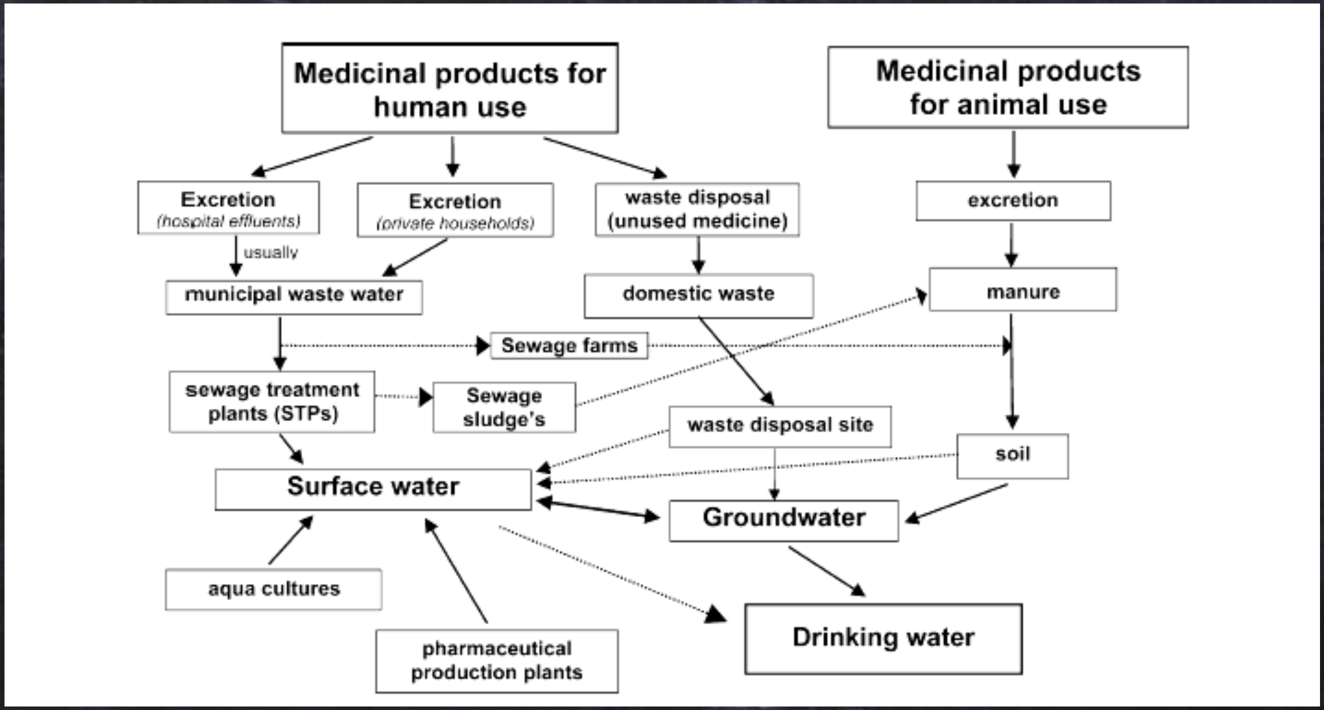
[d] This mass estimate is for the halogenated contaminants only (i.e., detergents are excluded).

Mackay and Cherry ES&T 1989

תרופות ומוצרי טיפוח

הקטגוריה כוללת תרופות והורמונים, חומרים קוסמטיים, תוספי מזון, סמים ותוצרי הפירוק שלהם.
כמויות משתנות נמצאו כמעט בכל מקום בו נבדקו, למשל: אוסטרליה, ברזיל, קנדה, קרואטיה, דנמרק, אנגליה, גרמניה, יוון, איטליה, ספרד, שוויץ, הולנד, וארה"ב.

קבוצה זאת של חומרים חסינה לכל תהליכי הטיפול הקונבנציונאליים ולכן מגיעה למאגרי המים ומוחזרת לשימוש חוזר. לדוגמא במים המסופקים בלונדון נמצאו שרידים של פרוצאק.



השפעות אפשריות

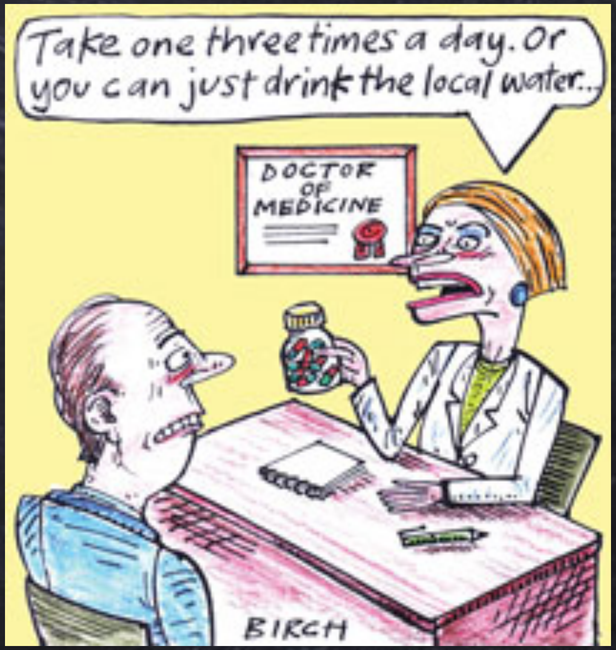
חשיפה כרונית לריכוזים נמוכים של קוקטיל תרופות בעלות השפעה לא רצויה

השפעה לא ספציפית על המערכת האנדוקרינית

זירוז התפתחות עמידות של חידקיים לתרופות

השפעה על המערכת האוקולוגית- שינויי בבעלי חיים

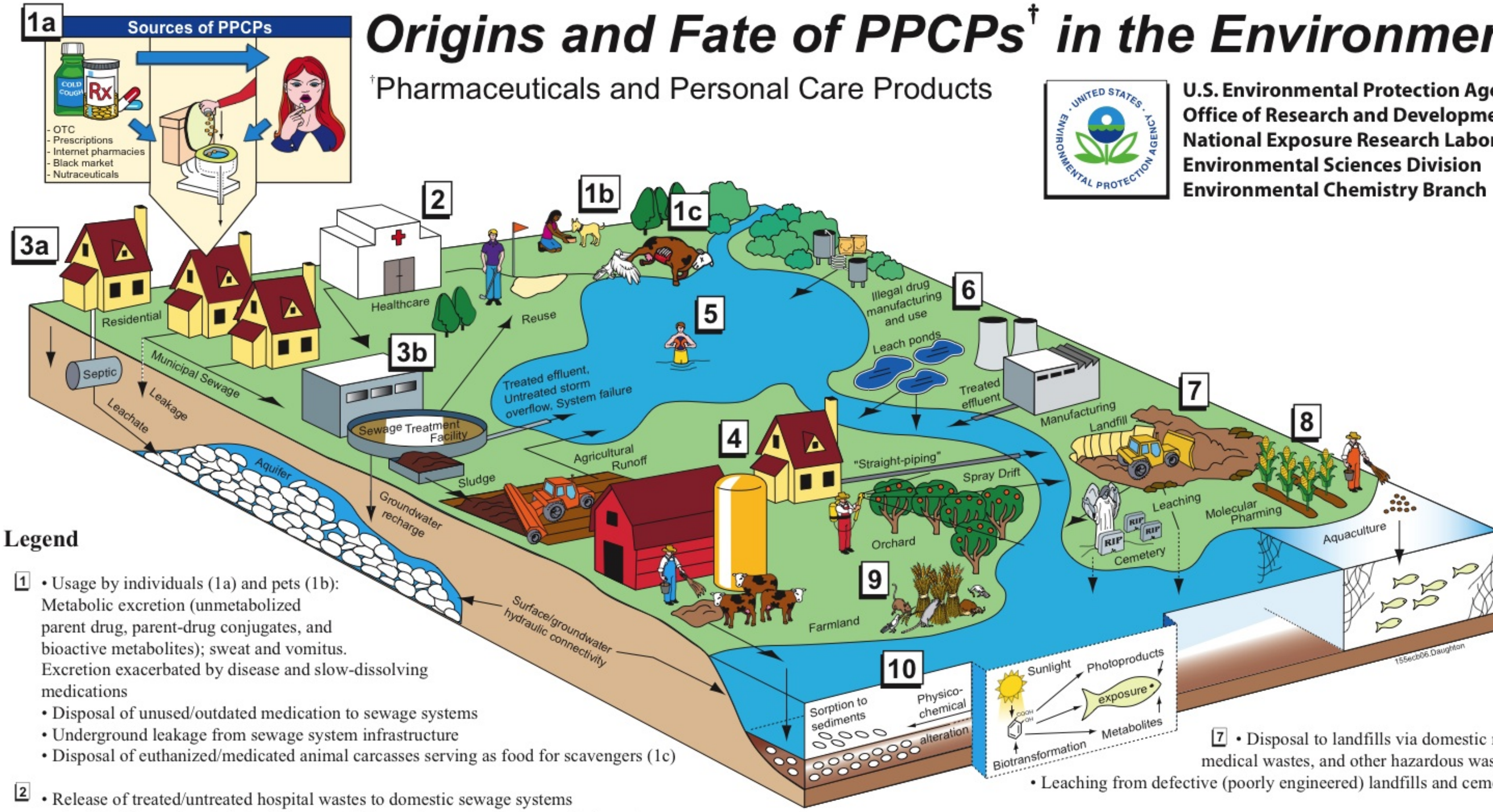
נכון להיום מתקני טיפול בשפכים לא מסוגלים לטפל במזהמים



Origins and Fate of PPCPs[†] in the Environment

[†]Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch



Legend

1 • Usage by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
• Disposal of unused/outdated medication to sewage systems
• Underground leakage from sewage system infrastructure
• Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2 • Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus

3 • Release to private septic/leach fields (3a)
• Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b)
• Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4 • Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
• "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
• Release from agriculture: spray drift from tree crops (e.g., antibiotics)
• Dung from medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5 • Direct release to open waters via washing/bathing/swimming

6 • Discharge of regulated/controlled industrial manufacturing waste streams
• Disposal/release from clandestine drug labs and illicit drug usage

7 • Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
• Leaching from defective (poorly engineered) landfills and cemeteries

8 • Release to open waters from aquaculture (medicated feed and resulting excreta)
• Future potential for release from molecular pharming (production of therapeutics in crops)

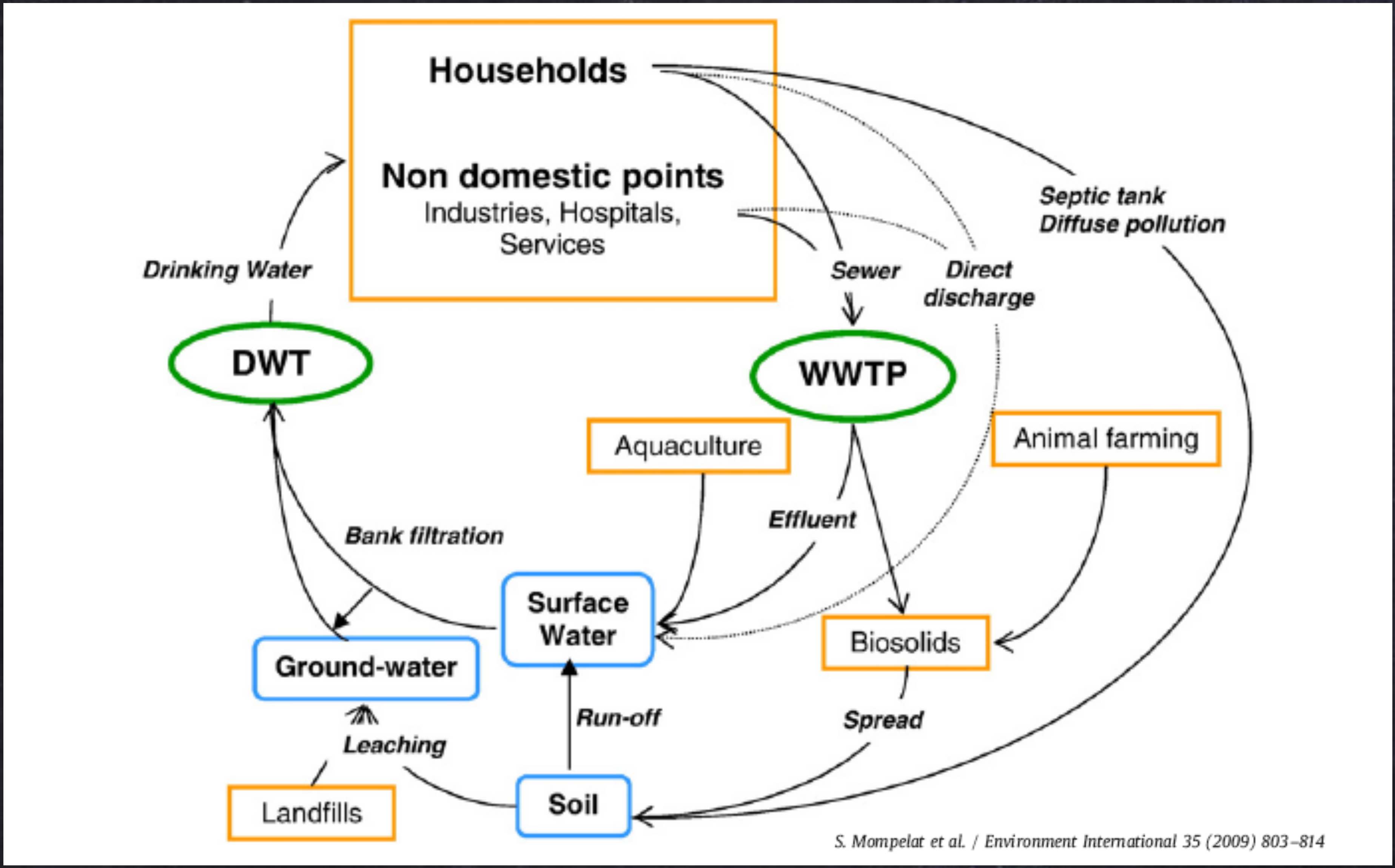
9 • Release of drugs that serve double duty as pest control agents:
examples: 4-aminopyridine, experimental multiple sclerosis drug → used as avicide; warfarin, anticoagulant → rat poison; azacholesterol, antilipidemics → avian/rodent reproductive inhibitors; certain antibiotics → used for orchard pathogens; acetaminophen, analgesic → brown tree snake control; caffeine, stimulant → *coqui* frog control

10 Ultimate environmental transport/fate:
• most PPCPs eventually transported from terrestrial domain to aqueous domain
• phototransformation (both direct and indirect reactions via UV light)
• physicochemical alteration, degradation, and ultimate mineralization
• volatilization (mainly certain anesthetics, fragrances)
• some uptake by plants
• respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

Christian G. Daughton, U.S. EPA-Las Vegas

March 2006
(original February 2001)

http://epa.gov/nerlesd1/chemistry/pharma/images/drawing.pdf
from: http://epa.gov/nerlesd1/chemistry/pharma/


Households
Non domestic points
Industries, Hospitals, Services
Drinking Water
DWT
Sewer
Direct discharge
Septic tank
Diffuse pollution
WWTP
Aquaculture
Animal farming
Effluent
Bank filtration
Surface Water
Ground-water
Biosolids
Run-off
Spread
Leaching
Landfills
Soil
S. Mompelat et al. / Environment International 35 (2009) 803–814

PPCPs- Cont

PPCPs in wastewater

Occurrence of psychoactive stimulatory drugs in wastewaters in north-eastern Spain. Huerta-Fontela et al. (2008) Sci. Tot. Environ.

"Most of the studied controlled drugs (8 out of 11) were found in both influent and effluent samples from several wastewater treatment plants. Cocaine and its metabolite were detected in wastewaters at concentrations ranging from 4 ng/L to 4.7 µg/L and from 9 ng/L to 7.5 µg/L respectively while concentrations of amphetamine type stimulatory drugs ranged from 2 to 688 ng/L."...."From the total concentrations found in wastewater influents estimations of the cocaine and ecstasy consumption were performed. For cocaine the results were approximately 14 doses per 1000 inhabitants (15–64 years old) per day and for ecstasy, approximately 4 doses per 1000 young adults (15–34 years old) per day for ecstasy."

Barbiturates have been widely used as sedative hypnotics in the mid-1960s and since then mainly as veterinary drugs. An average concentration of 0.53 *µg/L barbiturates was detected in all* samples investigated in the river Mulde

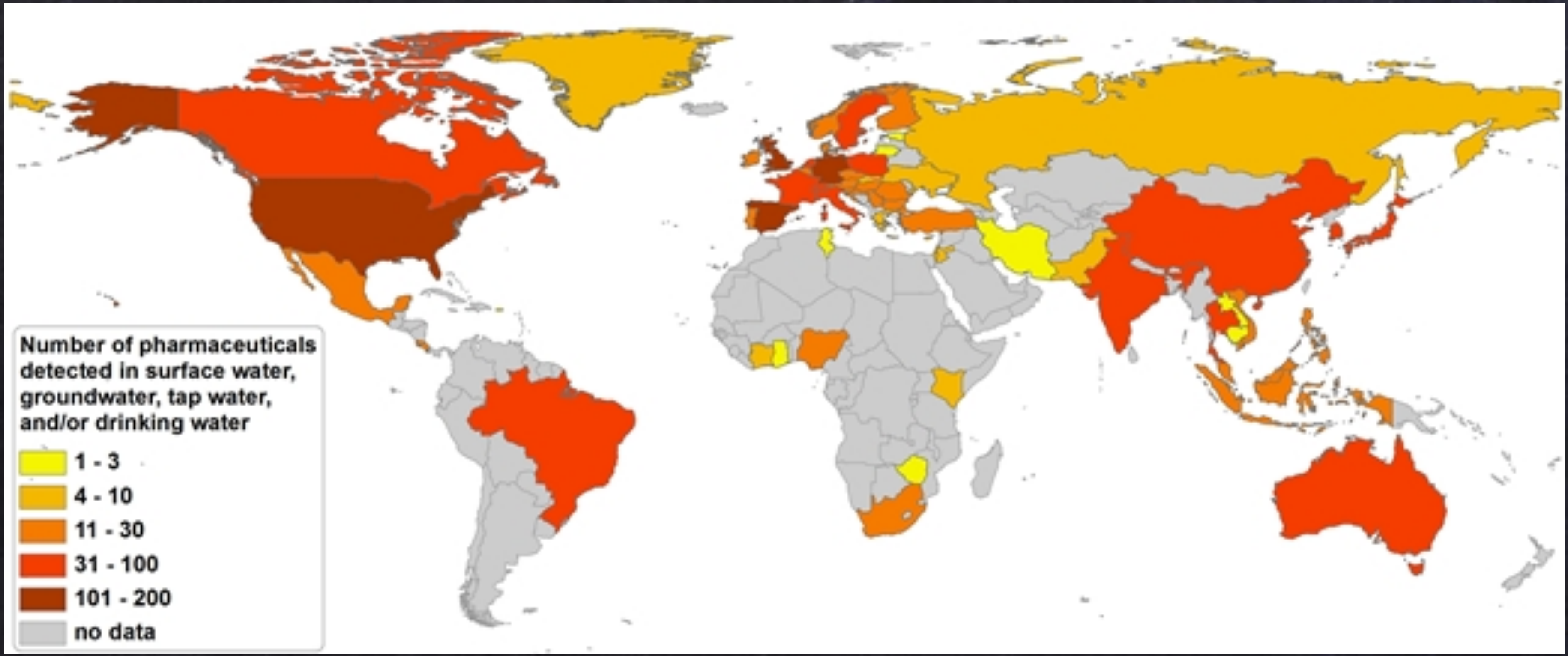
(Germany) Peschka et al., 2006, ES&T.

ריכוזי תרפות ותוצאי פירוק של תרופות במי ברז

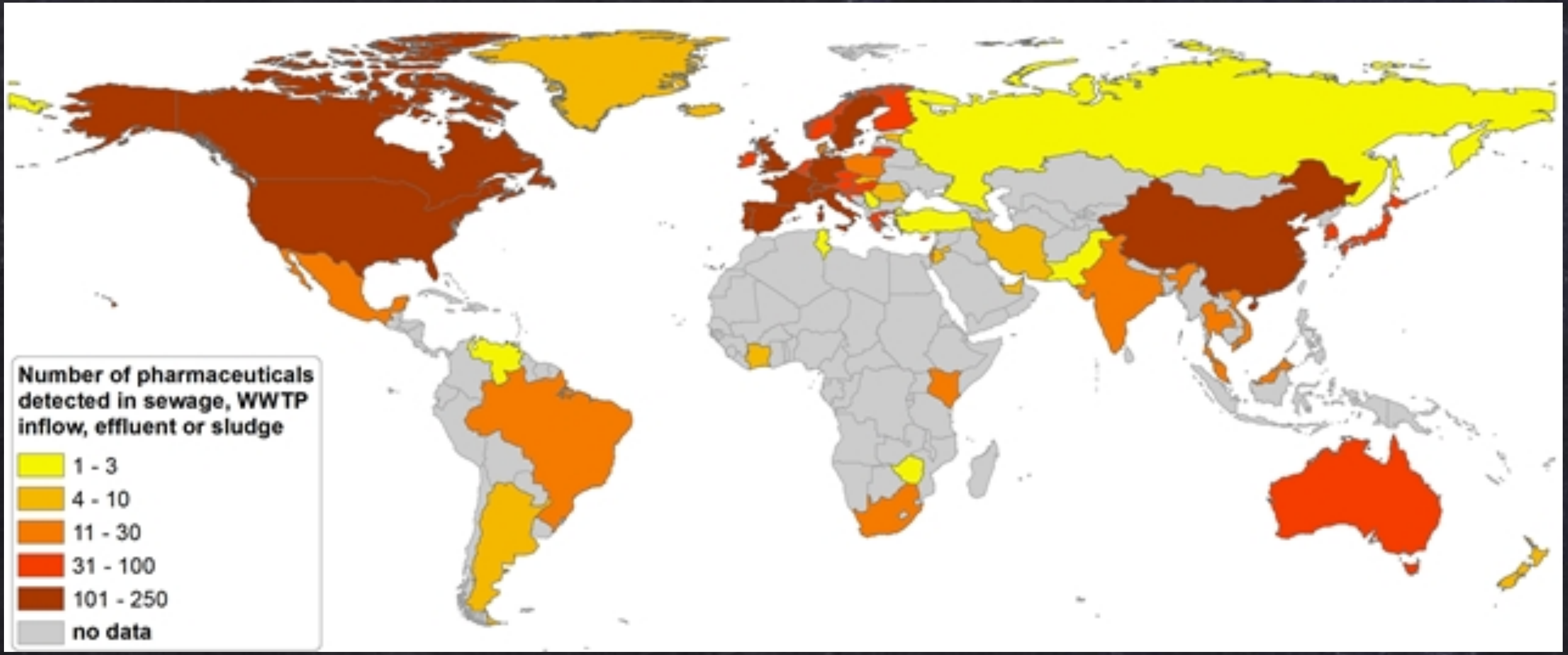
Therapeutic use	Compound	Maximal concentration detected (ng/L)	Country
Antibiotics	Triclosan	734	USA
Anticonvulsants	Carbamazepine	24 / 140-258/43.2/60	Canada/ USA/France/Germany
	Dilantin	1.3	USA
	Primidone	40	Germany
Antidepressants, anti-anxiety	Amitryptilline	1.4	France
	Diazepam	10/23.5	UK/Italy
	Meprobamate	5.9	USA
Antineoplastics	Bleomycin	13	UK
Iodinated X-ray contrast media	Diatrizoate	1200	Germany
	Iopromide	< 50	Germany
Lipid regulators	Bezafibrate	27	Germany
Non-steroidal anti-inflammatory drugs (NSAIDs) and analgesic and analgesics	Gemfibrozil	70	Canada
	Acetaminophen	210.1	France
	AMDOPH	900-1250	Germany
	Diclofenac	6-35/2.5	Germany/France
	DP	1.10	Germany
	Ibuprofen	3/0.6/8.5/1350	Germany/France/Finland/USA
	Ketoprofen	8.0/3.0	Finland/France
	PDP	0.24	Germany
	Phenazone	250-400	Germany
	Propyphenazone	80-240	Germany
Opioidanalgesics	Codein	30	USA
Psycho-stimulants	Caffeine	60-119	USA
		22.9	France

S. Mompelat et al. / Environment International 35 (2009) 803–814

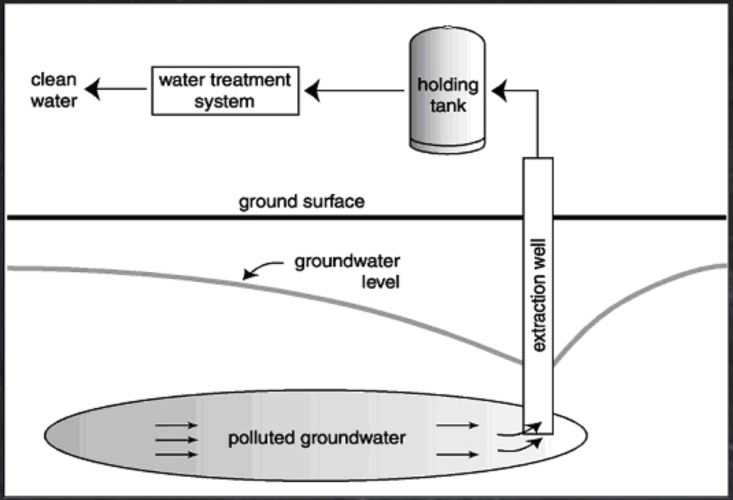
מספר חומרים רפואיים שנמצאו במקורות מים או מי שתייה במדינות שונות

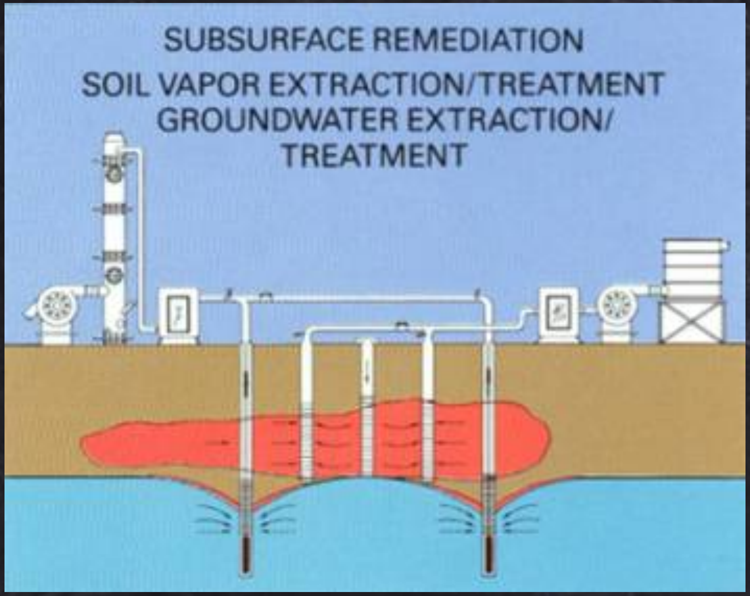


מספר חומרים רפואיים שנמצאו במתקני טיפול בשפכים או בבוצה במדינות שונות



שיטות טיפול





pump & treat – שאב וטפל

שאיבת מים או אויר מאזור מזוהם
, טיפול מעל הקרקע והחזרת
המים למאגר.

בעיות:
טיפול ארוך ויקר בד"כ
פחות יעיל בריכוזים נמוכים ולכן
בד"כ לא יאופשר הגעה ליעדים
של רמות ניקיון.
לא יעיל בכל מבנה קרקע מאוד
רגיש להטרוגניות.

Pump & Treat

Contaminated groundwater is pumped to the surface using a series of extraction wells, where it is subsequently treated to remove the contaminants, and then either reinjected into a groundwater aquifer or discharged into a nearby watercourse.

Surface treatment technologies often include liquid phase granular activated charcoal and air stripping.

The well design, pumping system, and treatment are dependent on the site characteristics and contaminant type. It is not uncommon to find many wells extracting groundwater at the same time. These wells may be screened at different levels to maximize effectiveness.

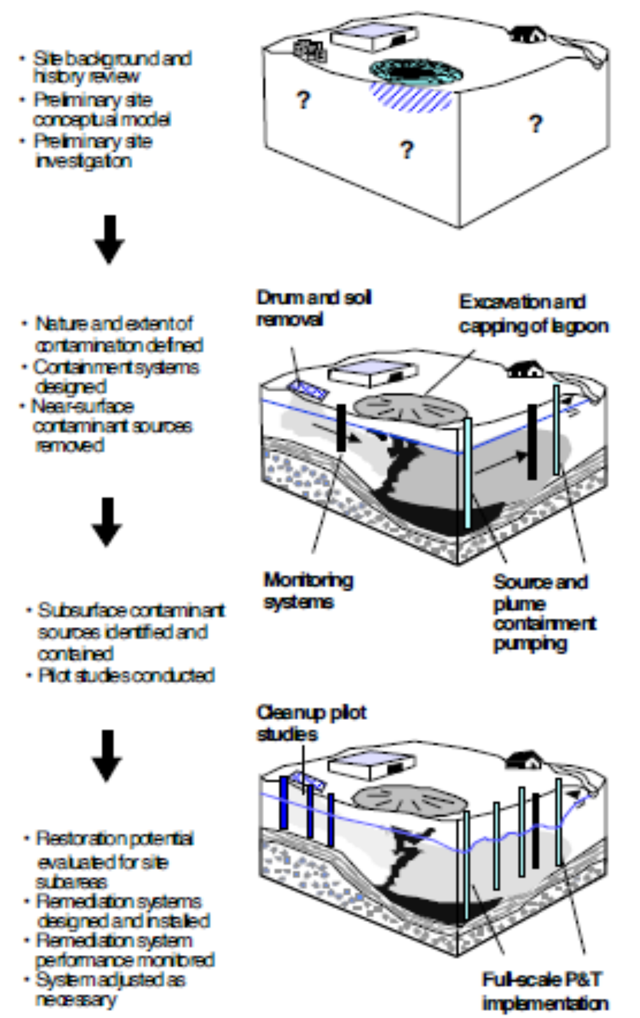


Figure 6. Iterative phases of site characterization and remediation (modified from U.S. EPA, 1993a; NRC, 1994).

Applicability

Pump-and-treat systems remove groundwater contaminated with a variety of dissolved materials, including volatile and semi volatile organic contaminants, fuels, explosive and dissolved metals.

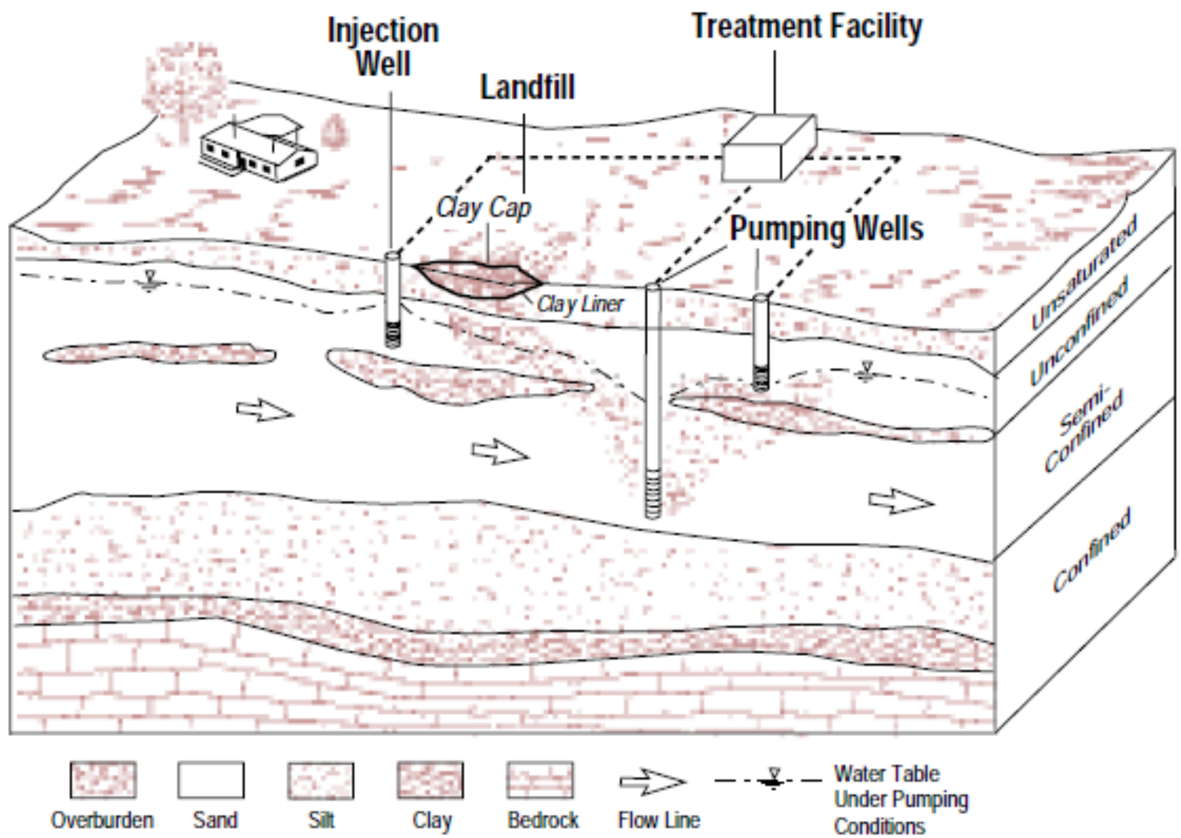
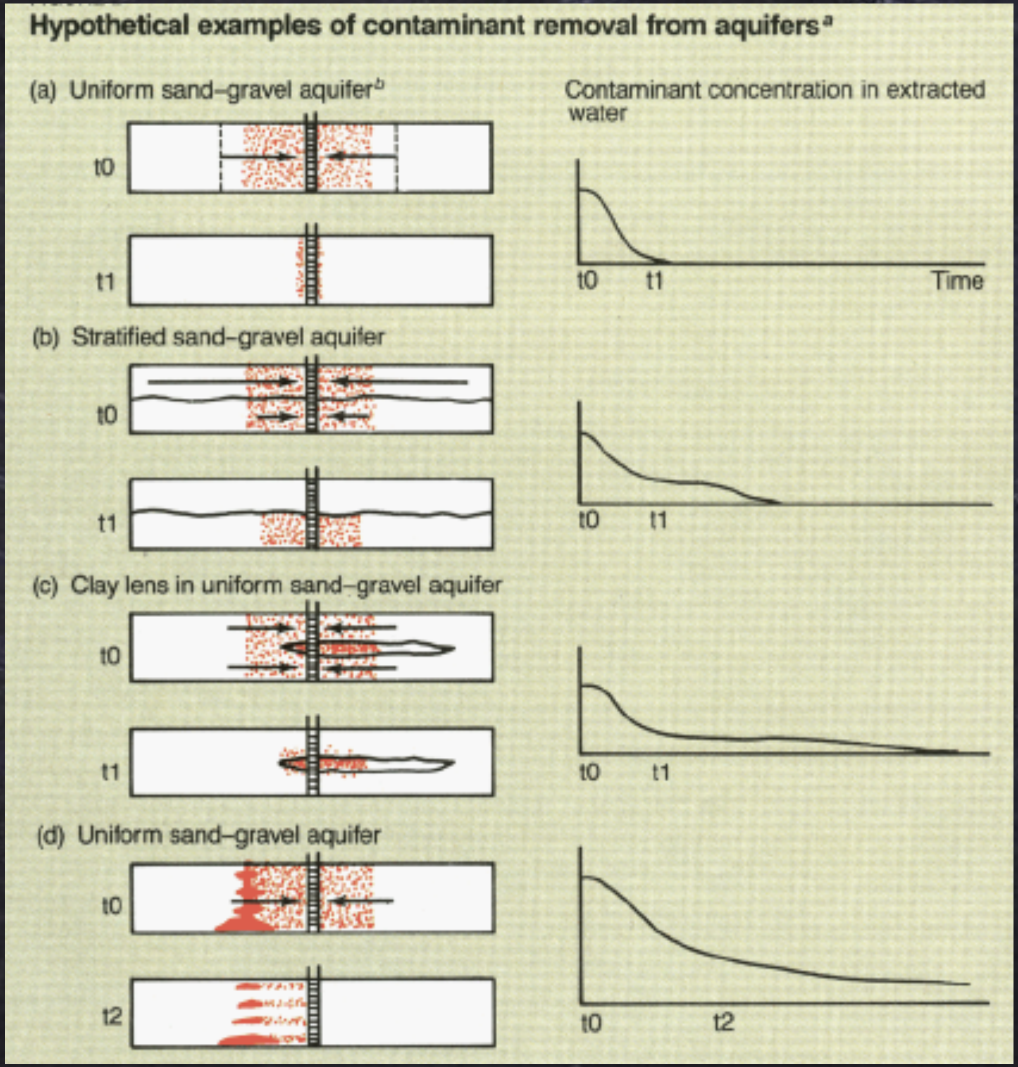


Figure 1. Example of a P&T system (after Mercer et al., 1990).

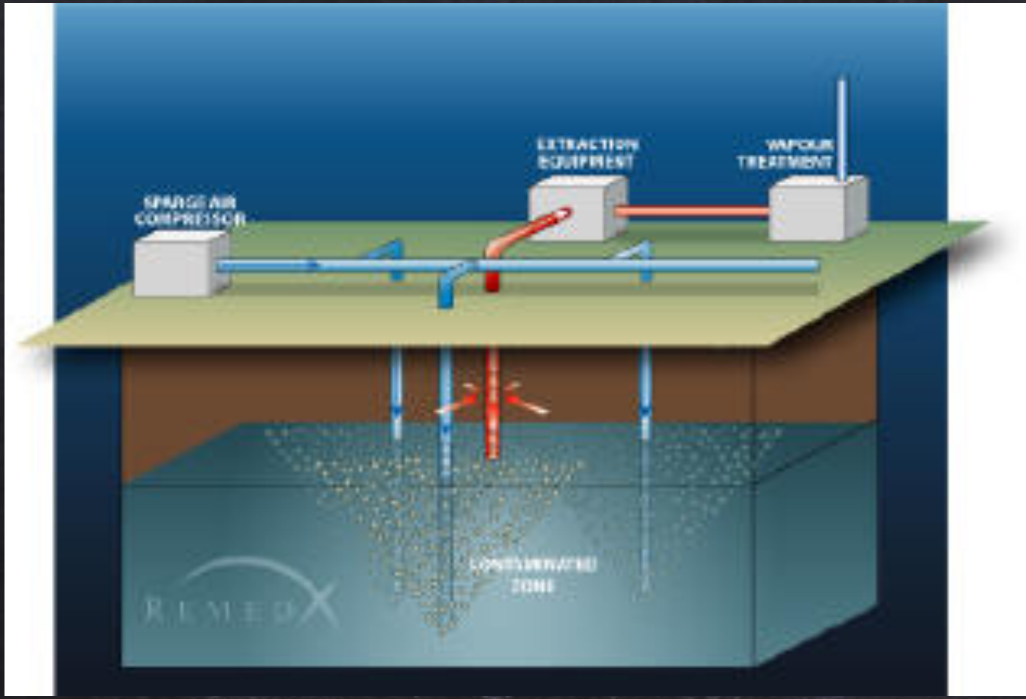
Limitations and Concerns

Pump-and-treat systems often take a very long time (e.g., 50 -100 years) to meet cleanup goals.

Pumping depresses the groundwater level, leaving residuals sorbed to the soil. After the groundwater level returns to its normal level, contaminants sorbed onto soil become dissolved. This phenomenon is called "rebound" . Rebound tests should be performed frequently in the first few years after the system is turned off, and after major precipitation or flooding events.



ביוונטיג, ובעבוע אויר



הזרמת אוויר באזור מזוהם על
מנת לנדף חומרים אורגנים ו/או
להגביר פעילות ביולוגית טבעית
לפרוק מזהמים.

בעיות:
נידוף מוגבל רק חומרים בעלי לחץ
אדים גבוהה ממים.
קשה לשלוט על זרימת האוויר לקבל
חזית נידוף אחידה

Exhibit VII-1
Air Sparging System With SVE

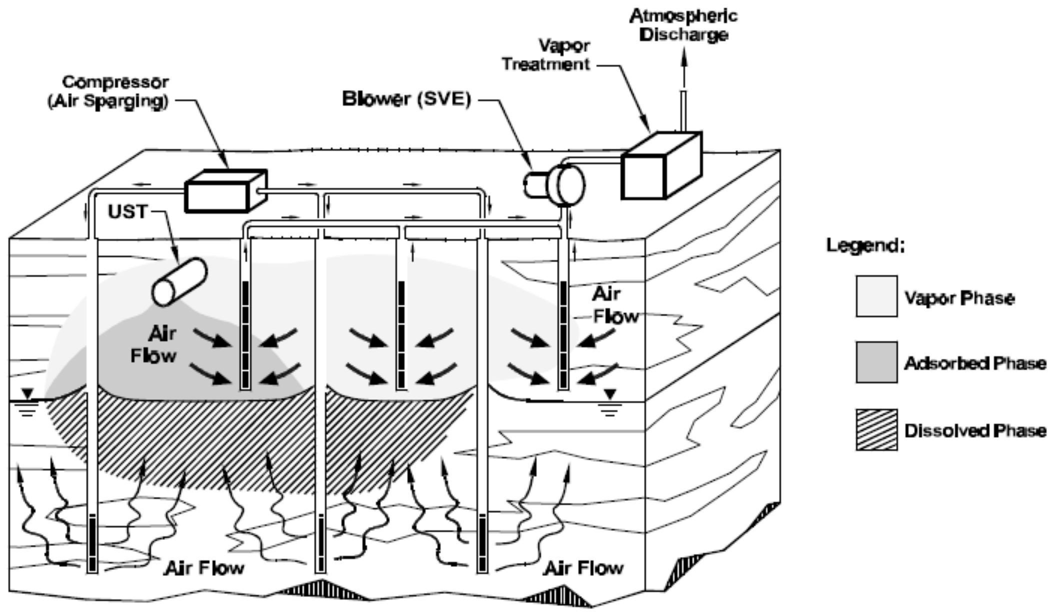


Exhibit VII-4
Iniital Screening for Air Sparging Effectiveness

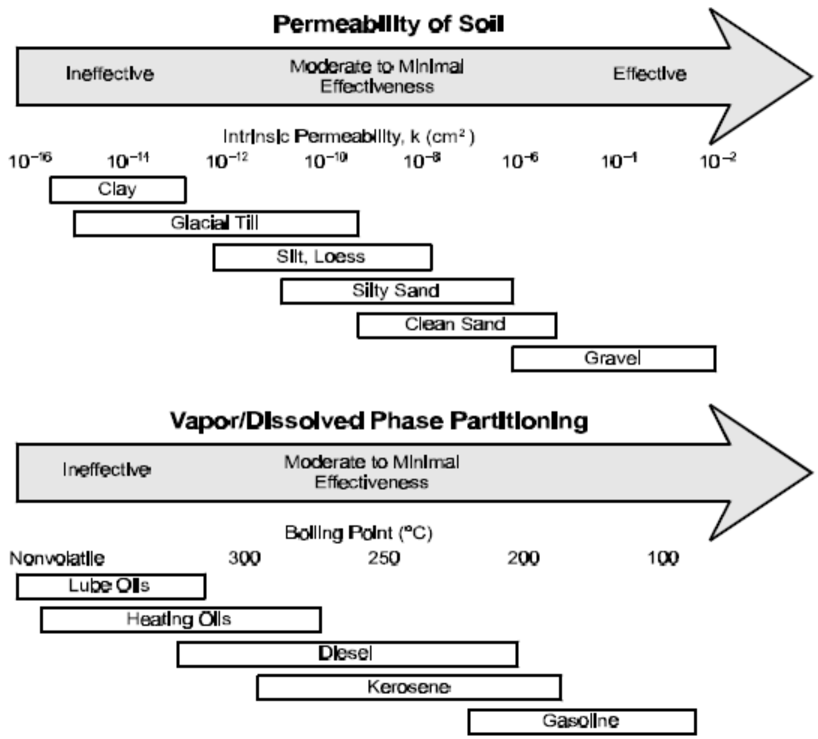
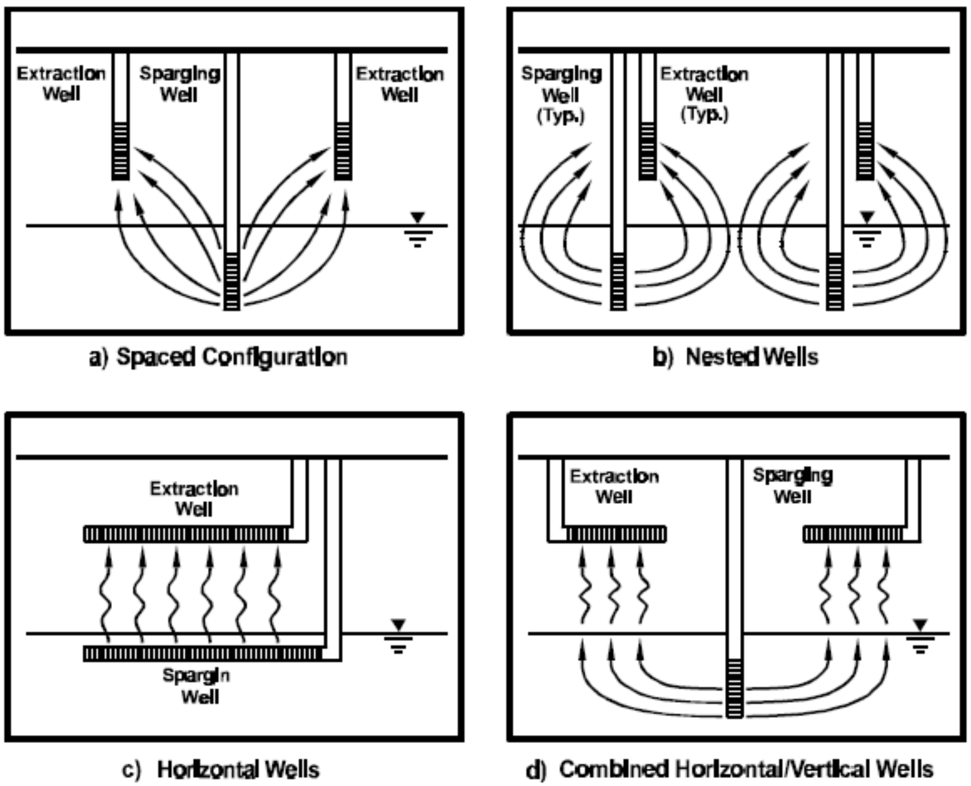
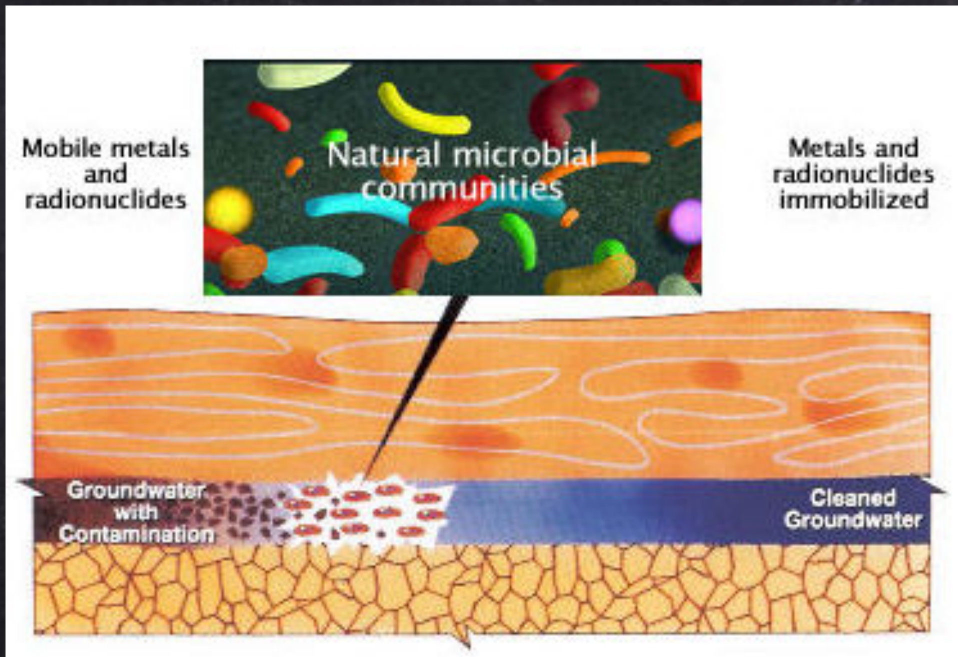


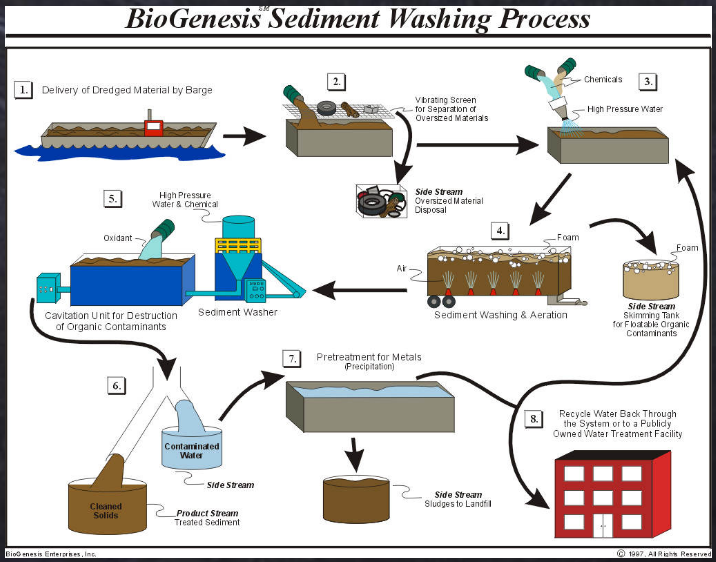
Exhibit VII-16
Air Sparging/Soil Vapor Extraction Well Configurations



Bioremediation – טיפול ביולוגי



טיפול על ידי עידוד פעילות ביולוגית – מציאת אוכלוסיה מיקרוביולוגית קיימת בעלת פעילות מבוקשת ויצירת תנאים אופטימלים לשגשוגה שכתוצאה מכך תביא לפרוק המזהמים.



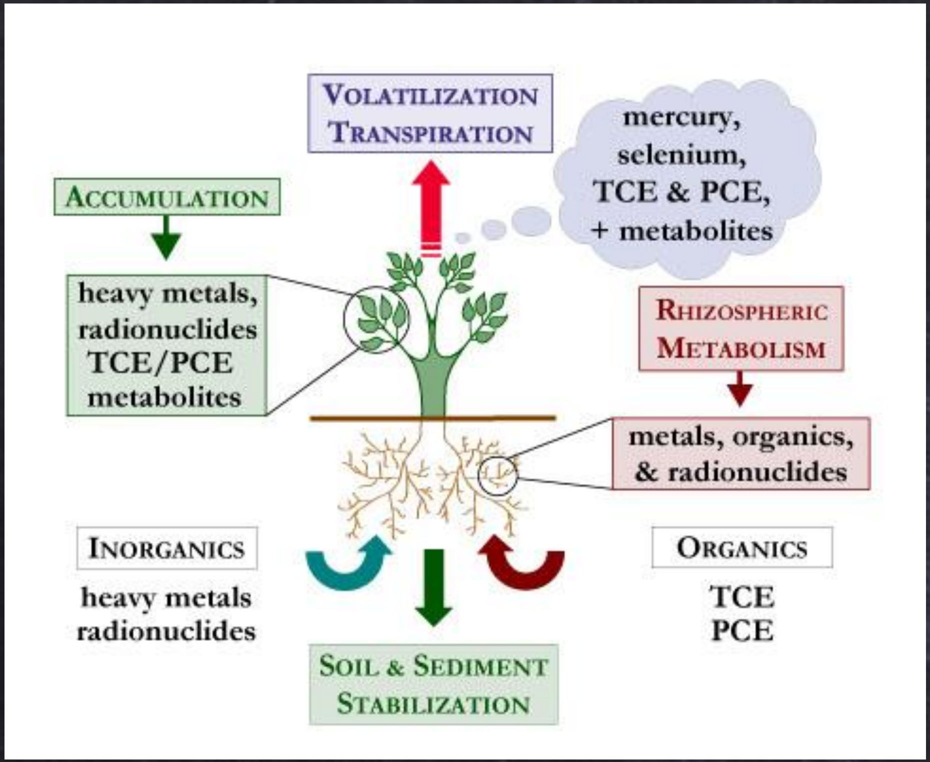
בעיות:

רגישות לתנאים סביבתיים (טמפ. , חומרי הזנה, חומציות, מזהמים אחרים)

תחרות עם אוכלוסיות אחרות לאו תמיד אופקטיבית בתנאים של ריכוזים גבוהים או נמוכים.

<table>
<tr><th>Technology</th><th>Examples</th><th>Benefits</th><th>Limitations</th><th>Factors to consider</th></tr>
<tr><td>In situ</td><td>In situ bioremediation
Biosparging
Bioventing
Bioaugmentation</td><td>Most cost efficient
Noninvasive
Relatively passive
Natural attenuation processes
Treats soil and water</td><td>Environmental constraints
Extended treatment time
Monitoring difficulties</td><td rowspan="2">Biodegradative abilities of indigenous microorganisms
Presence of metals and other inorganics
Environmental parameters
Biodegradability of pollutants
Chemical solubility
Geological factors
Distribution of pollutants</td></tr>
<tr><td>Ex situ</td><td>Landfarming
Composting
Biopiles</td><td>Cost efficient
Low cost
Can be done on site</td><td>Space requirements
Extended treatment time
Need to control abiotic loss
Mass transfer problem
Bioavailability limitation</td></tr>
<tr><td>Bioreactors</td><td>Slurry reactors
Aqueous reactors</td><td>Rapid degradation kinetic
Optimized environmental parameters
Enhances mass transfer
Effective use of inoculants and surfactants</td><td>Soil requires excavation
Relatively high cost capital
Relatively high operating cost</td><td>See above
Bioaugmentation
Toxicity of amendments
Toxic concentrations of contaminants</td></tr>
</table>

Phytoremediation – טיפול בעזרת צמחים



עקרון הטיפול: גידול צמחים המסוגלים לרכז מהמים או מהקרקע את המזהמים.

בעיות:
לא תמיד עובד בריכוזים גבוהים או נמוכים מאוד.

חלק מהחומרים רק מנודפים כך שאנחנו מעבירים את הזיהום לאטמוספרה ולא מטפלים בו.

רוב הזיהומים מופיעים בתערובות כך שגידול צמחים בסביבה כזו הוא מסובך יותר.

Processes mediated by plants for treating environmental problems

Phytoextraction - uptake and concentration of substances from the environment into the plant biomass.

Phytostabilization - reducing the mobility of substances in the environment, for example by limiting the leaching of substances from the soil.

Phytotransformation - chemical modification of environmental substances as a direct result of plant metabolism, often resulting in their inactivation, degradation (phytodegradation) or immobilization (phytostabilization).

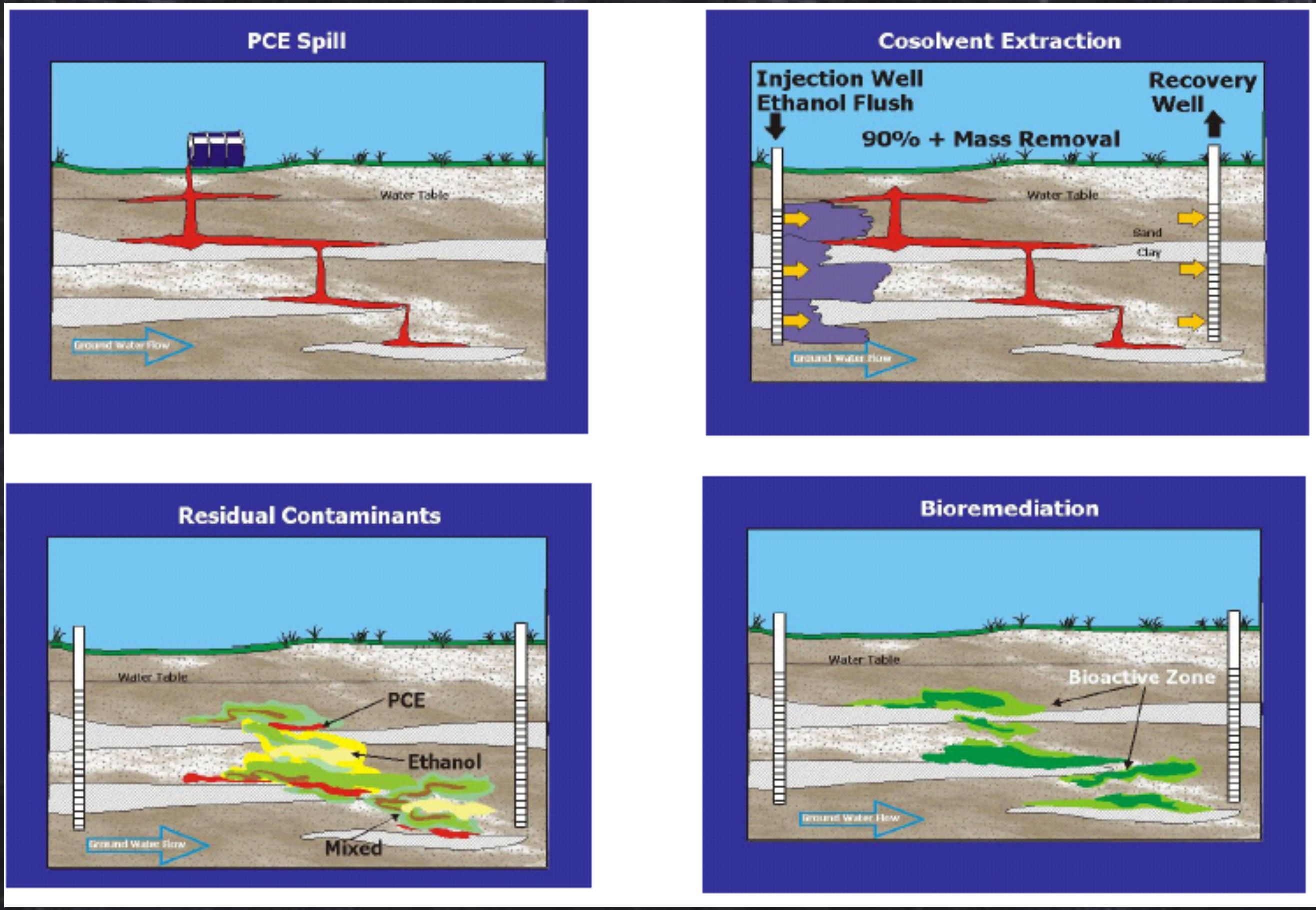
Phytostimulation - enhancement of soil microbial activity for the degradation of contaminants, typically by organisms that associate with roots. This process is also known as rhizosphere *degradation*.

Phytovolatilization - removal of substances from soil or water with release into the air, sometimes as a result of phytotransformation to more volatile and / or less polluting substances.

Rhizofiltration - filtering water through a mass of roots to remove toxic substances or excess nutrients. The pollutants remain absorbed in or adsorbed by the roots.

Cosolvent/surfactant enhanced dissolution

Chemical extraction does not destroy wastes but is a means separating hazardous contaminants from soils, sludges, and sediments, thereby reducing the volume of the hazardous waste that must be treated. The technology uses an Extracting chemical and differs from soil washing, which generally uses water or water with wash-improving additives. Commercial-scale units are in operation. They vary in regard to the Chemical employed, type of equipment used, and mode of operation.



Factors that may limit the applicability and effectiveness of the process :

- Some soil types and moisture content levels will adversely impact process performance.
- Higher clay content may reduce extraction efficiency and require longer contact times.
- Organically bound metals can be extracted along with the target organic pollutants, which restricts handling of the residuals.
- Traces of solvent may remain in the treated solids; the toxicity of the solvent is an important consideration.
- Solvent extraction is generally least effective on very high molecular weight organic and very hydrophilic substances.
- After extraction, any residual in treated soil needs to be destroyed.
- Capital costs can be relatively high and the technology may be more economical at larger sites.
- Meeting highly stringent heavy metals criteria may prove uneconomical.

Chemical treatment – In-Situ Chemical Oxidation

In-situ destruction of organic contaminants may be accomplished using chemical oxidation technologies. A variety of chemical oxidants and application techniques can be used to bring oxidizing materials into contact with subsurface contaminants to remediate the contamination. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting hydrocarbons to carbon dioxide and water and ultimately irreversibly reduce concentrations of petroleum hydrocarbons in soil and groundwater.

Chemical oxidation technologies are predominantly used to address contaminants in the source area saturated zone and capillary fringe. Cost concerns can preclude the use of chemical oxidation technologies to address large and dilute contaminant plumes.

- The four most commonly used oxidants for ISCO: permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) and iron (Fe), persulfate ($S_2O_8^{2-}$), and ozone (O_3).
- Each oxidation technology requires specific use of materials handling and injection methods.
- The persistence of the oxidant in the subsurface is important since this affects the contact time for advective and diffusive transport and ultimately the delivery of oxidant to targeted zones in the subsurface.
- Radical intermediates formed using some oxidants (H_2O_2, $S_2O_8^{2-}$, O_3) that are largely responsible for various contaminant transformations react very quickly and persist for very short periods of time (<1 sec).

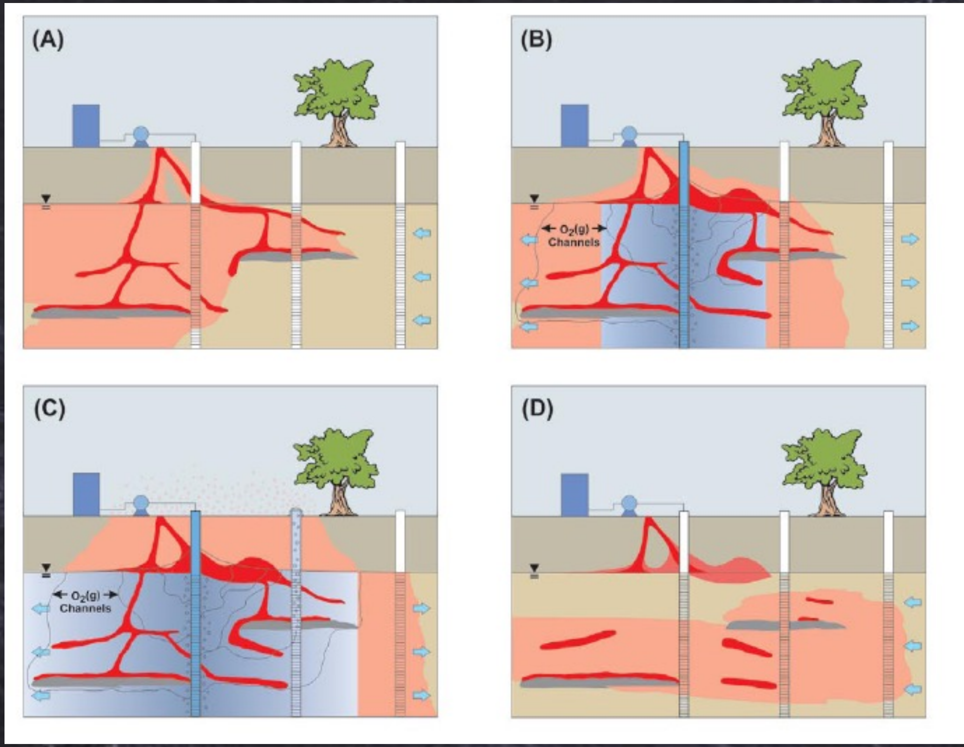
In-Situ Fenton Oxidation

The classic Fenton reaction specifically involves the reaction between H_2O_2 and ferrous iron (Fe(II)) yielding the hydroxyl radical (·OH) and ferric (Fe(III)) and hydroxyl ions (OH^-). Fe(III) reacts with H_2O_2 or the superoxide radical ($\cdot O_2^-$) yielding Fe(II). This general sequence of reactions continues to occur until the H_2O_2 is fully consumed. Since H_2O_2 injected into the subsurface reacts with many chemical species other than Fe(II), this technology is often referred to as catalyzed hydrogen peroxide (CHP).

Table 4. Fenton and Related Chemical Reactions

$H_2O_2 + Fe(II) \longrightarrow Fe(III) + \cdot OH + OH^-$	(1)
$H_2O_2 + Fe(III) \longrightarrow Fe(II) + \cdot O_2^- + 2\,H^+$	(2)
$\cdot O_2^- + Fe(III) \longrightarrow Fe(II) + O_2(g) + 2\,H^+$	(3)
$\cdot OH$ + target contaminant $\longrightarrow$ reaction byproducts	(4)
$\cdot OH + H_2O_2 \longrightarrow \cdot HO_2 + H_2O$	(5)
$2\,H_2O_2 \longrightarrow O_2 + 2\,H_2O$	(6)

Due to the fast reaction rates of ·OH, the transport distance of ·OH is limited to only a few nanometers. Therefore, a basic principle of Fenton oxidation is that the contaminant, Fe(II), and H_2O_2 must be in the same location at the same time.



Conceptual model of in-situ Fenton oxidation fate and transport mechanisms. (A) Cross-section of hazardous waste site containing DNAPL in the saturated and unsaturated zones. Injection well is constructed in the source area and two monitoring wells located in the upgradient direction (downgradient monitoring wells not shown); (B) H_2O_2 is injected and reacts ,contaminants are transformed. DNAPL movement, and enhanced volatilization of contaminants also occur; (C) O_2 (g) sparging of the ground water in monitoring wells, artesian conditions, may occur; (D) H_2O_2 injection ceases and is fully reacted. Loss of the target contaminant(s) in the source zone is achieved by oxidation transformation but may not be differentiated from other fate and transport mechanisms. Contaminant mass transfer and transport results in rebound.

In-Situ Ozone Oxidation

O_3 is a gas and a strong oxidant that is sparingly soluble in water and upon reaction does not leave a residual (i.e., SO_4^{2-}, $MnO_{2(s)}$) other than O_2. Analysis of dissolved O_3 in aqueous solutions can be performed using an colorimetric method

In-situ O_3 oxidation involves the injection of a mixture of air and O_3 gas directly into the unsaturated and/or saturated zones.

Direct Oxidation

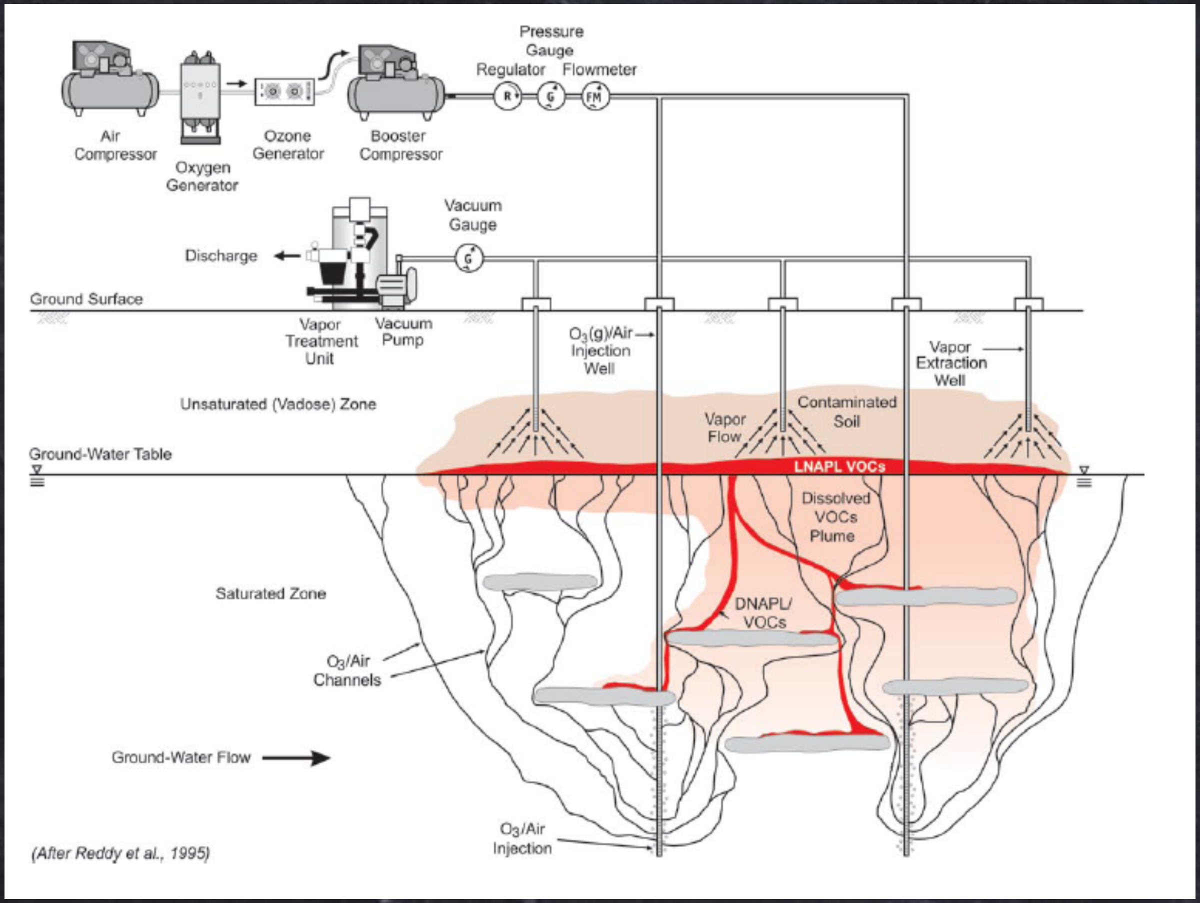
$$O_3 + C_2HCl_3 + H_2O \longrightarrow 2\,CO_2 + 3\,H^+ + 3\,Cl^-$$

·OH Formation

$$O_3 + H_2O \longrightarrow O_2 + 2\cdot OH \quad \text{(Slow)}$$

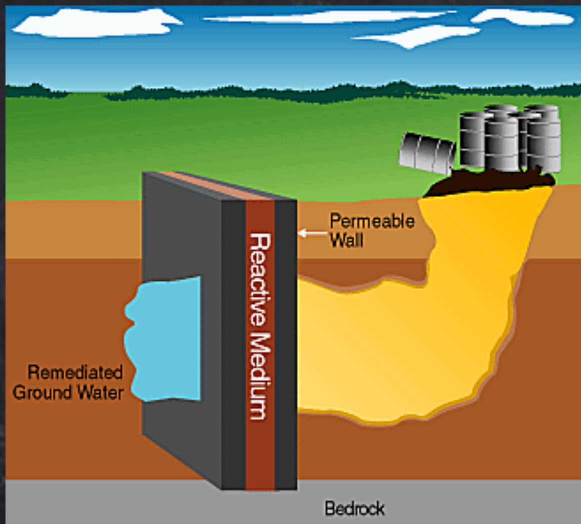
$$2\,O_3 + 3\,H_2O_2 \longrightarrow 4\,O_2 + 2\cdot OH + 2\,H_2O \quad \text{(Fast)}$$

General Ozone Oxidation and Related Chemical Reactions



General conceptual model of in-situ ozonation in the saturated zone with soil vacuum extraction to capture volatile emissions and O_3(g).

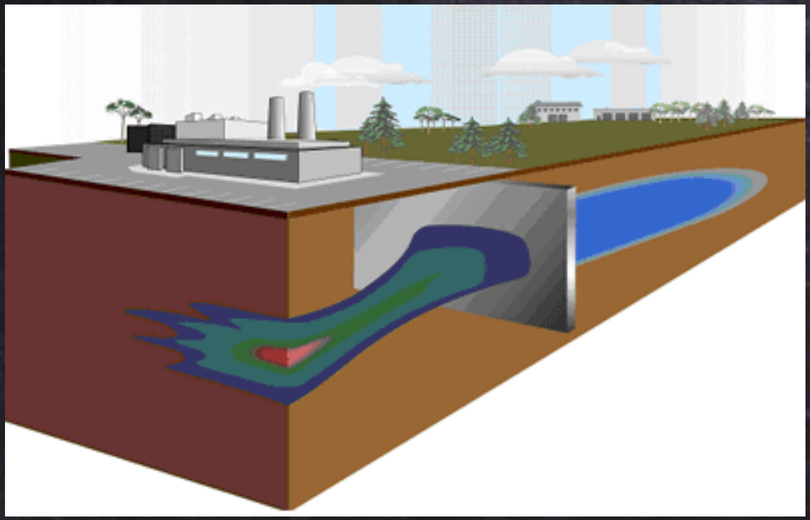
Permeable reactive barriers – מחסומים חדירים אקטיביים

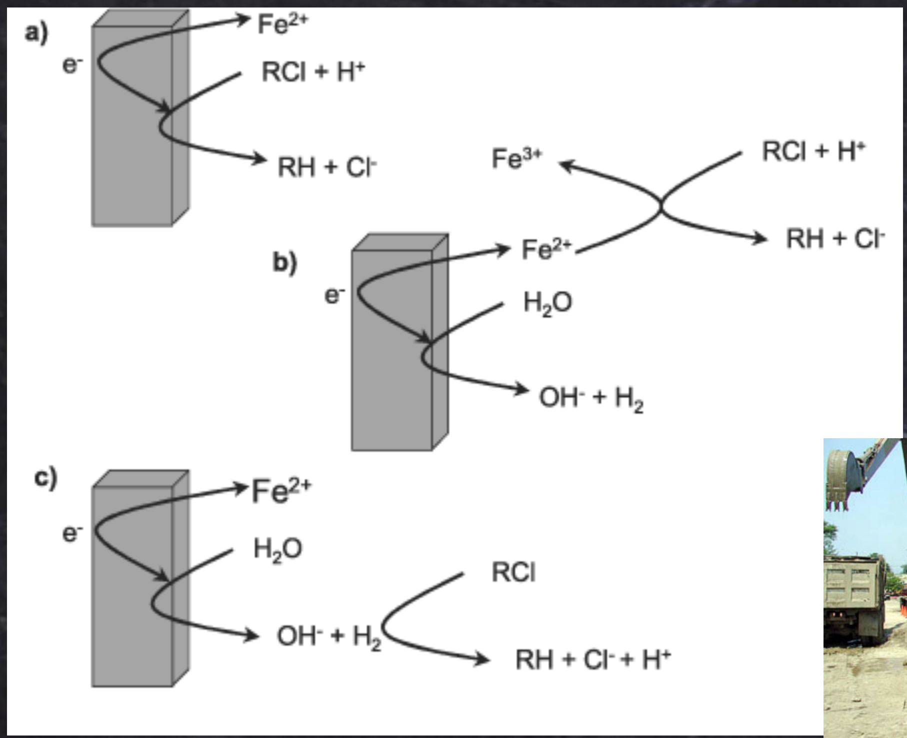


Permeable reactive barriers have the potential to lower the cost and increase the effectiveness of groundwater cleanup.

יצירת מחסום מחומר או חומרים המאופשרים מעבר מים דרכם ומכילים חומרים פעילים שמפרקים או מפרידים את המזהמים מהמים.

בעיות:
בד"כ מוגבל לעומק נמוך בלבד ולשטח קטן יחסית
מושפע במידה רבה מרכיבים נוספים הנמצאים במים (מלחים, מינרלים,חומרים אורגנים,ומיקרואורגניזמים).
שינויים במשטרי זרימה או בקצב יכולים להפריע או לעצור פעילות.




a)
e-
Fe2+
RCl + H+
RH + Cl-
Fe3+
RCl + H+
RH + Cl-
b)
e-
Fe2+
H2O
OH- + H2
c)
e-
Fe2+
H2O
RCl
OH- + H2
RH + Cl- + H+

מניעת ביטול מפגעים פוטנציאלים

איסוף, ביטול והחלפה של מקורות זיהום
כמו מיכלים תת קרקעיים ישנים, קרקע
מזוהמת או צנרת מתכלה. שימוש
בתהליכי ייצור "ירוקים" או בחומרים
ידידותיים לסביבה.

מגבלות:
מניעה תמיד עדיפה על טיפול
איסוף מקורות בעייתיים מוגבל לזיהום
נקודתי וקרוב לפני השטח.
תהליכים או חומרים חדשים צריכים
להיבדק היטב על מנת למנוע יצירת
מפגעים חדשים ויותר מסובכים.

סיכום

1. מורשת העבר משאירה לנו לא מעט אתגרים בצורה של "פצצות זמן סביבתיות"
2. קיימות שיטות לטיפול בהרבה מהמזהמים אבל הדרך עוד ארוכה לפתרון מלא.
3. יש לבחון את החומרים והמוצרים שאנו מפתחים ומיצרים היום כדי להבטיח שהם לא הבעיה הסביבתית הבאה.
4. בעולם בו שוק המים הופך יותר ויותר משמעותי ומחסור במים מוגדר אחת הבעיות המרכזיות במאה ה - 21 יש לשים דגש על איכות המשאבים שעומדים לרשותנו.

תודה, שאלות?