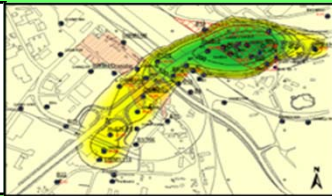
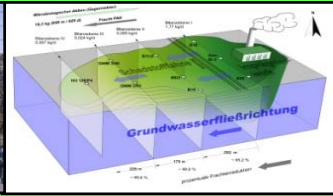


## Risk based Dioxin-Management in EC: European Community: PCDD/F-Contaminations and Methodology for Site Investigations, Health Risk Assessments & Remediation

**Dr. Frank P.M. KARG**

*Scientific Director of HPC Group International  
President-CEO of HPC Envirotec SA / France  
Member of Borad of Directors of HPC AG / Germany*



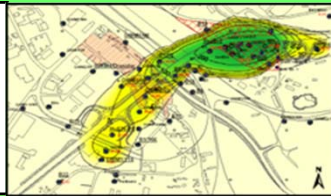
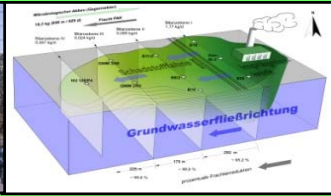


**HPC Group & INOGEN Joint Venture Company**

**global thinking**

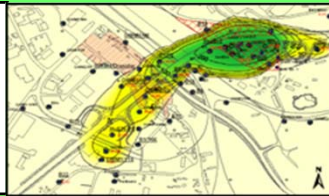
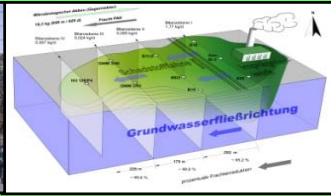


**local delivery**



- **Site Remediation Projects (Investigations HRA, REM, etc.):** Soils, Soil gas, Water, Air, Food stuffs, etc.: About 58 800 Contaminated Site Remediations Projects Worldwide (HPC Group).
- **Health Risk Assessments (HRA) :** Analysis of existing Data, Definition and Implementation of Toxicological Data (Contaminated Sites, Industrial Facilities, Landfills, Agriculture Pesticide use, Mining sites, Maritime Contamination, REACH, Military Chemistry.....). More than 1 380 HRA worldwide.
- **Design, Supervision & Control** and **Realization of Site Remediation Programs:** MNA, ENA, Green Remediation, etc.
- **Research Programs:** Destruction & Degradation of Toxic & Military Chemicals (French Army, German Army....), **Maritime & Costal Contaminations, Public Health Threats by Environmental Risks:** physical, chemical, biological and nuclear (INVS: National Institute for Health Surveillance/France).
- **Investment Safety by Environmental Risk Management & Environmental Due Diligences (M&A),**





# HPC-Projects

Goals:

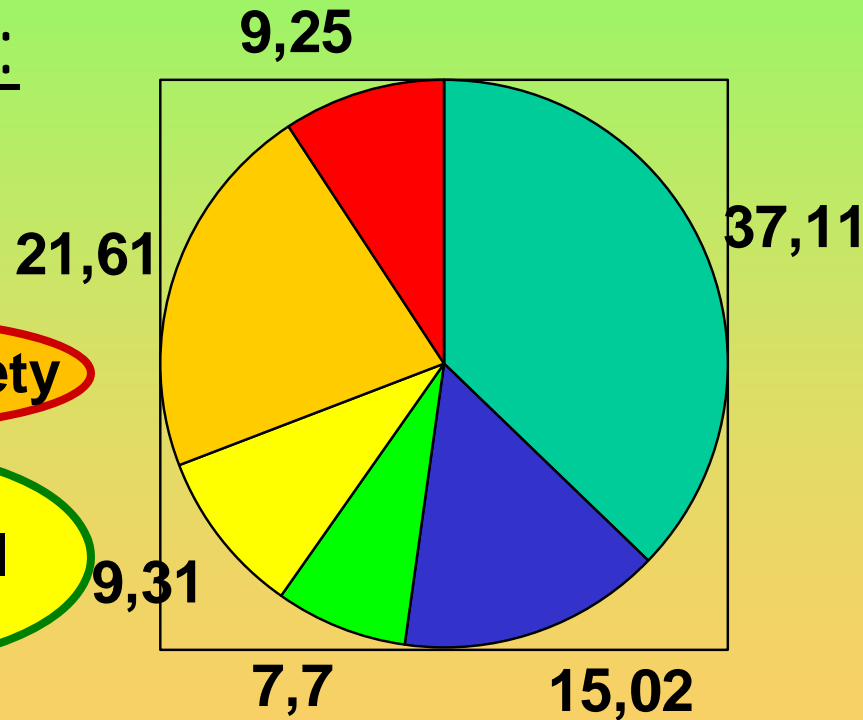


**HSSE-Safety**

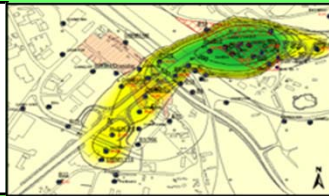
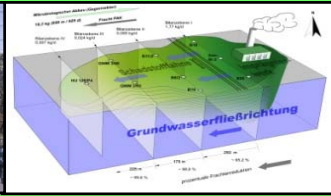
**Legal & Financial Safety**



**Investment Safety**

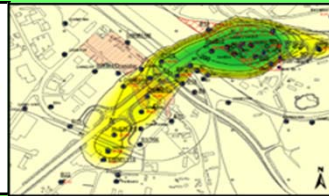
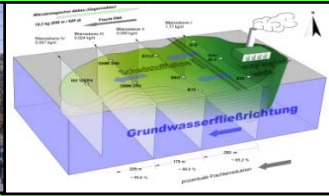


- Petrol, Chemical & Pharma Industry
- Investments & Real Estate
- Armement & Armys
- Municipalities / Gouvernements
- Divers: Mining, Automotive, Steel...
- R&D



**Object: Safe Remediation of Dioxin (Agent Orange)  
Contaminated Sites to Ensure best health Safety &  
Real Estate & Investment Safety**

- **International Investments**, for new Commercial, Industrial and Residential use, **are only realized**, if **Pollution Risks** & Remediation **Cost** can be managed (for ex. : Excavation of contaminated Soil for Construction, Foundations, etc.) .
- **Before Investment Decisions are taken;**  
**The Pollution Impact must be clear** for Health (Workers, Residents, etc.), for Ground & Surface Water and for Ecosystem & Food Stuff Production (Plants, Fish, Meat, etc.)

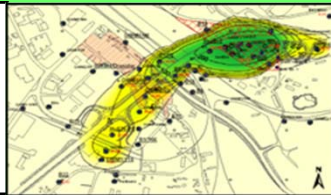
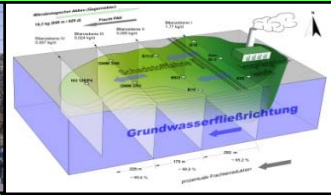


## **Methodology: International Management of Contaminated Sites for Legal & Financial Budget Safety**

International State-of-the-Art Management of Contaminated Sites (for ex. in Europe, USA & Canada, Japan, China, etc.) is since some years ensured as following:

- **Historical Survey** concerning Polluting Activities Zones & Pollutants.
- **Site Investigations** (concerning soil, soil gas, ground & surface water, food stuffs).
- **HRA: Health Risk Assessment** for future site activities and Real Estate Projects.
- **Mapping of SS-RG (Site specific Remediation Goal)** exceeding.
- **Remediation technical-economic Feasibility study** and Cost estimate.
- **Remediation Design & Planning.**
- **Application of Remediation Technologies.**
- **EHS-Management** during Remediation.
- **Environmental Monitoring.**



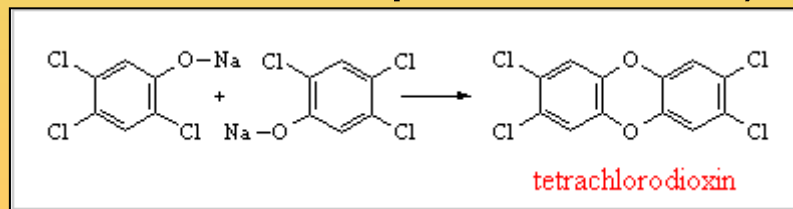


## Historical Survey: Example: Contaminated Sites by Ranch Hand Mission (U.S.-AF):

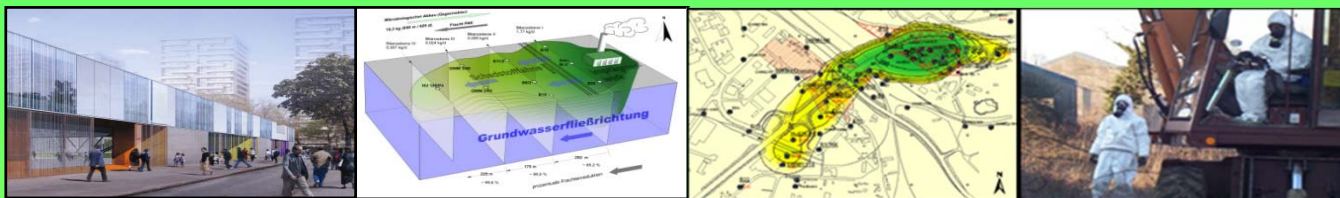
- During the war in Vietnam, the U.S.-Air Force sprayed up to 72 million liters of herbicides over the the homes, and the people of Vietnam (“Operation Ranch Hand”: 1961 - 1971),



- **Agent Orange** was a 50/50 mixture of two herbicides; 2,4-D and 2,4,5-T  
Orange stripe across the barrels, contains 2,3,7,8-TCCD (tetrachloro-dibenzo-para-dioxine)



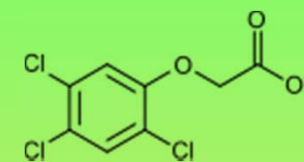
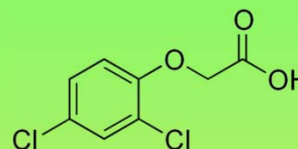
TCDD-Impurity in Agent Orange-Mixtures from 2,4,5-Trichloro-sodium phenolate use for the 2,4,5-T-Production.



## Historical Survey & Pollutant Definition:

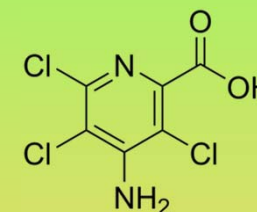
- **Agent Orange:  $30 \times 10^6$  liters,**

→ 1/1 mixture of 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid).



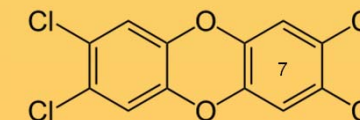
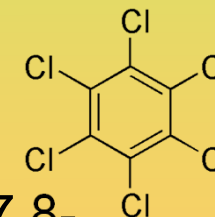
- **Agent White:  $17 \times 10^6$  liters,**

→ Tordon 101 =: 4/1 mixture of 2,4-D and Picloram (4-amino-3,5,6-trichloro-picolinic acid) or tri-isopropanolamine salt of P. (+ about 200 ppm HCB)



- **Agent Green:  $5 \times 10^6$  liters.**

→ 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) + traces of 2,3,7,8-tetrachloro para dibenzo dioxine (2,3,7,8-TCDD),



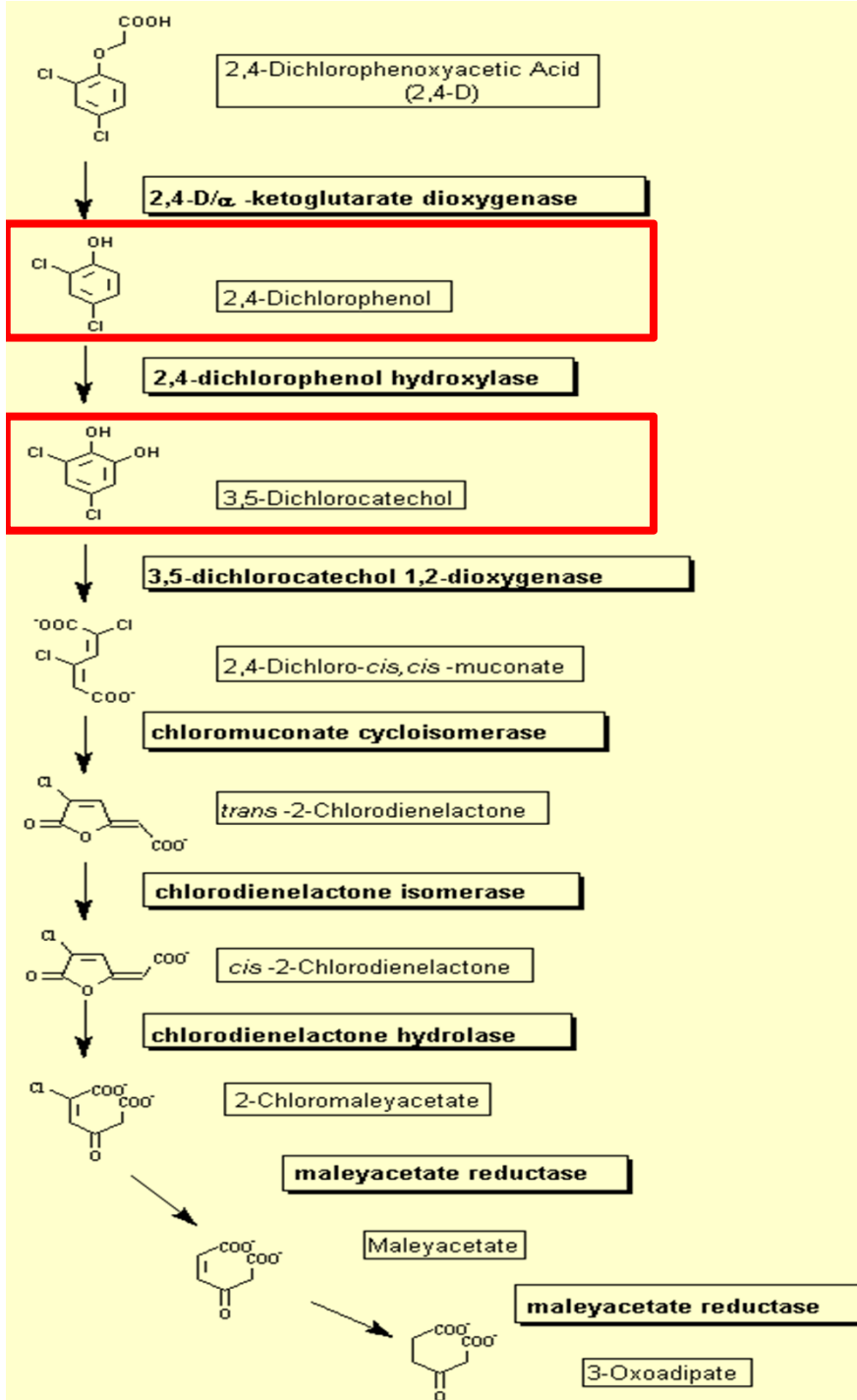


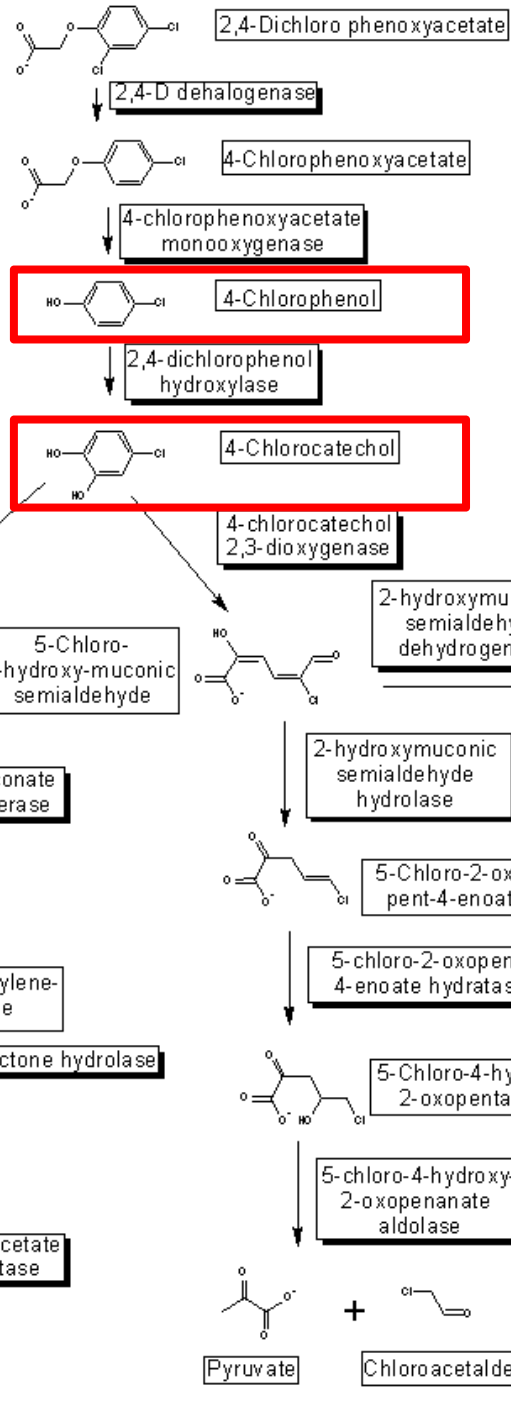
**Historical Survey & Pollutant Definition:**

**Degradation of 2,4-D:**

Identification of toxic degradation products (metabolites)

**+ 2,4-DCP  
+ 3,5-DC-Catechol**





• **Historical Survey & Pollutant Definition:**

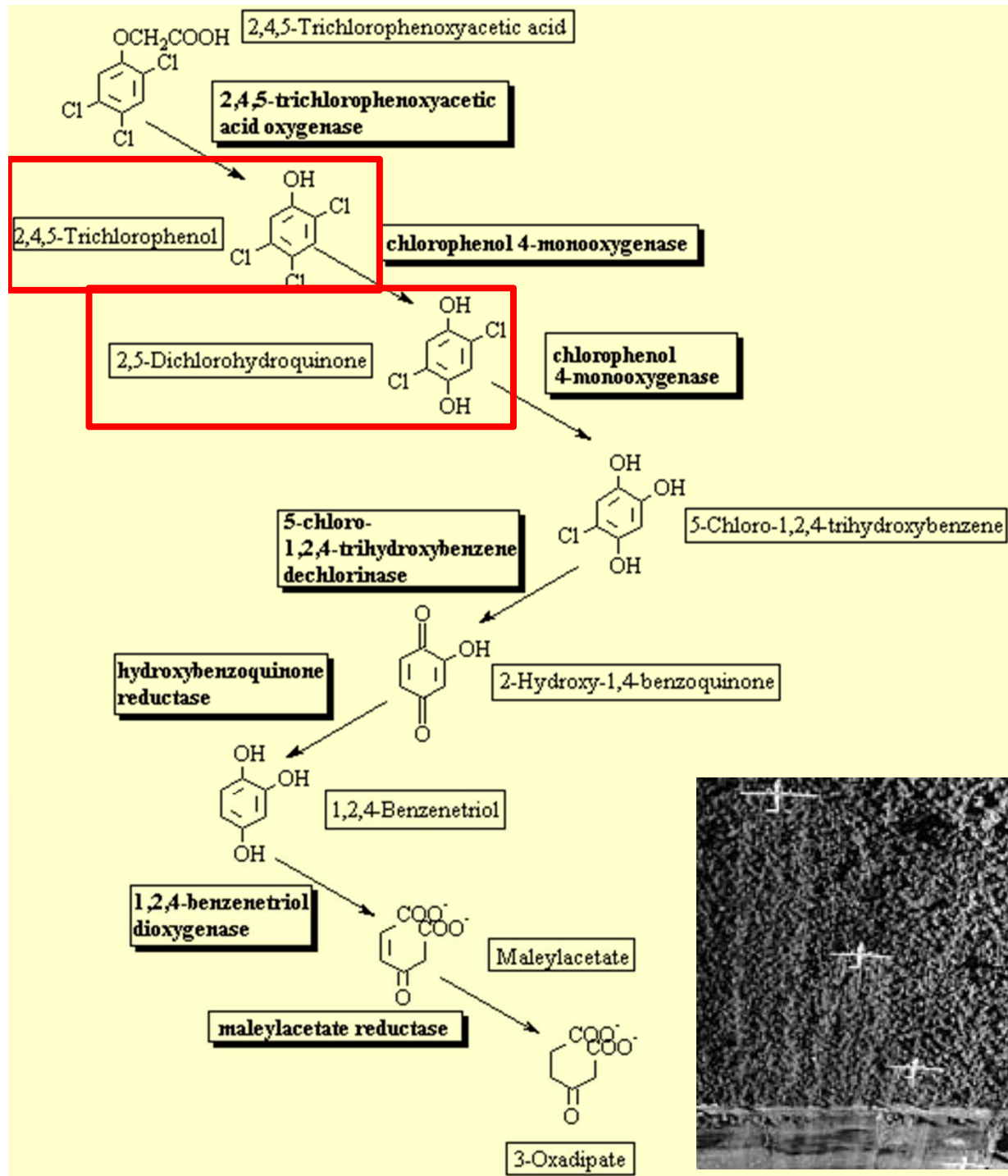
**Degradation of 2,4-D:**

[http://umbbd.msi.umn.edu/2,4-d/2,4-d\\_map.html](http://umbbd.msi.umn.edu/2,4-d/2,4-d_map.html)

Identification of toxic degradation products (metabolites)

**+ 4-CP**  
**+ 4C-Catechol**





## Historical Survey & Pollutant Definition:

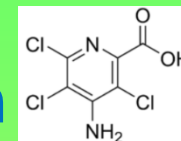
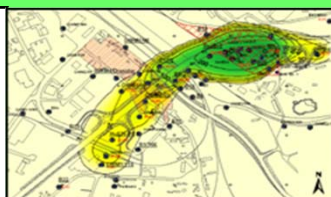
### Degradation of 2,4,5-T

[http://umbbd.msi.umn.edu/2,4,5-t/2,4,5-t\\_map.html](http://umbbd.msi.umn.edu/2,4,5-t/2,4,5-t_map.html)

Identification of toxic degradation products (metabolites)

+ 2,4,5-TCP  
+ 2,5-DC-Hydroquinone

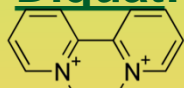
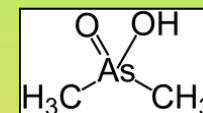
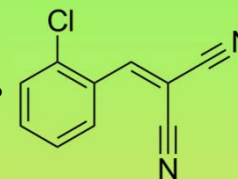




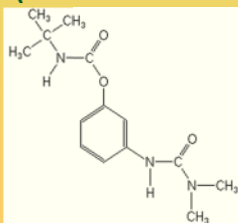
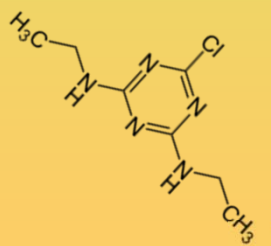
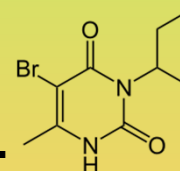
AW

## Other Agents: Used by the US-AirForce in Vietnam

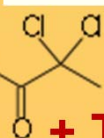
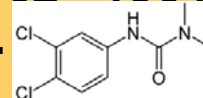
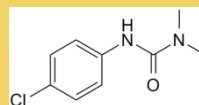
- **Agent Orange:** 2,4-D and 2,4,5-T; used between January 1965 and April 1970.
- **Agent Orange II (Super Orange):** 2,4-D and 2,4,5-T; used in 1968 and 1969.
- **Agent Purple:** 2,4-D and 2,4,5-T; used between January 1962 and 1964.
- **Agent Pink:** 2,4,5-T; used between 1962 and 1964.
- **Agent Green:** 2,4,5-T; used between 1962 and 1964.
- **CS:** 2-chlorobenz almalono nitrile (CWA!): 9 million litres ?
- **Agent White (AW):** Picloram and 2,4-D.
- **Agent Blue:** contained cacodylic acid (arsenic). 4.74 million litres
- **Dinoxol:** 2,4-D- and 2,4,5-T-butoxyethylester; used 1962-1964.
- **Trinoxol:** 2,4,5-T; used between 1962 and 1964.
- **Diquat:** used between 1962 and 1964.



- **Bromacil:** Used between 1962 and 1964.
- **Tandex** (simazine and karbutilate 2:1) : 1962 -1964.



- **Monuron:** 1962 - 1964.
- **Diuron:** 1962 - 1964.
- **Dalapon:** 1962 - 1964.

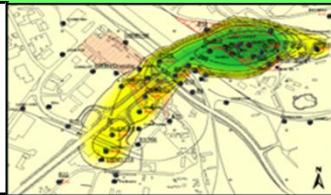
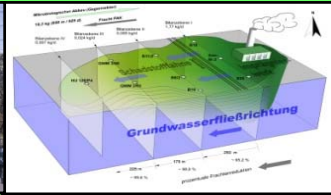


+ Toxic Metabolites & Impurities.....!

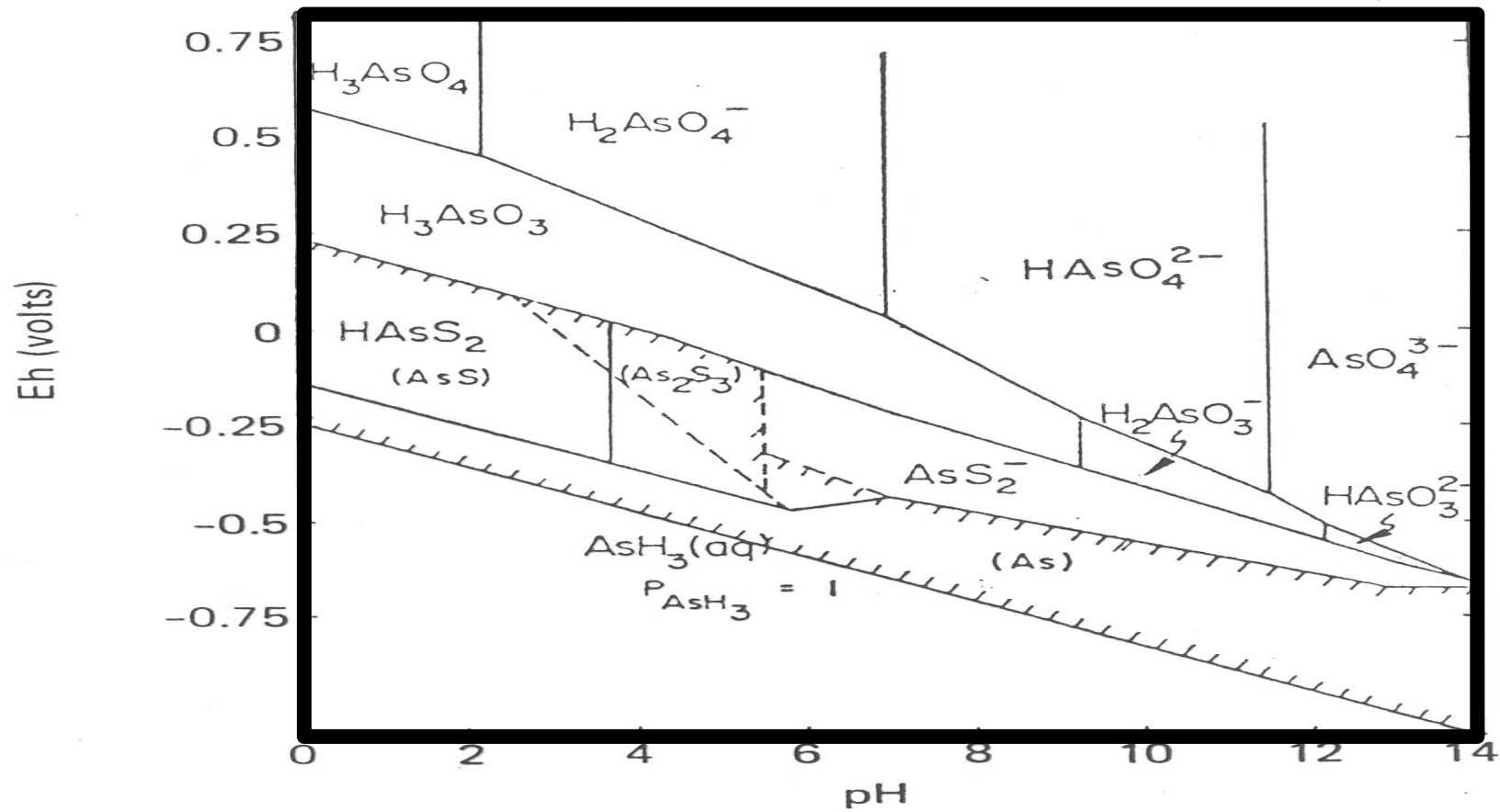


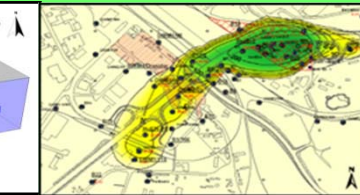
### Diseases:

- Acute and Subacute Transient Peripheral Neuropathy
- AL Amyloidosis
- Chloracne
- Chronic Lymphocytic Leukemia
- Hodgkin's Disease
- Multiple Myeloma
- Non-Hodgkin's Lymphoma
- Porphyria Cutanea Tarda
- Prostate Cancer
- Respiratory Cancers
- Soft Tissue Sarcoma
- Type 2 Diabetes Mellitus



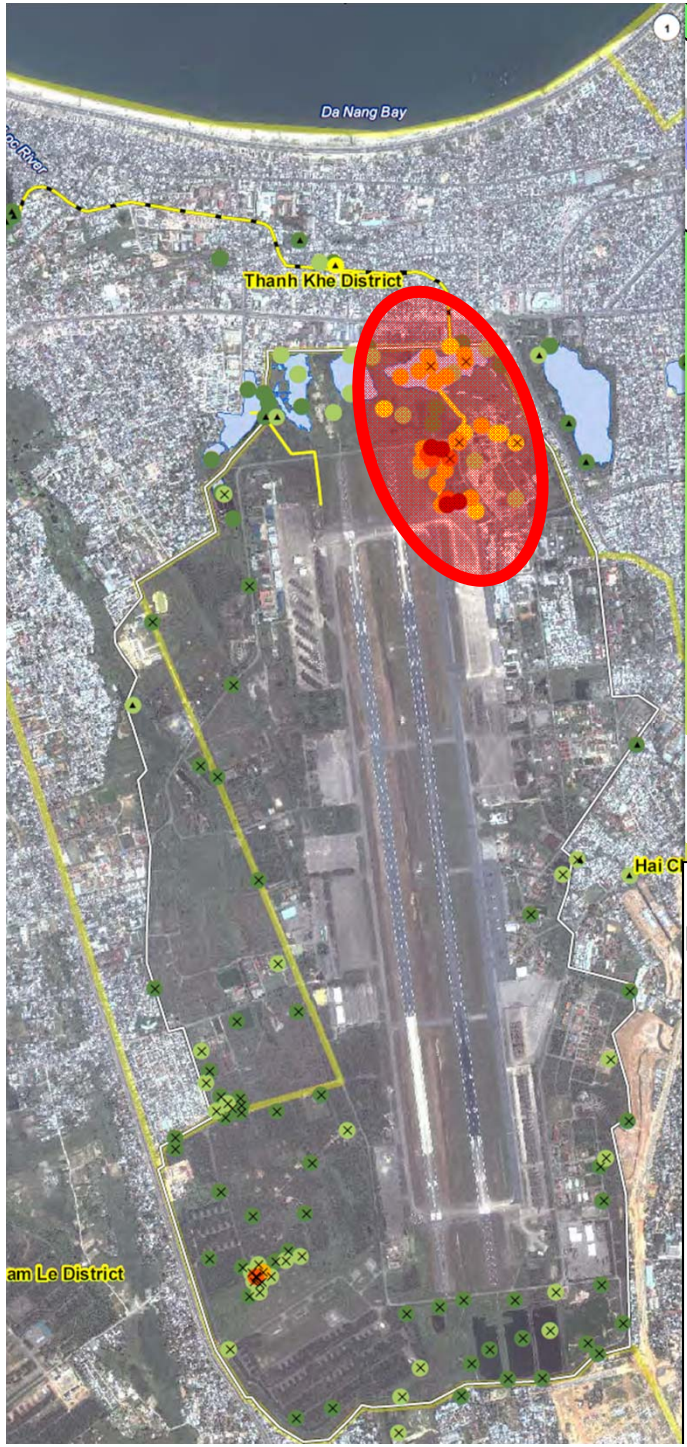
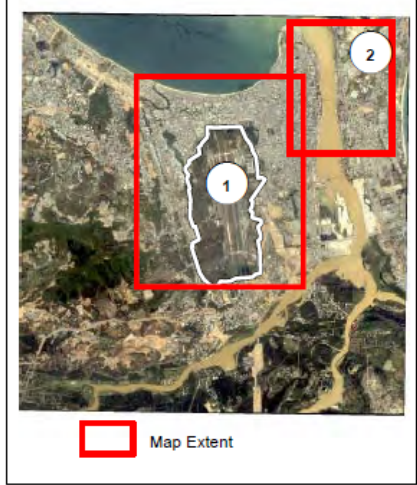
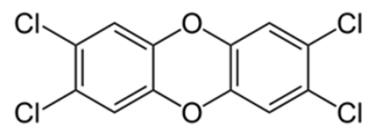
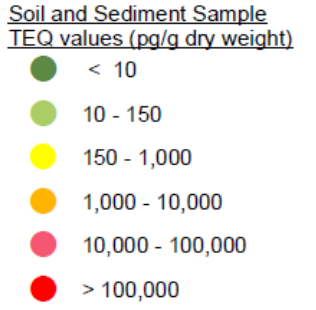
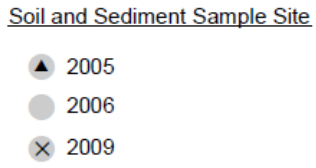
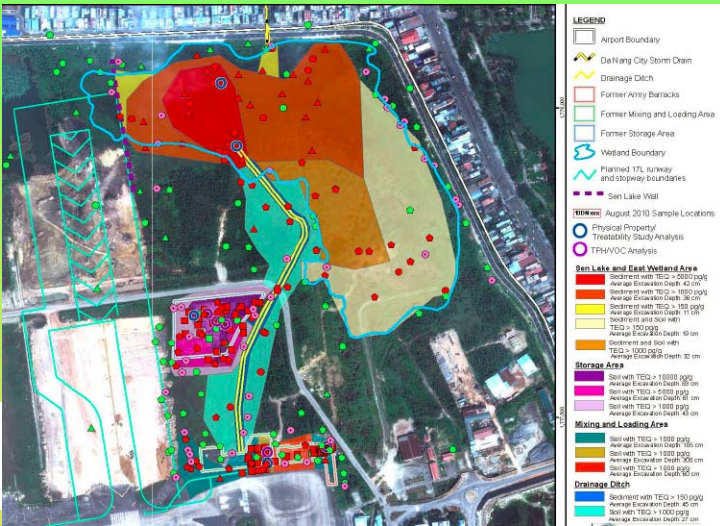
**Eh-pH-Diagramme des stabilités (Ferguson & Gavis : 1972) : Eau**

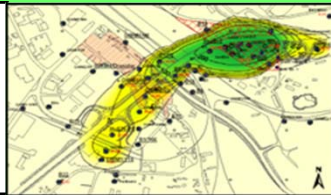
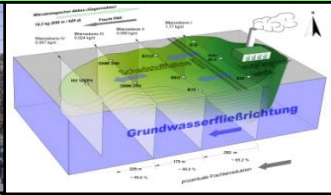




# Example: Da Nang Airport: TCDD

Overview of all dioxin sampling locations in Da Nang, Viet Nam by Hatfield/10-80 Division/ Office 33 in 2005, 2006, and 2009.

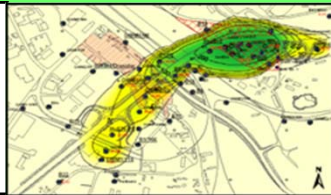
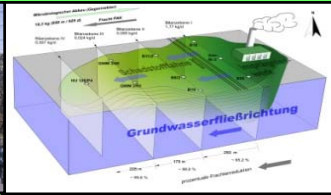




## Site Investigations

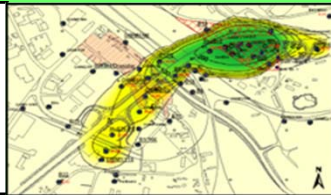
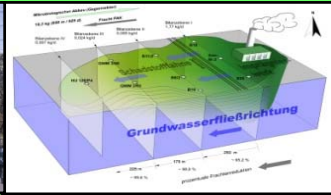
- Soil Drillings,
- Soil, Soil gas and Sediment Sampling & Analyses,
- Groundwater (Monitoring Wells) and Surface Water Sampling & Analysis,
- Ambient Air Sampling & Analysis,
- Food Stuffs Sampling & Analysis.





## HRA: Health Risk Assessment Steps:

1. Identification of all Contaminants, including toxic break down Products, as microbiological Metabolites, etc.,
2. Definition of Site uses & Exposure Scenarios with their specific Exposure Pathways,
3. Calculation of daily Exposure Doses (mg/kg/day) for Ingestion, Inhalation and dermal Contact,
4. Choice of TRD: Toxicological Reference Doses (as RfD, RfC, UR, etc.)
5. Quantification of Risks and Identification of Action Needs,
6. Definition of SS-RG: Site Specific Remediation Goals as acceptable Concentrations for acceptable Risks.



## Health Risk Assessment: Acceptable Risks

- Individual Cancer Risk :  $ICR \leq 10^{-5}$

- WHO 1996: International Symposium

Exposure and Risk Assessment with Respect to Contaminated Soil: YOUNES.  
Munich (28-29/02/1996),

- Germany: BA 161a : 28/08/1999,

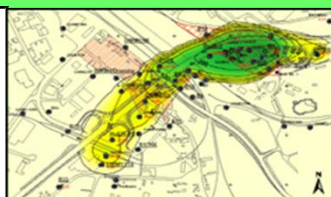
- France: Ministry Circulars DPPR/SEI/BPSE/BS/MB: 10/12/1999 and 08/02/2007,

- U.S.A. / DOH: Department of Health: 2006: There is no overall DEP (Data Execution Policy) on acceptable cancer risk level; this varies by program. Act 2 authorizes a range of 10E-4 to 10E-6 for the Land Recycling program. The calculation of the generic Statewide health standards used a level of 10E-5 :

$$ICR = DED \cdot UR \quad (\text{Daily Exposure Dose} \cdot \text{Unit Risk} = \text{Slope Factor})$$

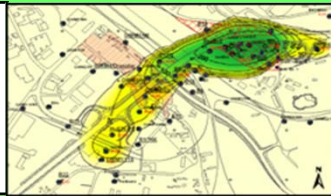
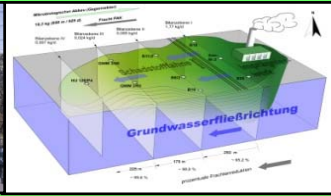
- Systemic (Non-Cancer) -Risk: Risk Index:  $RI \leq 1$

$$RI = TRD / DED \quad (\text{Toxic Reference Dose} / \text{Daily Exposure Dose})$$

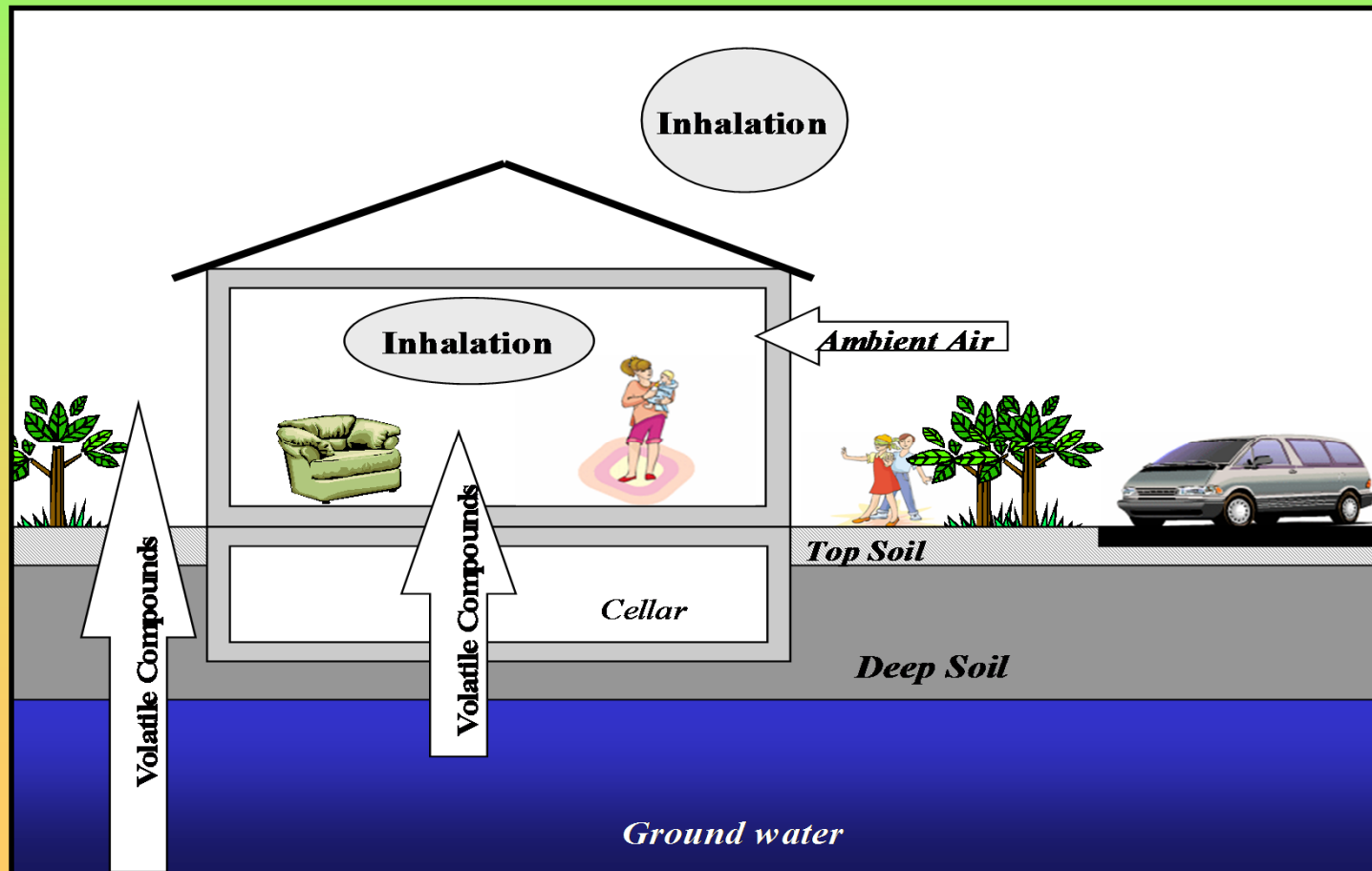


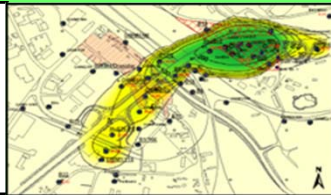
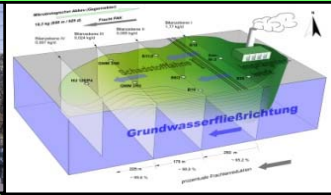
## HRA: Health Risk Assessment: TRD Examples

Substance	Nature du risque	Valeur toxicologique chronique			Espèce	Critère / Facteur de sécurité	Organisme	
		Voie d'exposition	Organe(s) cible(s)	Valeur				application d'un FET
<b>2,3,7,8-TCDD</b>	NC	Ingestion	Systèmes hépatique, neurologique, immunitaire, développement foetal et thyroïdien	7E-10 mg/kg	-	homme	LOAEL / 30	IRIS 2012
		Inhalation	développement, système immunitaire, cutané, neurologique, hépatique, circulatoire	4E-08 mg/m <sup>3</sup>	-	rat	NOAEL / 100	OEHHA 2003
	C	Ingestion	développement, système immunitaire, cutané, neurologique, hépatique, circulatoire	130000 [mg/kg/j] <sup>-1</sup>	-	souris	1	OEHHA 2002
		Inhalation	développement, système immunitaire, cutané, neurologique, hépatique, circulatoire	38000 [mg/m <sup>3</sup> ] <sup>-1</sup>	-	souris	1	OEHHA 2002
<b>2,4,6-Trichlorophénol</b>	NC		Systèmes cutané, circulatoire, oculaire, hépatique, immunitaire et respiratoire	0,003 mg/kg/j	-	Rat	NOAEL / 100	RIVM 2000
	C	Ingestion		0,011 [mg/kg/j] <sup>-1</sup>	-	Rat	-	IRIS 1994
		Inhalation		0,0031 [mg/m <sup>3</sup> ] <sup>-1</sup>	-	rat	-	IRIS 1994
<b>2,4-D (acide 2,4-Dichloro-phenoxyacétique)</b>	NC	Ingestion	Systèmes circulatoire, hépatique et rénal	0,01 mg/kg/j	-	rat	NOAEL / 100	IRIS 1988
		Inhalation	-	-	-	-	-	-
<b>2,4,5-Trichlorophenoxy acetic acid</b>	NC	Ingestion	Système rénal et développement foetal	0,01 mg/kg/j	-	rat	NOAEL / 300	IRIS 1989
		Inhalation	-	-	-	-	-	-



- **HRA: Health Risk Assessment:** Exposure Pathways:  
Conceptual Scheme





- HRA: Health Risk Assessment: Exposure Quantification**

## Exposure Quantification: Ingestion of soils, water or food:

$$DED_{ing} = C_m \cdot \frac{Q_{ing}}{P} \cdot F_a \cdot \frac{Ex}{Ve} \cdot F_{exa} \cdot F_{exd}$$

DED<sub>ing</sub> = Daily Exposure Dose [mg/kg/d]

C<sub>m</sub> = Concentration Pollutants Concentration in the exposure medium : C<sub>soil</sub> [mg/kg], C<sub>water</sub> [mg/l], C<sub>food</sub> [mg/kg]

Q<sub>i</sub> = Ingested Soil quantity and/or food [kg/d] or water [L/d], distinct from the Adults (Q<sub>ing.A</sub>) and the Children (Q<sub>ing.C</sub>)

P(a) = Adult Body Weight [70 kg]

P(e) = Child Body Weight [15 kg]

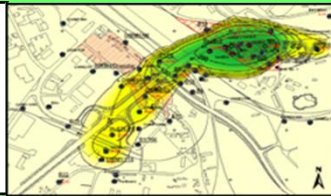
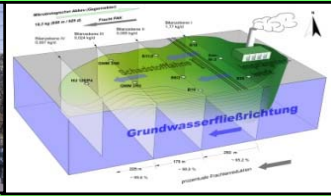
F<sub>a</sub> = Absorption Factor (if failing: 100 % = [1])

Ex = Exposure years in Lifetime (Adult or Child) [y]

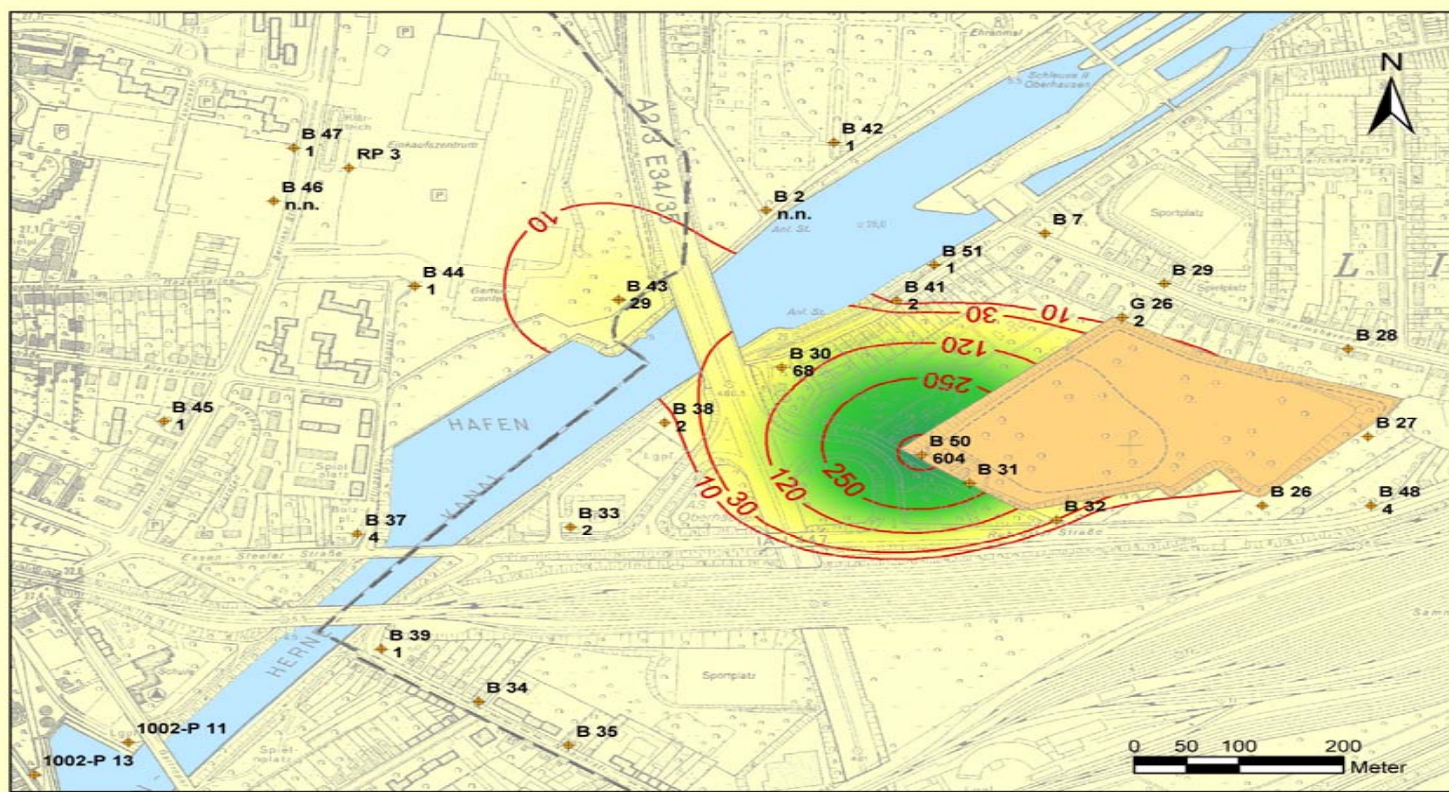
Ve = Lifetime: Adult or Child [y]. In case of carcinogenic Pollutants: Ve = Ex [y]

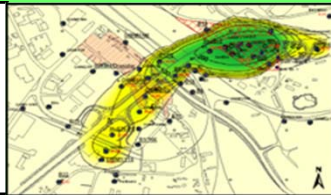
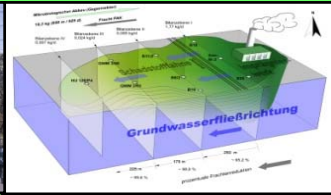
F<sub>exa</sub> = Yearly Exposure [d/365 d]

F<sub>exd</sub> = Daily Exposure [hrs/24 hrs]



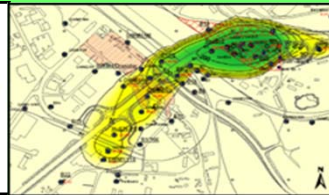
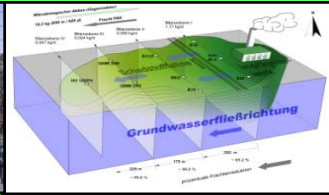
## SS-RG: Mapping of Remediation Goal Exceeding





## HR-Management: Additional Medical Needs:

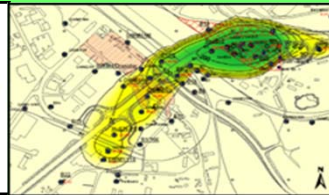
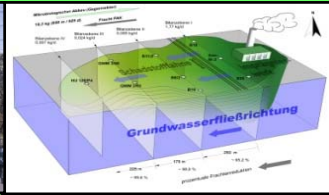
1. **Epidemiological studies**, including compilation between Site investigation & Health Risk Assessment Results, Geographical Pathologies and Environmental Chemistry, etc.,
2. **Medical Laboratory equipment for sampling PCDD/F-, As-, POP- etc. Analyses in Laboratories in Blood, water, Soil and Food-Stuffs,**
3. **Medical Laboratory Equipment for Agent-Orange, etc. related Pathology-Diagnostic: Oncology, Neurotoxicity; Hepatotoxicity, Nephrotoxicity, Endocrine disruption, etc.,**
4. **Bio-Medical-Analysis Equipment** (Metabolites, Bio-monitoring Parameters, etc.), X-Ray-Tomography, Magnetic Resonance Nuclear Spin Tomography, Ultrasound-Equipment, Computer- Equipment for interpretation, etc. and **trained Staff.**
5. **Clinical – Therapeutic Equipment (4.2 Million AO-sick People in Viet-Nam ! (Oncology, Neurology, Hepathology, etc.).**



## Dioxin Strategy from the European Community (EC 2007):

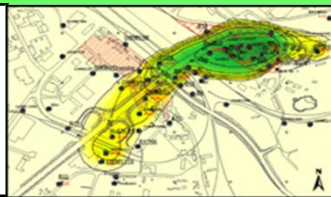
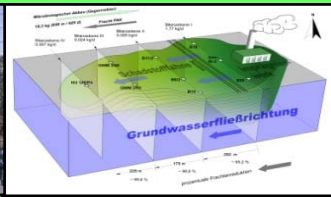
→ **Integrated approach to regulations on feed and food to reduce the exposure to dioxins:**

1. The introduction of strict but feasible **maximum levels in feed and food** taking into account the results obtained in lowering the presence of dioxins in the environment.
2. The introduction of **action levels** to trigger action when levels in feed or food are found **clearly above background level**. These action levels have an early warning function.
3. The introduction of **target levels** to be achieved over time so as to bring the exposure of the majority of the European population within the limits recommended by the Scientific Committee on Food.



## Exposure by Food:

- **Environmental chemical background exposure** to dioxins in the EC is still at a level where **chronic health effects may occur**.
- Estimations concerning an **average total dietary exposure** to dioxins: **0.9-3.0 pg I-TEQ/kg body weight/day** (assuming an average body weight of 70 kg).
- The **WHO recommended a TDI** (maximum Total Daily Intake) of **1-4 pg TEQ/kg body weight/day**, including exposure to dioxin-like PCBs.
- This means that, for many people, **total exposure will exceed** even the upper limit of **the recommended TDI**.

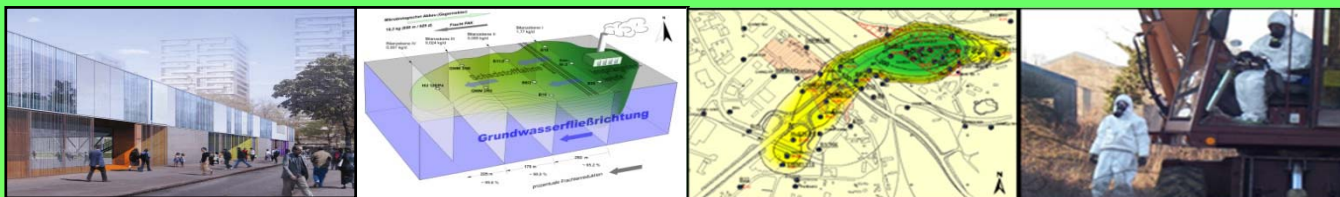


## Exposure by Food:

- These are generally individuals consuming **higher than average amounts of fatty foods, especially fatty fish and fish products**, but also **meat and milk products**.
- It is also important to consider the implications of the concentrations of dioxin in human **breast milk** for the daily intake of breast-fed **babies**.

Concentrations of PCDD/PCDF measured in EU Member States

Environmental Matrix	Measured Typical Range	Max. Concentration Contaminated Sites	Units <sup>*</sup>
Soil	<1 – 100	100,000	ng I-TEQ/kg d.m.
Sediment	<1 – 200	80,000	ng I-TEQ/kg d.m.
Air (ambient) (bulk deposition)	<1 – 100s <1 – 100s	14,800	fg I-TEQ/m <sup>3</sup> pg I-TEQ/m <sup>2</sup> d
Sewage Sludge	<1 – 200 (average 10 – 40)	1,200	ng I-TEQ/kg d.m.
Spruce/Pine Needles (biomonitors)	0.3 – 1.9	100	ng I-TEQ/kg d.m.



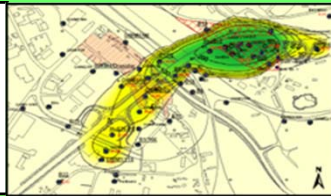
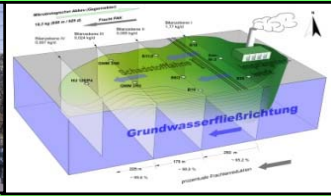
## Contaminated Sites:

### Generic German Action Values for Dioxins in soil.

Total of 2, 3, 7, 8 - TCDD-Toxicity equivalence (according NATO/CCMS)

Compounds	Action Value [ng I-TEq/kg TM]*			
	Dioxins/Furans (PCDD/F)	Children - Playing Grounds	Residential Area	Parc- & Sports Green Spaces
	100	1.000	1.000	10.000

**Site Specific Remediation Goals (SS-RG)** are based on site specific HRA (Health Risk Assessment) or TERQ (Toxicological Exposure Risk Quantification) to **ensure elimination of residual non-acceptable risks.**



## HRA: Health Risk Assessment Methodology Application

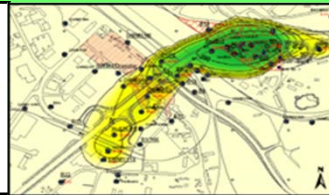
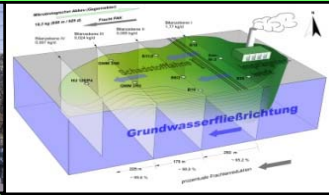
### Example: Residential and Recreation site use (Park)

**Goal:** → *Real Estate Revalorization by Remediation*

#### Definition of the exposure pathways

Potential exposure channel	Exposure scenario		Medium considered (HESP® model)
	residential	recreational	
• inhalation of pollutant in gaseous form	YES	YES	(3)
• inhalation of dust on which the pollutant is adsorbed	YES	YES	(1)
• inhalation of contaminated water vapour when taking a shower	YES	NO	(5)
• direct ingestion of soil	YES	YES	(1)
• ingestion of home grown fruits and vegetables	NO	NO	(2)
• ingestion of contaminated water from the supply	YES	NO	(5)
• ingestion of water from a private well	NO	NO	(4)
• absorption of soil and dust through the skin	YES	YES	(1)
• absorption through the skin of pollutant from the contaminated water supply when taking a shower	YES	NO	(5)

- (1) : surface layer of the soil corresponding to the horizon ( 0 - 0,3 m ),  
 (2) : concentration in the soil ( 0 - 1 m layer ) via the air in the soil,  
 (3) : migration of volatile and semi-volatile pollutants via the air in the soil to the surrounding air,  
 (4) : well water.



## Exposure Quantification: Example Ingestion of soils, water or food:

$$DED_{ing} = C_m \cdot \frac{Q_{ing}}{P} \cdot F_a \cdot \frac{Ex}{Ve} \cdot F_{exa} \cdot F_{exd}$$

**DED<sub>ing</sub>** = Daily Exposure Dose [mg/kg/d]

**C<sub>m</sub>** = Concentration Pollutants Concentration in the exposure medium : C<sub>soil</sub> [mg/kg], C<sub>water</sub> [mg/l], C<sub>food</sub> [mg/kg]

**Q<sub>i</sub>** = Ingested Soil quantity and/or food [kg/d] or water [L/d], distinct from the Adults (Q<sub>ing.A</sub>) and the Children (Q<sub>ing.C</sub>)

**P(a)** = Adult Body Weight [70 kg]

**P(e)** = Child Body Weight [15 kg]

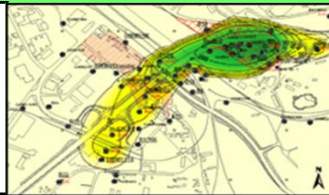
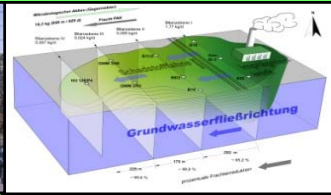
**F<sub>a</sub>** = Absorption Factor (if failing: 100 % = [1])

**Ex** = Exposure years in Lifetime (Adult or Child) [y]

**Ve** = Lifetime: Adult or Child [y]. In case of carcinogenic Pollutants: Ve = Ex [y]

**F<sub>exa</sub>** = Yearly Exposure [d/365 d]

**F<sub>exd</sub>** = Daily Exposure [hrs/24 hrs]



## Acceptable / Unacceptable Risks:

- Individual Cancer Risk :  $ICR \leq 10^{-5}$

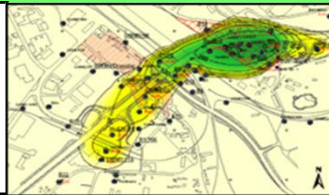
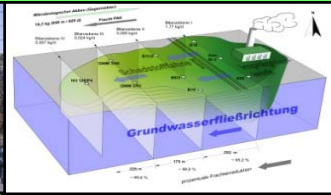
$$ICR = DED \cdot UR$$

Daily Exposure Dose (mg/kg/d) • Unit Risk or Slope Factor (mg/kg/d)<sup>-1</sup>

- Non-Cancer-Risk: Risk Index:  $RI \leq 1$

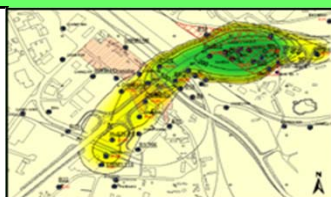
$$RI = DED / TRD$$

Daily Exposure Dose (mg/kg/d) / Toxic Reference Dose or ADI (mg/kg/d)  
per toxicological target Organ



## Acceptable Risks (for ex.: ICR Individual Cancer Risk):

- **WHO:** WHO: World Health Organisation, M. Younes: International Symposium “Exposure and Risk Assessment with Respect to Contaminated Soil”, Munich from February 28 & 29/1996: Acceptable Individual Cancer Risk: **ICR =  $10^{-5}$**  (= 1 additional Cancer per 100 000 Persons),
- **Austria:** UBA<sub>AT</sub>: Umweltbundesamt (2011): Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **UK:** DEFRA: Department for Environment, Food and Rural Affairs (2002): Report CLR9TOX1-10: Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **Canada:** According HEALTH CANADA (2002) : “Atlantic Provinces” (NS, NB, PEI, and Nfld./Lab.): Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **France:** MEDD: Circular from February 08/2007: Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **Germany:** Bundesanzeiger BA 161a from August 28/1999 : Toxicological Screening Level (PW) for Acceptable Cancer-Risk: **ICR =  $10^{-5}$** , Proved intervention level: **ICR =  $5 \cdot 10^{-5}$**
- **Italy:** Decreto 52/2006 from 2006: Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **Netherlands:** RIVM (2001): Document 711701 025 Re-Evaluation of Human-Toxicological Maximum Permissible Risk levels: Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **Switzerland:** Anhang 1 der Altlastenverordnung (AltIV): BAFU: 31/03/2009 & Art. 2 Verordnung über Belastungen des Bodens (VBBo) SR 814.12 from 01/07/1998 (State 01/07/2008), in Art. 12 of Verordnung über die Sanierung von belasteten Standorten AltIV. from 26/08/98, State 01/08/2011: Acceptable Cancer Risk: **ICR =  $10^{-5}$** ,
- **USA:** DOH: Acceptable Cancer Risk: **ICR =  $10^{-6}$  -  $10^{-4}$** . In the most cases and States an Acceptable Cancer Risk of **ICR =  $10^{-5}$**  is used.
- **Australia, Hong-Kong, Denmark, Japan, New Zealand, Norway, Sweden:** **ICR =  $10^{-5}$**  is used.



**US- EPA toxic  
equivalency  
(TEQ)  
Factors:**

**Case Study:  
Bitterfeld Site  
in Germany\*:**



Compound	TEF
Polychlorinated dibenzo- <i>p</i> -dioxins (PCDDs)	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
Polychlorinated dibenzofurans (PCDFs)	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003

**SCENARIO : Industrial site with Workers on Site (adults only): Bitterfeld / Germany**

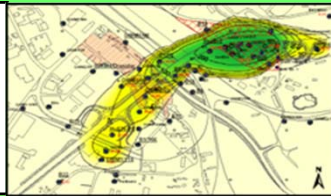
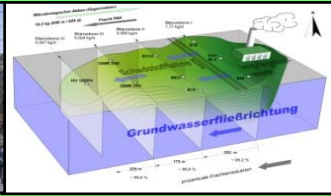


Pollutant	Health risk		Pollutant	Health risk	
	Non carcinogenic	Carcinogenic		Non carcinogenic	Carcinogenic
Lead	0.109	-	m,p-xylene	0,167	-
Cadmium	0.00124	0.00081x10 <sup>-5</sup>	o-xylene	0.0422	-
Chrome VI	0	0	Trichloroethylene	2.5	-
Chrome III	0.0000227	-	Tetrachloroethylene	0.00624	0.16x10 <sup>-5</sup>
Arsenic	0.0160	0.261x10 <sup>-5</sup>	1,1,1-trichloroethane	0.0713	-
Nickel	0.00109	-	<b>PCDD/F (total TEQ)</b>	-	<b>11x10<sup>-5</sup></b>
Mercury	0.657	-	Naphthalene	2.62	-
Zinc	0.000782	-	1,2,3-trimethylbenzene	0.01	-
Selenium	0.000241	-	1,2,3-Trichlorobenzene	0.00175	-
Antimony	0.00270	-	1,3,5-Trichlorobenzene	0.00314	-
Ethyl benzene	0.0000428	-	1,3-Dichlorobenzene	0.0000499	-

**PCDD/F-  
Cancer Risk  
ICR = 11·10<sup>-5</sup>**

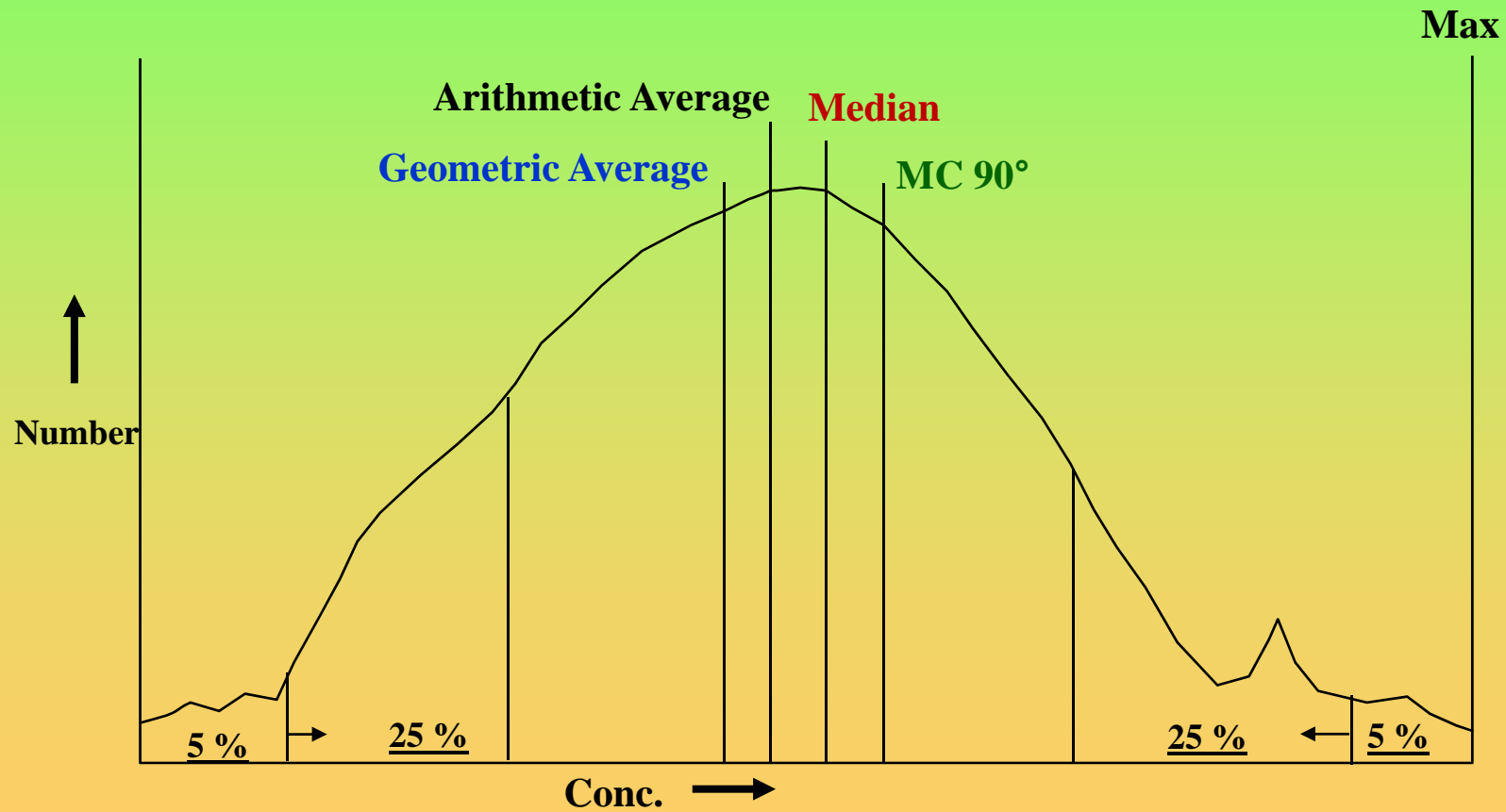
<b>Total of carcinogenic risks ICR :</b>	<b>11.16x10<sup>-5</sup></b>	<b>Limit value: ICR =10<sup>-5</sup></b>
<b>Total of non carcinogenic risks (*) RI :</b>		<b>Limit value: RI = 1</b>
<b>Neurotoxicity: Pb + Hg + tri- &amp; tetrachloro-ethylene + trichloroethane</b>	<b>3.4(*)</b>	<b>Limit value: RI = 1</b>
<b>Blood toxicity: Pb + As + Zn + Sb</b>	0.129(*)	<b>Limit value: RI = 1</b>
<b>Liver toxicity: tetrachloroethylene + chloro-benzene + ethylbenzene</b>	0.0625(*)	<b>Limit value: RI = 1</b>
<b>Fetotoxicity : xylenes</b>	0.209(*)	<b>Limit value: RI = 1</b>

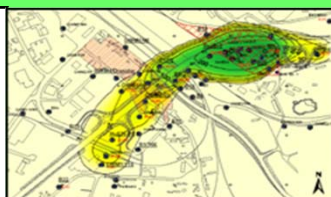
**Total  
Cancer Risk  
ICR = 11·10<sup>-5</sup>**



# Statistics & Uncertainties: Example Pollutant Concentrations

## Statistical Distributions:





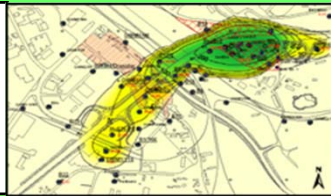
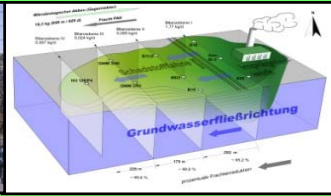
## Uncertainties: Example Inhalation Rates

### Inhalation Rates US vers. Europe

Cible	Activity							
	Relaxation		Slight		Average		Intensive	
	MES	MOD	MES	MOD	MES	MOD	MES	MOD
Children (6 ans)	9,6	20	19	20	48	20	58	20
Children (10 ans)	9,6	20	24	20	77	20	101	20
Adult (m)	7,2	20	12	20	38	20	70	20
Adult (f)	17	20	19	20	60	20	115	20

MES : Volumes mesurés [m<sup>3</sup>/j] : AML (D)

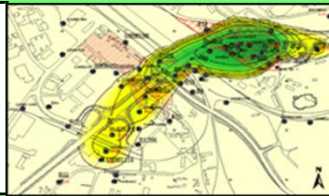
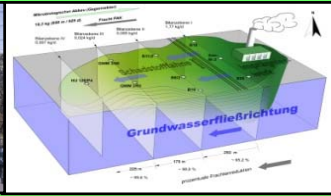
MOD : Volumes généralisés [m<sup>3</sup>/j] : U.S.A. → **under- and over-Risk-Evaluations !**



## Remediation of Contaminated Soil, Groundwater, etc.: Goals:

- **Remediation & Decontamination Success** for final Site (use HRA (Health Risk Assessment) Site Specific Remediation Goals (SS-RG) for acceptable future Health Risks (Maximum Individual Cancer Risk: ICR =  $10^{-5}$ , etc., cf. HRA).
- **Remediation feasibility for the different SS-RG: Applicable Strategies & Technologies** (for example):
  - A. Site Use Restrictions and Access limitations,
  - B. Capping and/or Excavation & Confinement or Dumping (+ Stabilization or Immobilization),
  - C. ISCO: In-situ Chemical Oxidation ( $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ , etc),
  - D. In-situ Dechlorination by nano- or  $\mu\text{Fe}^0$ , Enzymes, etc.,
  - E. Microbiological Degradation (ex-situ or in-situ: DNBA or ENA or for ex. in in Combination with C, D or F) and / or F. Phyto-Remediation,
  - G. Thermal Treatments (Thermo Desorption, Incineration, etc.).



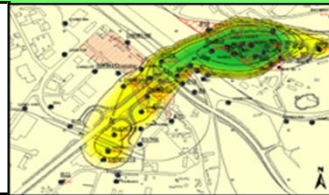
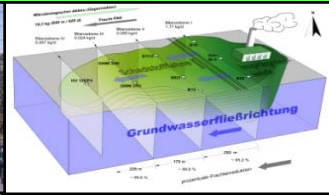


## **Remediation Plan: Remediation Design & Planning**

- A. Determination of Site Specific Remediation goals SS-RG: Risk Assessment based on European & US Knowledge and Site specific Exposure Scenarios.**
- B. Pollutant specific approach, based on initial Pollutants, Metabolites and Impurities.**
- C. Exact definition of Remediation Zones and Volumes & Excavation under Tente (?) →**
- D. Realization of Technical-Financial Feasibility study for Treatment, including all available Technology (Best Results for best Price).**
- E. Health & Safety (EHS) Procedures during Remediation Actions for Workers & Neighborhood.**
- F. Surveillance and Control of Work (EHS, Separation of excavated Soil), Final Controlling, Cost Limitation.**
- G. Final Remediation Report and Final Health Risk Assessment.**







## PCDD/F & Arsenic Treatment Strategy:

### 1. **Site specific Health Risk Assessment** (TERQ: Toxicological Exposure-Risk-Quantification):

- A. Application of site specific **Pollutant Cocktails** and (future) site uses,
- B. Definition of **Site-Specific Remediation Goals (SS-RG)**,
- C. **Mappings of SS-RG Exceeding** (for different site use scenarios),
- D. **Definition of Priority Zones** (Pollution Hot Spots + Sensible site use + urgent Urbanization & Real Estate Projects + Existing Health Risks, Social Aspects, etc.)

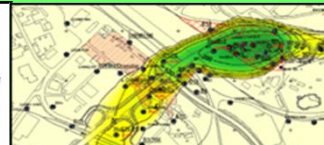
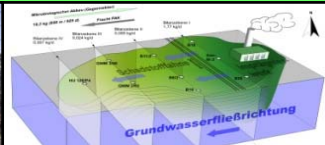
### 2. **Priority related Remediation** (according 1.D.):

#### 2.1. **Strong Hot-Spots after excavation:**

- **Thermal Treatments (ISPD, TD, Incin, PlAr)** or **Dumping** in Engineered Landfill,
- **PCDD/F-Dechlorination** (for ex. **ZVI**) and **As-Immobilization** (for ex. EHC-M) and subsequent microbiological and/or Enzymatic destruction.

#### 2.2. **In-situ Treatments (soil & sediments):**

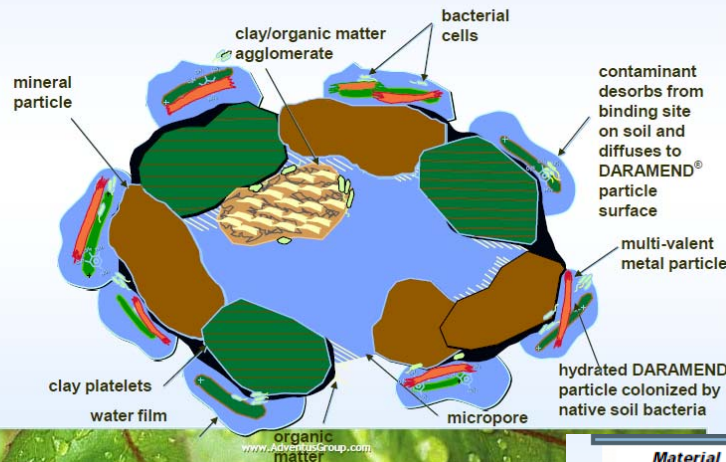
- **PCDD/F-Dechlorination** (for ex. **ZVI**) and **As-Immobilization** (for ex. EHC-M)
- and subsequent **microbiological** and/or **Enzymatic Destruction** of PCDD/F (for ex. by EnzFKINV-01, EnzERFU-02, EnzFKNOE-7F, etc.) and eventually
- **Application of specific fungi** and/or **Dehalococcoides ethenogenes Strain 195** (according PCR results). → Laboratory → Pilot Test → Vietnamese Applications.



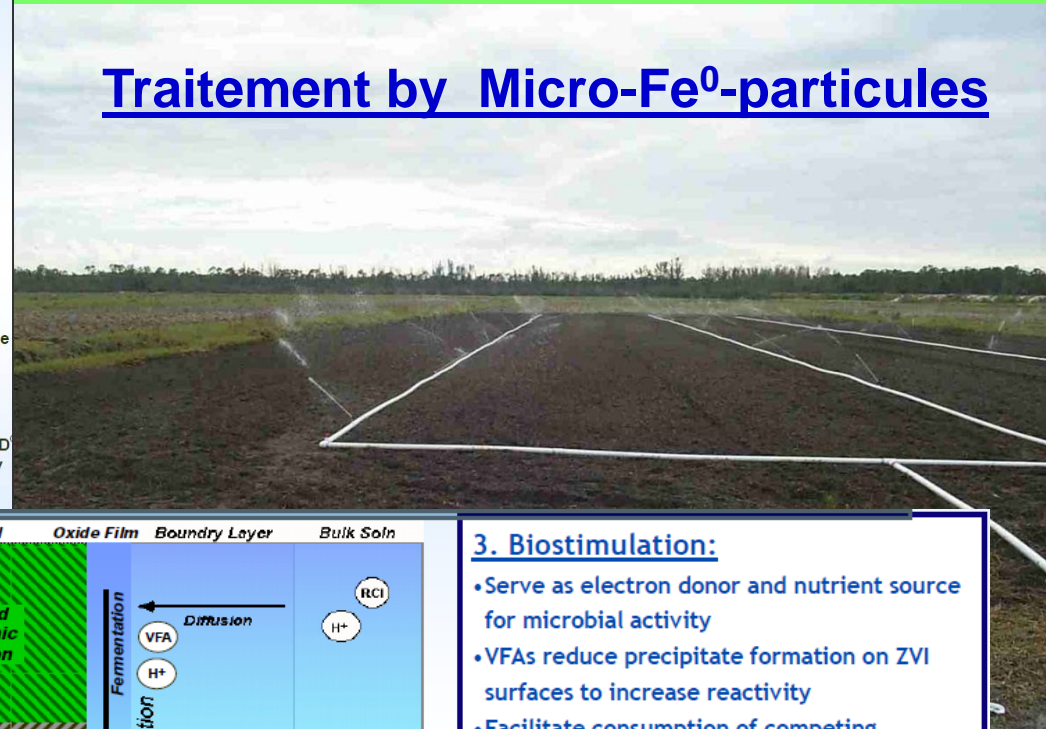
## Treatment examples



### DARAMEND® Soil Amendments (ZVI/carbon)

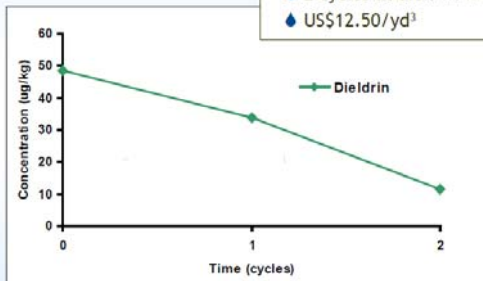


## Traitement by Micro-Fe<sup>0</sup>-particules

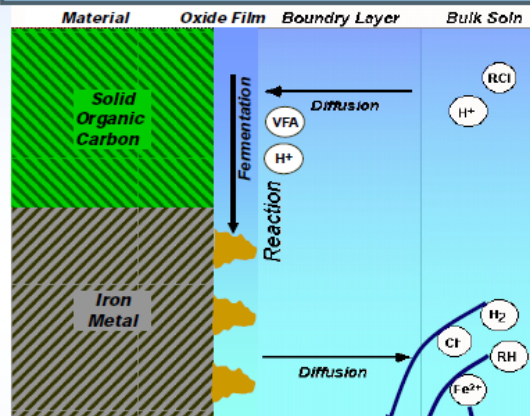


### Treatment of Dieldrin: Palm Beach County Florida

- 2,600 tons in situ
- 2 cycles at 0.5% w/w DARAMEND®
- US\$12.50/yd<sup>3</sup>



Source: FMC



#### 1. Direct Iron Effects:

#### Hydrocarbon generation:

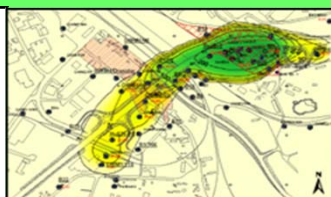
#### 2. Indirect Iron Effects: Dissolved iron precipitates to reactive minerals

#### 3. Biostimulation:

- Serve as electron donor and nutrient source for microbial activity
- VFAs reduce precipitate formation on ZVI surfaces to increase reactivity
- Facilitate consumption of competing electron acceptors such as O<sub>2</sub>, NO<sub>3</sub>, SO<sub>4</sub>
- Increase rate of iron corrosion/H<sub>2</sub> generation

#### 4. Enhanced Thermodynamics:

- Very low redox reached by addition of fermentable carbon and ZVI (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H<sup>+</sup> pressure

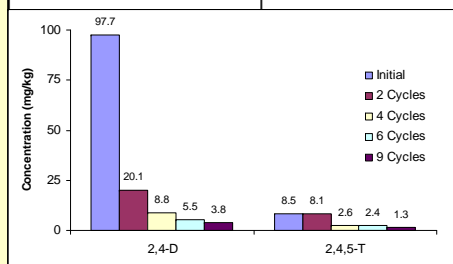


## Treatment examples

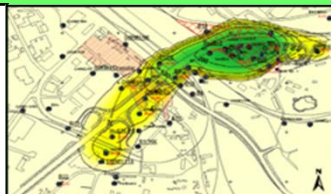
### SUMMARY REPORT FOR GRACE DEARBORN DARAMEND™ BIOREMEDIATION TOTAL DIOXINS/FURANS

## Daramend-Application

Analyte ppb	EPA Site Data (n=1)		PCDD/F- Reduction %	Environment Canada Lab Data (n=4)		PCDD/F- Reduction %
	Before Treatment	After Daramend		Before Treatment	After Daramend	
2,3,7,8-TCDD	ND	ND				
1,2,3,7,8-PeCDD	ND	0.116				
1,2,3,4,7,8-HxCDD	10.2	ND				
1,2,3,6,7,8-HxCDD	11.8	7.73				
1,2,3,7,8,9-HxCDD	1.75	2.22				
1,2,3,4,6,7,8-HpCDD	610	406				
OCDD	10,400	3830	- 63, 2 %	9,000	6,900	- 23, 3 %
2,3,7,8-TCDF	ND	ND				
1,2,3,7,8-PeCDF	ND	ND				
2,3,4,7,8-PeCDF	0.142	ND				
1,2,3,4,7,8-HxCDF	1.52	1.72				
1,2,3,6,7,8-HxCDF	ND	0.437				
2,3,4,6,7,8-HxCDF	ND	0.716				
1,2,3,7,8,9-HxCDF	1.58	0.477				
1,2,3,4,6,7,8-HpCDF	80.4	23.7				
1,2,3,4,7,8,9-HpCDF	4.41	2.15				
OCDF	733	346				
Total TCDD	1.24	ND		0.490	0.153	
Total PeCDD	ND	0.264		0.071	0.058	
Total HxCDD	81.8	45.2	- 44, 7 %	43.7	37.0	- 15, 3 %
Total HpCDD	1,320	890	- 32,6 %	1,940	920	- 52,6 %
Total TCDF	0.0832	ND				
Total PeCDF	2.19	2.54				
Total HxCDF	99.1	42.8				
Total HpCDF	508	161	- 68,3 %			
Total TEQ	20.83	9.91	- 52,4 %			



Source: FMC

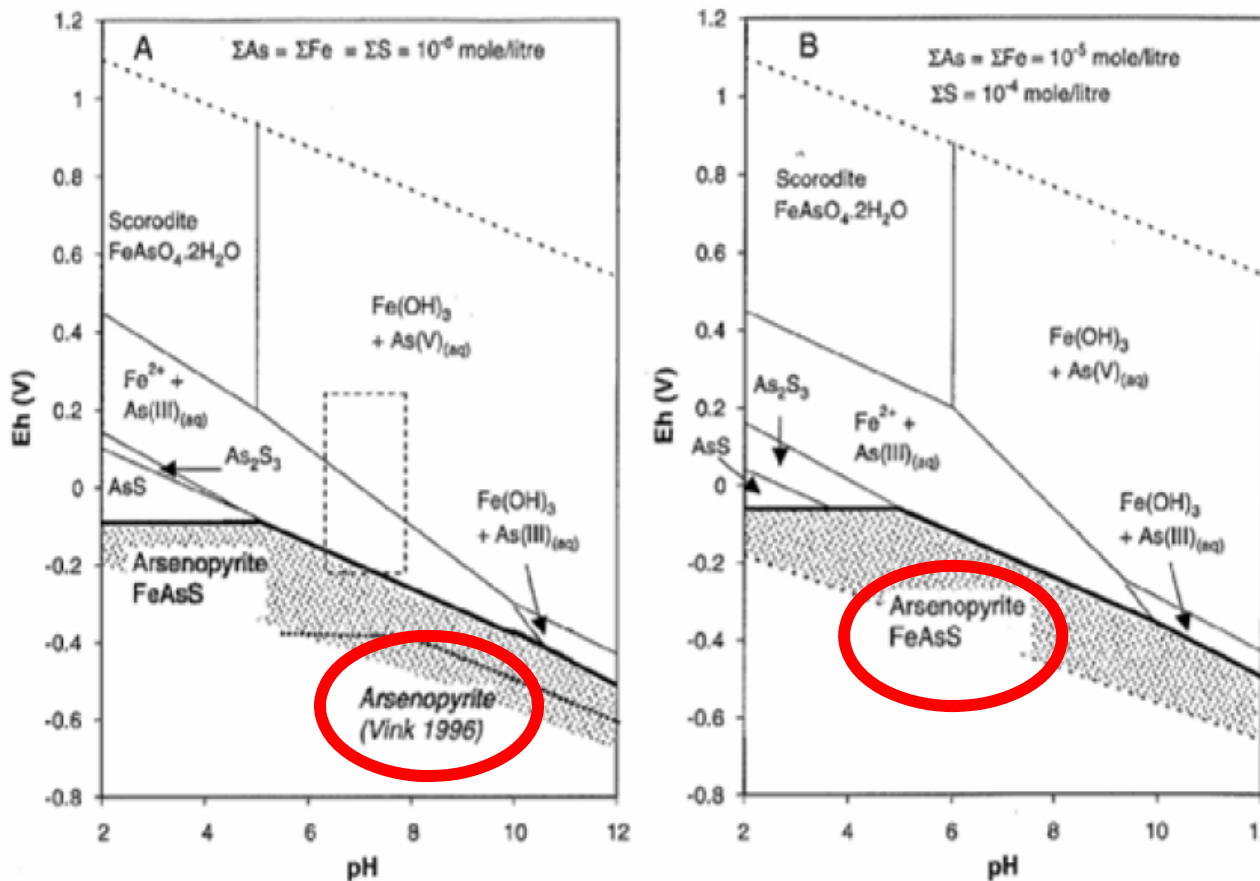


**Stabilisation of As  
by EHC-M & Sulfate**

**Arsenic Stabilisation via EHC-M (ZVI)**



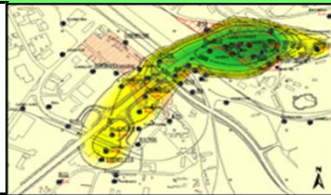
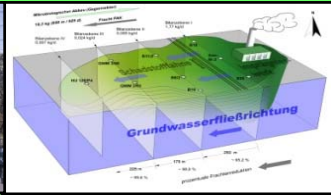
Eh-pH diagram for the As-Fe-O-S system showing the stability field of arsenopyrite (Craw et al 2003).



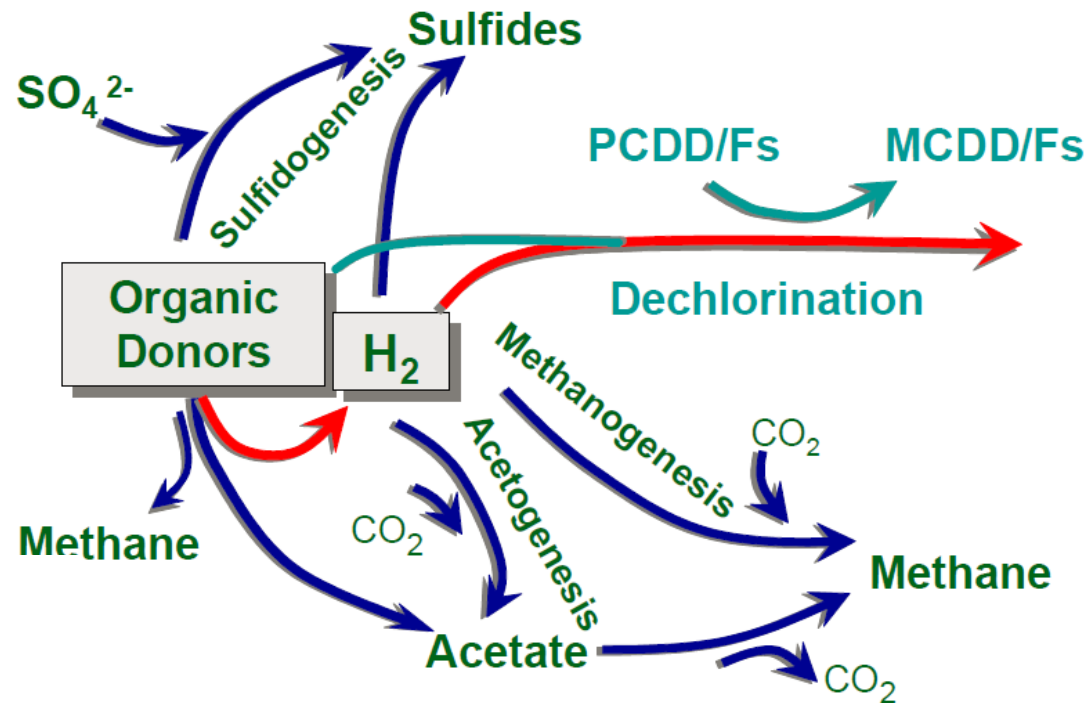
**Arsenic  
removal  
using  
EHC-M  
Technology  
is  
NON  
REVER-  
SIBLE**

**Back to  
stable  
Arseno-  
Pyrite  
!**

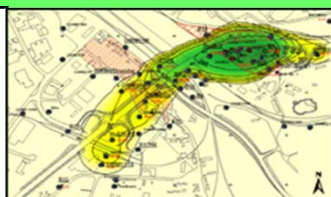
Source: FMC



## Microbial reductive dechlorination : Dehalococcoides ethenogenes Strain 195

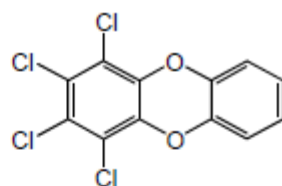


**Fig. 1.** Competing electron flow pathways in anaerobic sediments.

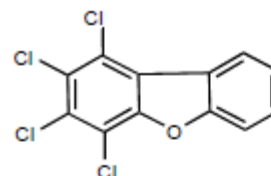


## Treatment examples

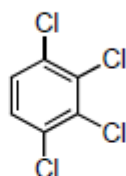
### Microbial reductive dechlorination : Dehalococcoides Ethenogenes Strain 195



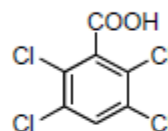
1,2,3,4-TeCDD



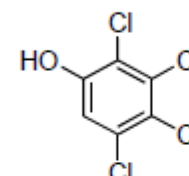
1,2,3,4-TeCDF



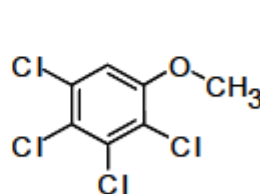
1,2,3,4-TeCB



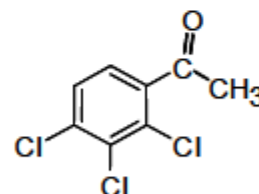
2,3,5,6-TeCBA



2,3,4,5-TeCP

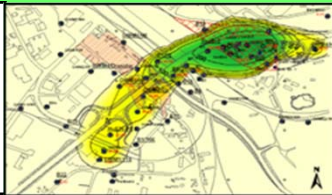
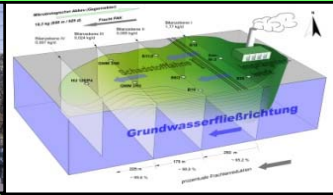


2,3,4,5-TeCA

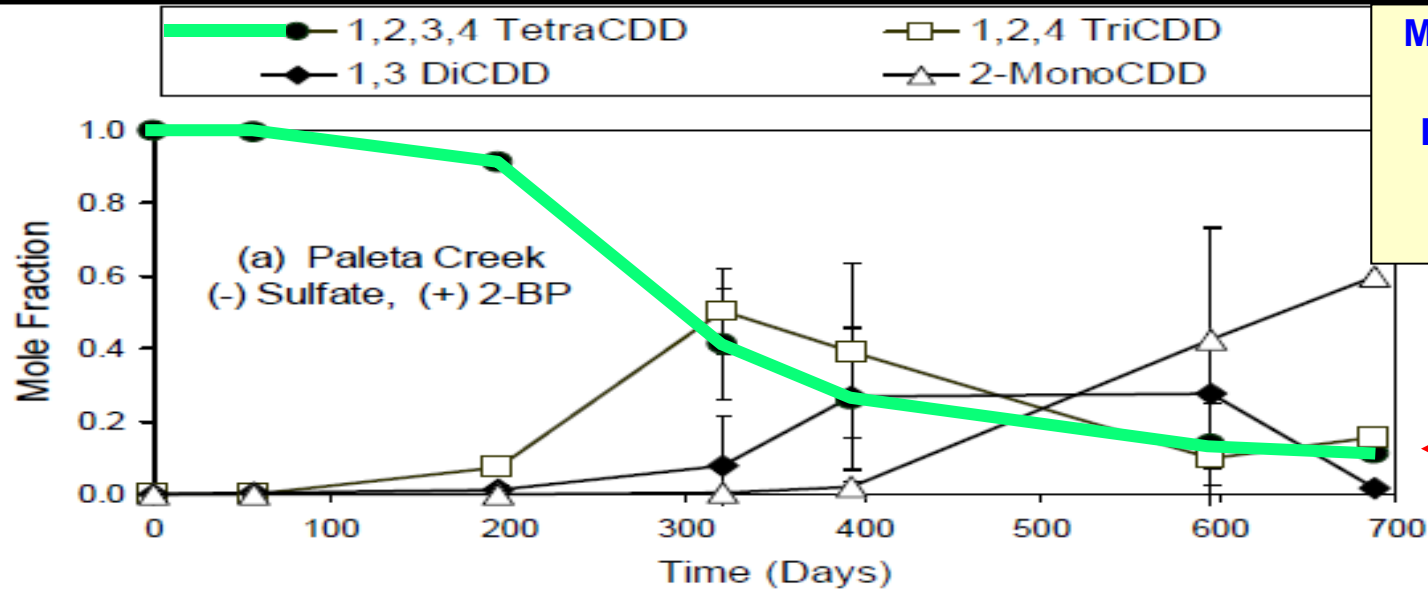


2',3',4'-TrCAP

Halogenated compounds used in this study (TeCDD, tetrachlorodibenzo-*p*-dioxin; TeCDF, tetrachlorodibenzofuran; TeCB, tetrachlorobenzene; TeCA, tetrachloroanisole; TeCP, tetrachlorophenol; TeCBA, tetrachlorobenzoic acid; TrCAP, trichloroacetophenone).

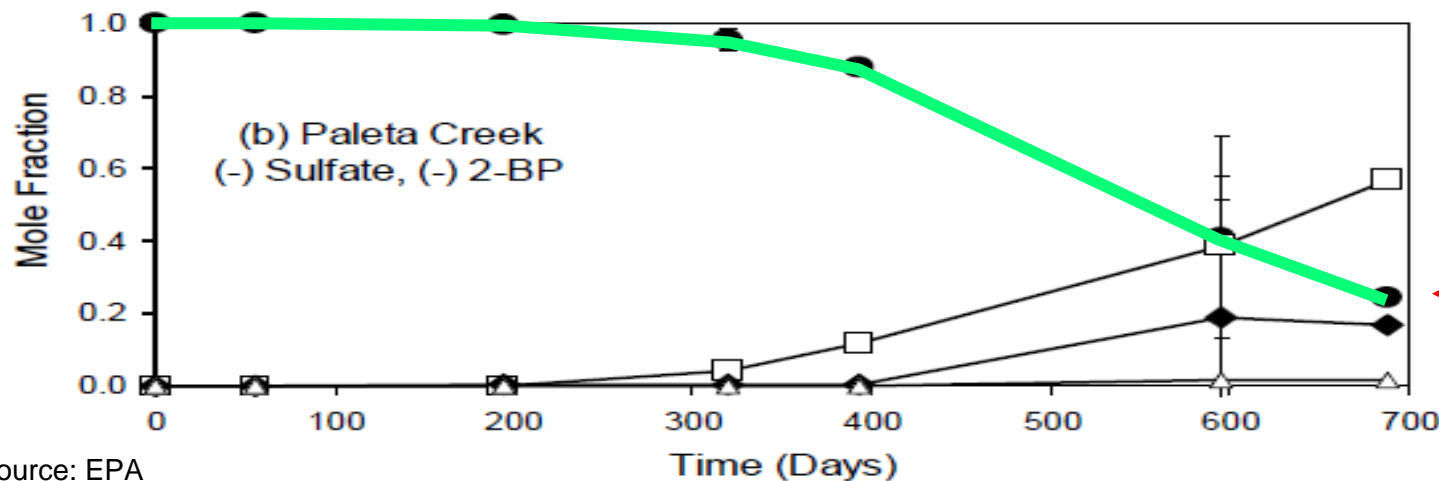


## Treatment examples

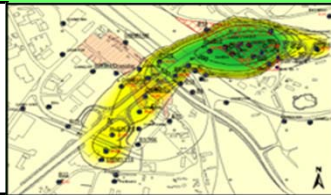
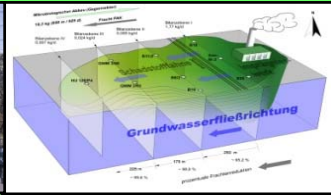


Microbial reductive dechlorination :  
Dehalococcoides  
Ethenogenes  
Strain 195

## Microbial reductive dechlorination : Dehalococcoides ethenogenes Strain 195



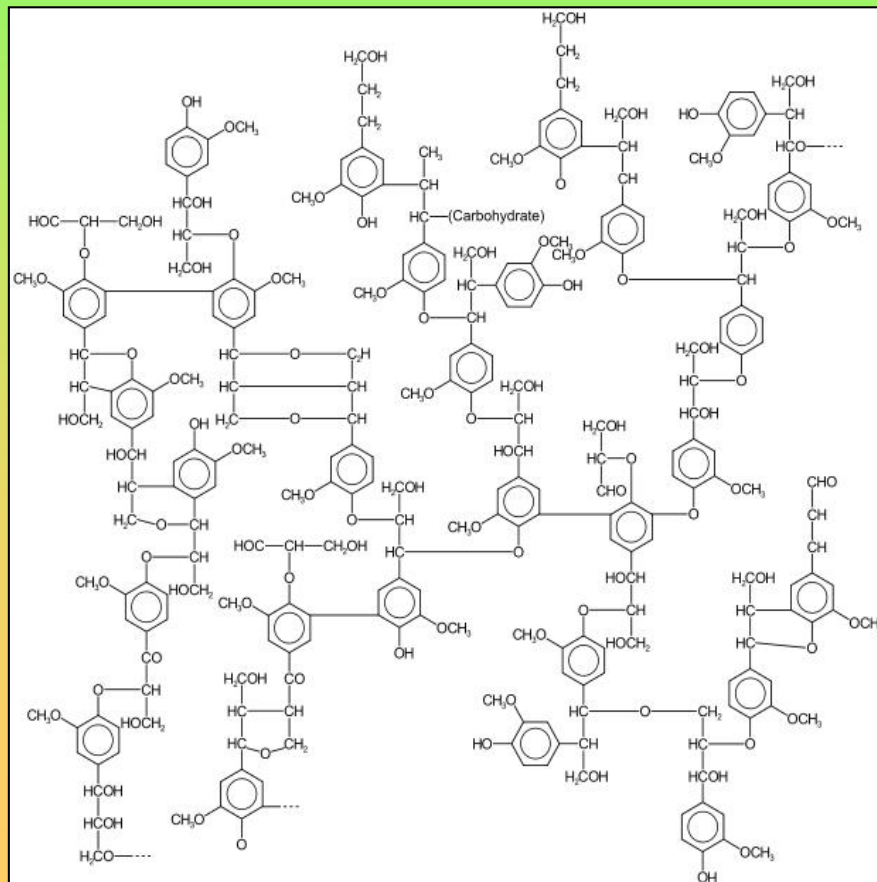
Source: EPA



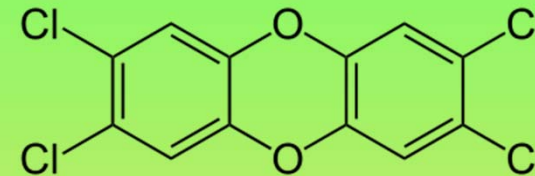
## Treatment examples

# Based on lignin degrading mechanism of fungi and/or Enzymes

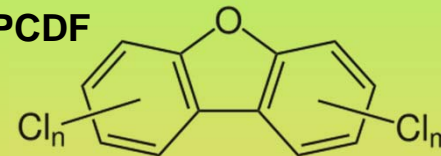
## LIGNINE STRUCTURE



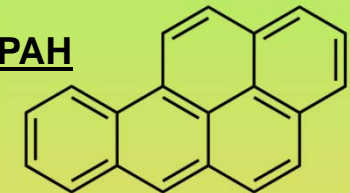
## PCDD



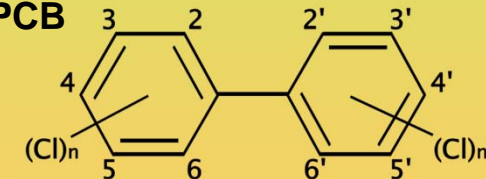
## PCDF



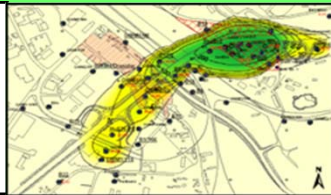
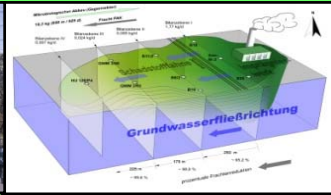
## PAH



## PCB



EnzFKINV-01, EnzERFU-02,  
EnzFKNOE-7F, etc.

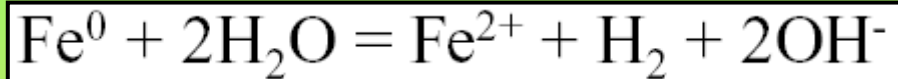


## Treatment examples

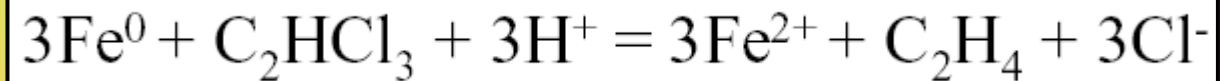
Soil and Water: *Traitements Fe<sup>0</sup>-Micro- & Nano-particles:*

→ μFe<sup>0</sup>: Best Technical & Cost Option (DAREMEND Technology)

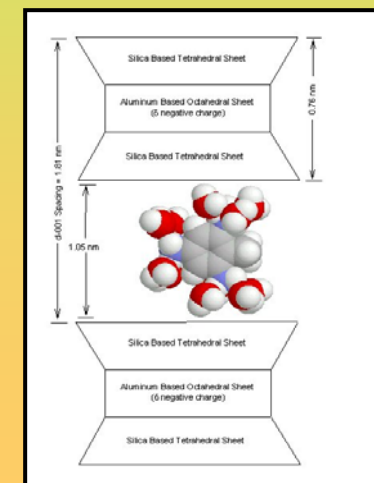
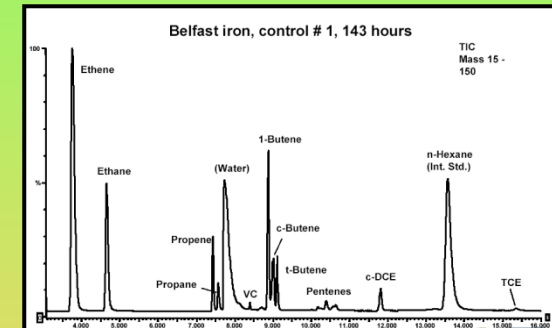
Reductive Destruction / hydrolysis (& microbiological activation):

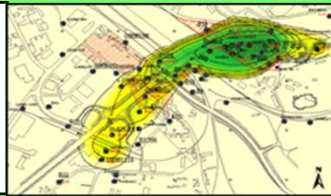
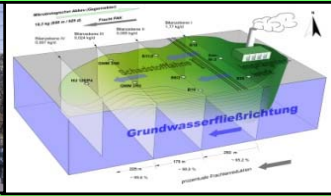


Ex.: Destruction du TCE



Dynamization via catalysers: Pd, Ni.





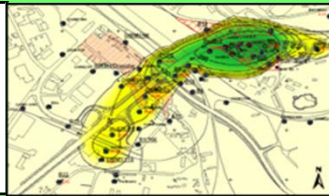
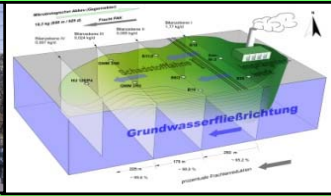
## Site Remediation Goals (Social-Political & Economical):

- Strong Environmental & Public Health,
- Stronger Economy without ill People for better Productivity, Export and Tourism, etc.,
- Stronger Vietnam by Strong Public Health & Economy !

### Via and by:

- Soil, Sediment and Water **Decontamination**,
- **Stop illnesses** by Dioxines, US-Pesticides, etc. for more efficient Workers,
- **Less Medical Costs** for less illnesses and better Family Functioning,
- **Producing cleaner a more healthy Food** (even for export: Fishery, etc.),
- **Optimize Real Estate & Urbanization Development** of cleaned Land (with Certification),
- **Claiming for De-Damaging Budgets** from the Toxic Chemicals Pollution Responsible.



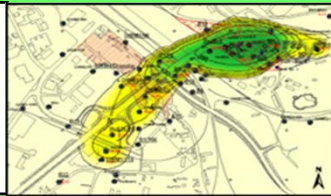
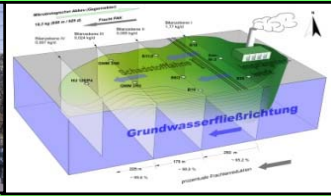


## Recommendations: Management of Contaminated Sites for Real Estate & Investment Safety

### Everytime:

- **Historical Survey** concerning Polluting Activities Zones & Pollutants.
- **Site Investigations** (concerning soil, soil gas, ground & surface water, food stuffs).
- **HRA: Health Risk Assessment** for future site activities and Real Estate Projects.
- **Mapping of SS-RG (HRA - Site specific Remediation Goal)** exceeding.
- **Remediation technical-economic Feasibility study** and Cost estimate.
- **Remediation Design & Planning.**
- **Application of Remediation Technologies.**
- **EHS-Management** during Remediation.
- **Environmental & Bio-Monitoring.**
- **Integrated transparent Real Estate & Urbanization Revalorization.**





## Recommendations: For Treatments:

### For example Bien Hoa :

➤ **Remediation technical-economic Feasibility Study and Cost estimate.**

- **Laboratory & Field Tests,**

➤ **Application of Remediation Technologies.:**

**In-situ chemical Dehalogenation & Microbiological Degradation of Dioxins (PCDD/F)**





# REPAIR

**REPA**ration-Foundation for **I**nternational **RE**mediation  
of War Damages

(in Viet-Nam, Kosovo, China, etc.)

**REPA**arations-Fundation für **I**nternationale  
**RE**habilitation

von Kriegsschäden

(in Viet-Nam, Kosovo, China, etc.)

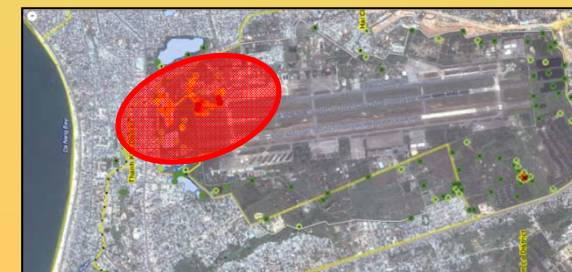
Fondation de **REPA**ration **I**nternationale pour la  
**RE**habilitation des Dommages de Guerre

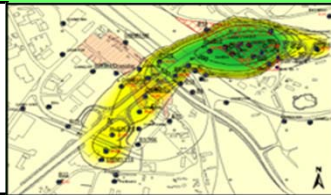
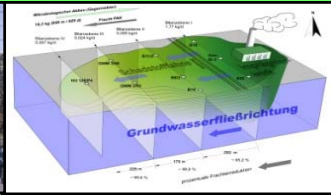
(en Viet-Nam, Kosovo, China, etc.)

# REPAIR Financing



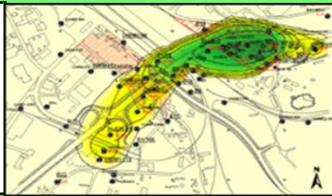
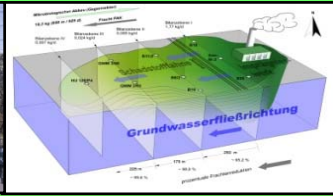
- Important War Pollution Damages are existing Worldwide. For ex., about 60 – 70 Million of liters of toxic Pesticides, strongly contaminated with Dioxins and Arsenic, etc. were used by the US-Forces during the Viet-Nam War. Dioxins (PCDD/F) and Arsenic, etc. are still existing in the Vietnamese Environment (Soil, Rivers, Groundwater Food chain, etc.).
- **A moral Co-responsibility** is existing for all Countries who furnished those Chemicals or who supported the USA during this « **Chemical-War** », as the NATO-Members (Germany, UK, etc.), Japan, Australia, etc.
- **The International Foundation « REPAIR »** for financing Remediation of contaminated Sites (Dioxins, Arsenic, etc.) and Health Faire of hundred of thousands « Agent-Orange » sick People (veterans and Children with genetic illnesses, cancer, etc.) **must be internationally supported !**
- The same principle must be applied for all War Pollution and Health Damages existing Worldwide (Viet-Nam, Kosovo, Pollution by Japanese Chemical Warfare Agents in China, etc.).





## Contact:

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Email : [frank.karg@hpc-envirotec.com](mailto:frank.karg@hpc-envirotec.com)
- **Mr. Eberhard REECK** / Co-President of « **REPAIR** »:  
Co/ HVR International, Herzbergstrasse 128-139, D-10365 BERLIN/ Germany  
Tel: ++49 306 093 0201 / Fax: ++49 336 250 1563 /  
Email : [hvr1992@aol.com](mailto:hvr1992@aol.com)



## Discussions & Actions

