



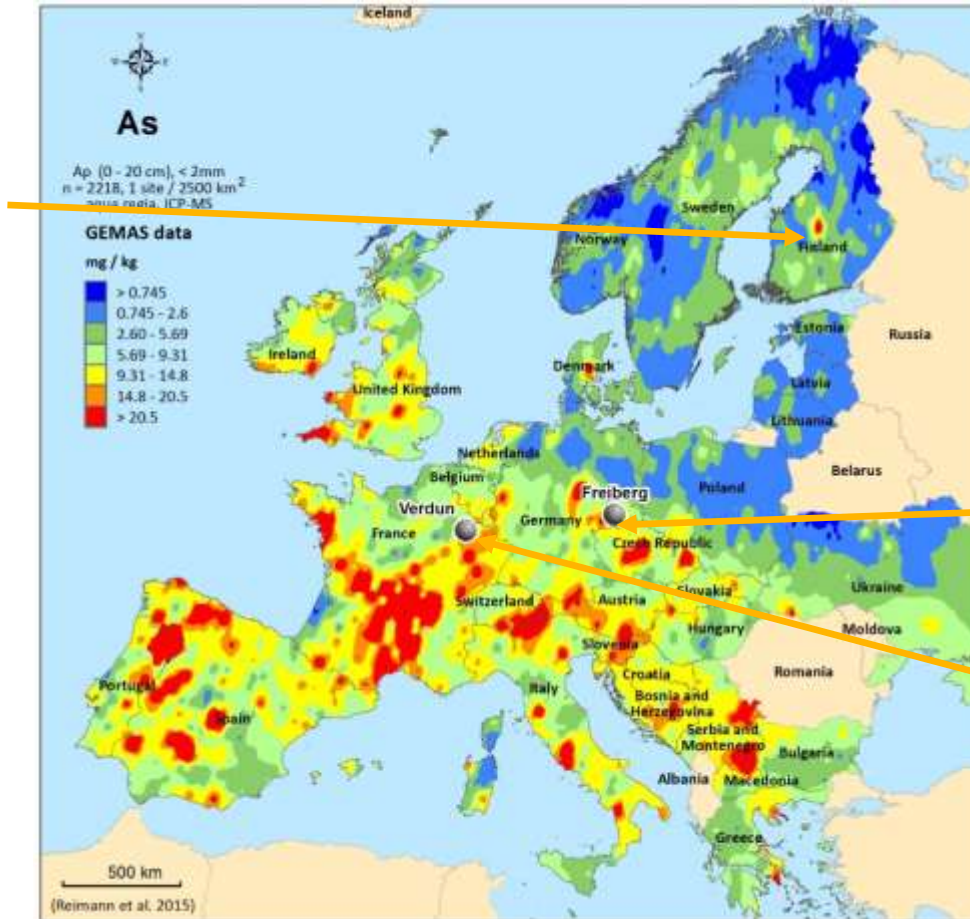
Risk Assessment and Management for Arsenic: Comparison of Tampere, Verdun and Freiberg areas

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Isabel Jordan GEOS and Daniel Hube BRGM
with
- the AgriAs project team



Arsenic in European agricultural soils

Tampere:
Key note for
characteristics



Arsenic concentration in European agricultural soils (0 – 20 cm).
Source: GEMAS data (Reimann et al. 2015).

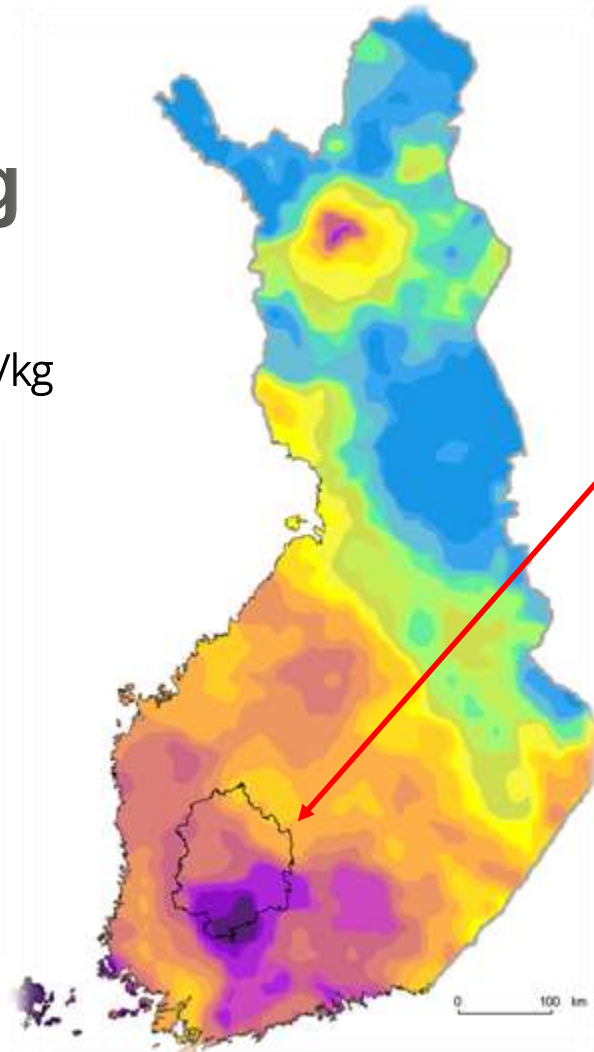
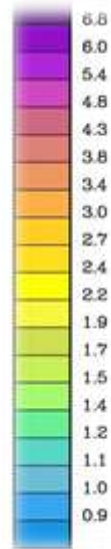
Dots: AgriAs target sites:

Freiberg: old mining district

Verdun: a former chemical ammunition breaking-down facility of the interwar period

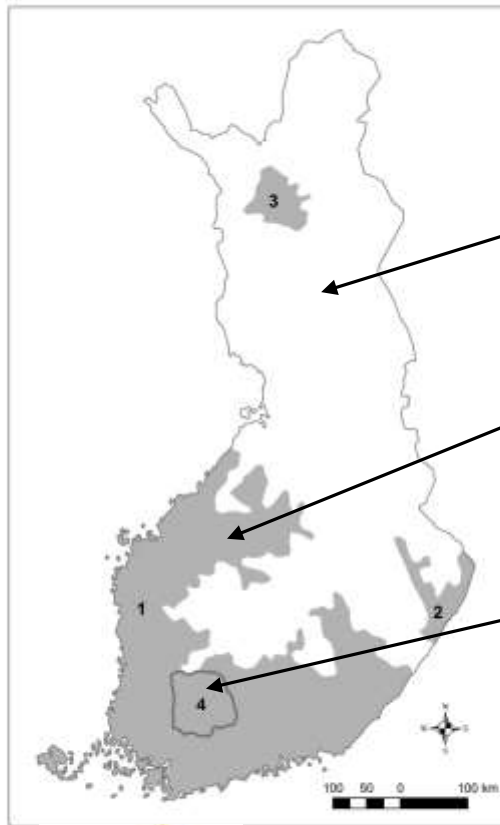
National till geochemical mapping

As mg/kg



Tampere region:
South part is an
Arsenic province

Arsenic provinces

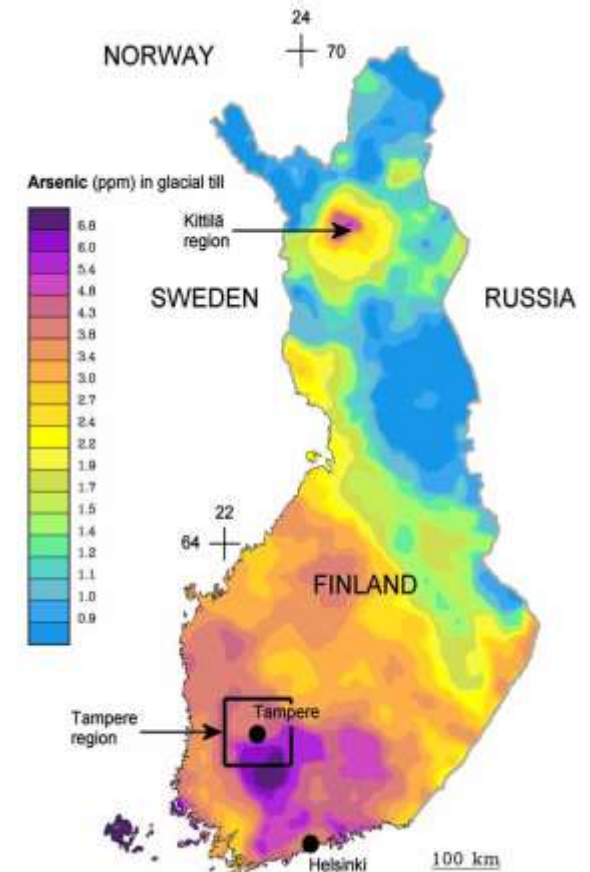


- Decree on the Assessment of Soil Contamination and Remediation Needs 2007: regional baselines can be used as threshold value for the assessment
- White areas:
 - Threshold value for As is 5 mg/kg
- Large grey As province 1 in Southern Finland:
 - As baseline 10 mg/kg
- The highest natural As concentrations are found in the Tampere – Häme region (province 4):
 - As baseline ca 30 mg/kg

RAMAS project 2004-2007



- Arsenic in the Tampere region in Finland: occurrence in the environment, risk assessment and risk management
- Aims
 - To locate the sources of natural and anthropogenic arsenic from the study area
 - To assess health and ecological risks
 - To present recommendations for preventive or remediation actions
 - To develop risk assessment and risk management tools
- Agricultural soil and As concentration in plants (wheat, potato, timothy) were studied from 15 sites



ASROCKS project 2011 – 2014

- The main objective of the ASROCKS project was to develop guidelines for the exploitation of natural aggregate resources, crushed bedrock, sand and gravel, in areas with higher than average arsenic concentrations in bedrock and soil.
- Study area: Tampere region, Finland
- Guidelines available from <http://projects.gtk.fi/ASROCKS/ohjeistus/>



LIFE10 ENV/FI/0062



Tampere region: Sources of arsenic and As concentration in rocks and soil

- As is mostly natural, derived from bedrock.
- In bedrock the highest concentrations were found from the narrow volcanic dominated Tampere Schist Belt. Up to 1000 mg/kg.
- Several mineralizations, e.g. Cu-W, Ni-Cu, Au-Cu. Arsenopyrite in gold-bearing quartz veins. Also old mining sites.
- The highest average As concentrations in the glacial tills were also found in the middle and southern part. Up to 9280 mg/kg. In topsoil max 1050 mg/kg
- Old wood preservation plants have been the most important anthropogenic sources of As in the Tampere region.
- RAMAS: As concentration low in plants: wheat grains 0.005 mg/kg, potatoes 0.011 mg/kg (lower than median values in EFSA study)
- Important pathway to humans: Deep wells drilled into the crystalline bedrock with elevated As concentrations.

Arsenic in Germany

Topsoil: As in mg/kg
1:1 000 000

- Background concentration of As in topsoil high in mountain regions
- Baseline concentrations:

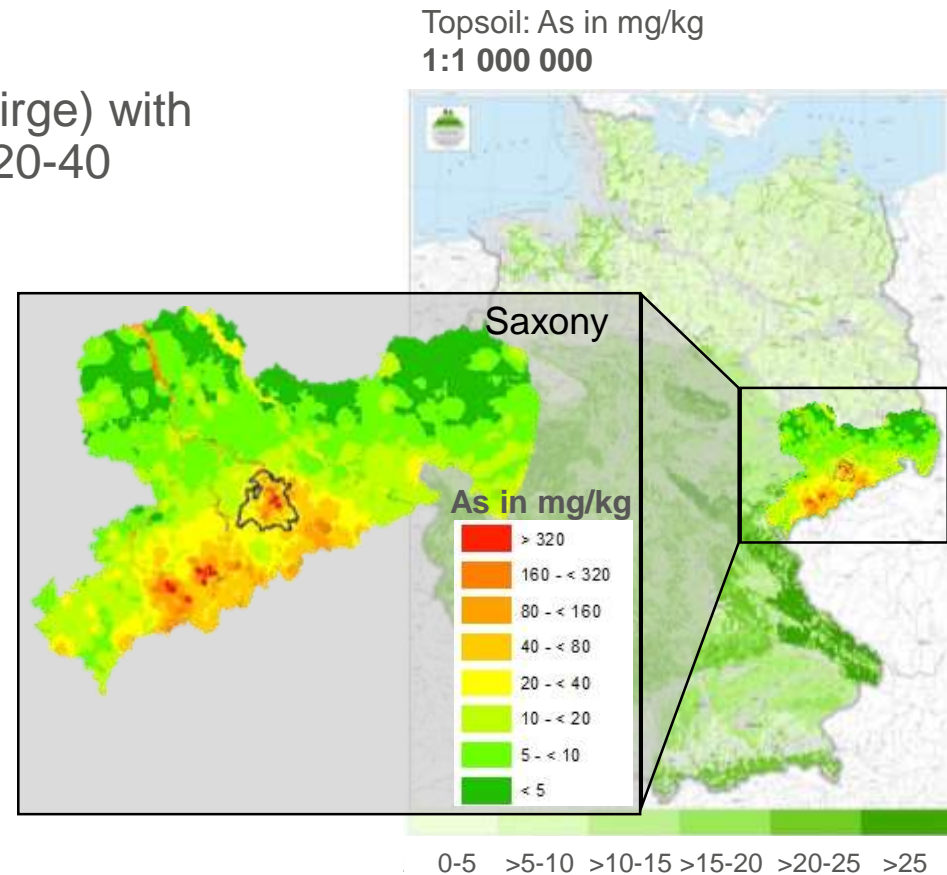
North:	0-10	mg/kg
Middle/ South:	10-25	mg/kg
Local Hotspots:	>> 25	mg/kg



Source: BGR (Bundesanstalt für Geowissenschaften und Rohstoffe)
https://www.bgr.bund.de/DE/Themen/Boden/Bilder/Bod_HGW_KarteAs_g.html

Saxony and Freiberg region

- Area of the ore mountains (Erzgebirge) with baseline concentration of As from 20-40 mg/kg
- Interpolated mean values: 320 mg/kg for topsoil, 80-320 mg/kg for alluvial plains
- Local hotspots with up to 5000 mg/kg



Source: BGR (Bundesanstalt für Geowissenschaften und Rohstoffe)
https://www.bgr.bund.de/DE/Themen/Boden/Bilder/Bod_HGW_KarteAs_g.html

Saxony and Freiberg region- As sources

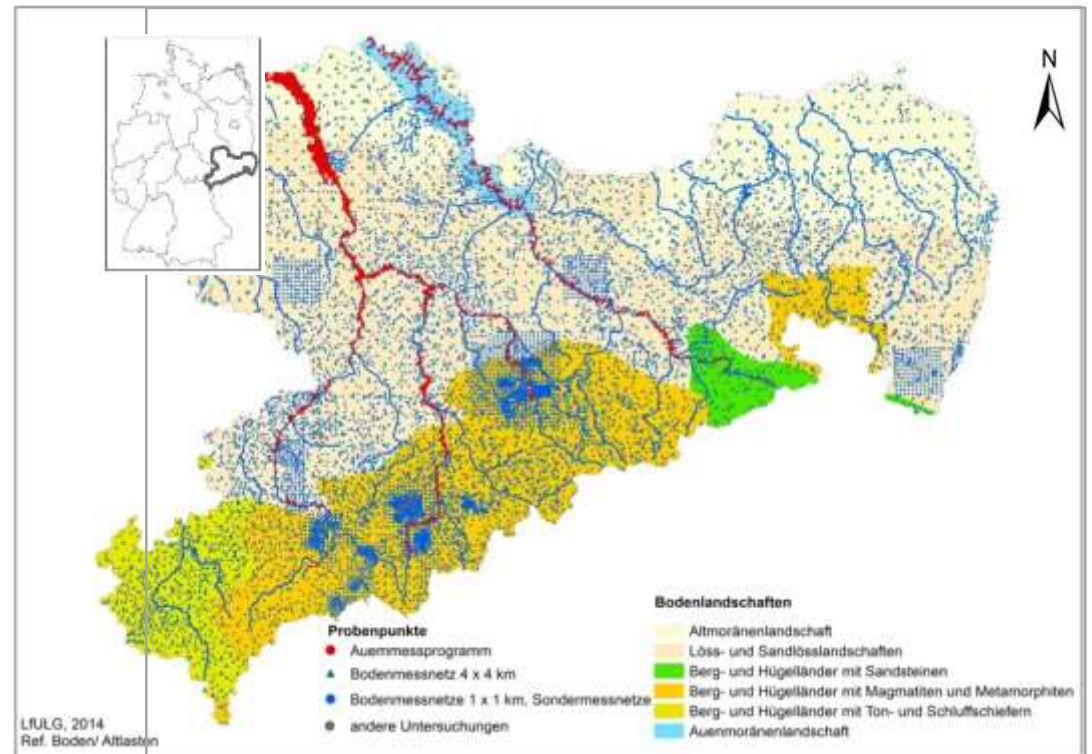
- High background concentrations of metals and metalloids due to geochemical situation: silver and lead in galena, zinc and cadmium in sphalerite, arsenic in arsenopyrite
- Mining and ore processing in the ore mountains (Erzgebirge) for more than 800 years led to mining heaps, tailings, dust deposition, discharged mining waters
- remarkable release of As (and other pollutants) which affect agricultural sites and alluvial plains
- Many sampling campaigns were carried out by the Saxon state office of environment, agriculture and geology (short: LfULG) for the evaluation of pollution



Saxony and Freiberg region

Scientific Soil Database (FIS Boden) 2017:

- > 61,000 Soil Profile Data
- > 220,000 Soil layer / horizon data
- > 22,000 Soil Profiles analyzed
- > 65,000 Soil samples analyzed
- > 2,057,000 Analytical data
- > 14,000 Data set of As in top soil



Source: LFULG Kernerat Boden, Atlanten 2014

maps are available online:

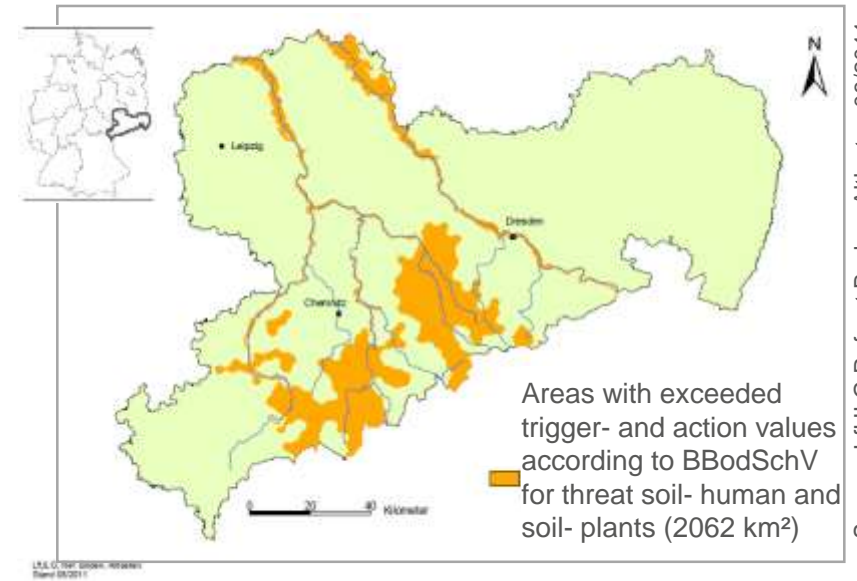
<https://www.umwelt.sachsen.de/umwelt/boden/11619.htm>

Saxony and Freiberg region

Trace element contaminated sites (TECS)

- identified areas with TE concentrations above threshold values given by the German Ordinance of Soil Protection (BBodSchV): 2062 km²
- 288 km² polluted with As > 50 mg/kg

→ potential risk on those sites!



Saxony and Freiberg region- Investigations

- Data on As in Soil
 - Pseudo-total (aqua regia)
 - availability by oral human ingestion (DIN 19738)
 - availability by plants - NH_4NO_3 extract (DIN 19730)
 - water solubility (water extract 1:10 – DIN 38414 part 4)
- Pot tests and field tests on transfer into plants
- Pot tests and field tests on cultivar selection and amendments
- Ecotoxicological tests with invertebrates
- Investigation on As transfer into sheep
- Permanent soil monitoring site close to Freiberg (As conc. > 800 mg/kg)
- examination of remediation measures (liming, iron based amendments, phytoremediation)



Source: H. Forberg, LfULG

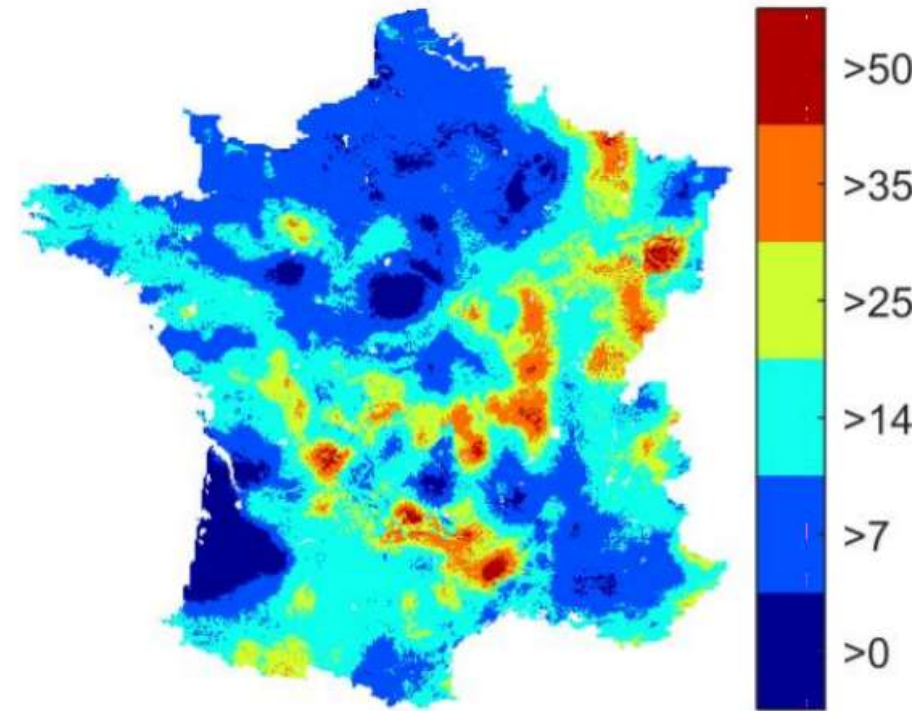
Saxony and Freiberg region- Investigations

- Evaluation on transfer into plants, food, fodder and derivation of guidelines for farmers,
 - Evaluation on human exposure ,
- development of the soil planning area Freiberg for an efficient management of polluted sites .



Arsenic in France

- The mean and median observed concentrations of topsoil arsenic in France of approximately 12 and 18 mg/kg respectively
- Anomalies are primarily attributed to geology and mineralisation although mining activities within the Massif Central and the use of pesticides to the south west of this region are also cited.



Categorical predicted map of expected arsenic concentrations (mg/kg)

Source: Ben P. Marchant, Nicolas Saby, Dominique Arrouays. A survey of topsoil arsenic and mercury concentrations across France. *Chemosphere*, Elsevier, 2017, 181, pp.635-644

Arsenic contamination in relation to industrial scale destruction of old chemical ammunition of the Great War

Ammunition has been used in an unprecedented scale during the First World War (1914 – 1918).

Chemical warfare began in April 1915 in Yper (Belgium).

During the interwar period, authorities challenged with disposal of large amounts of old ammunition: ~ 2,5 millions tons.

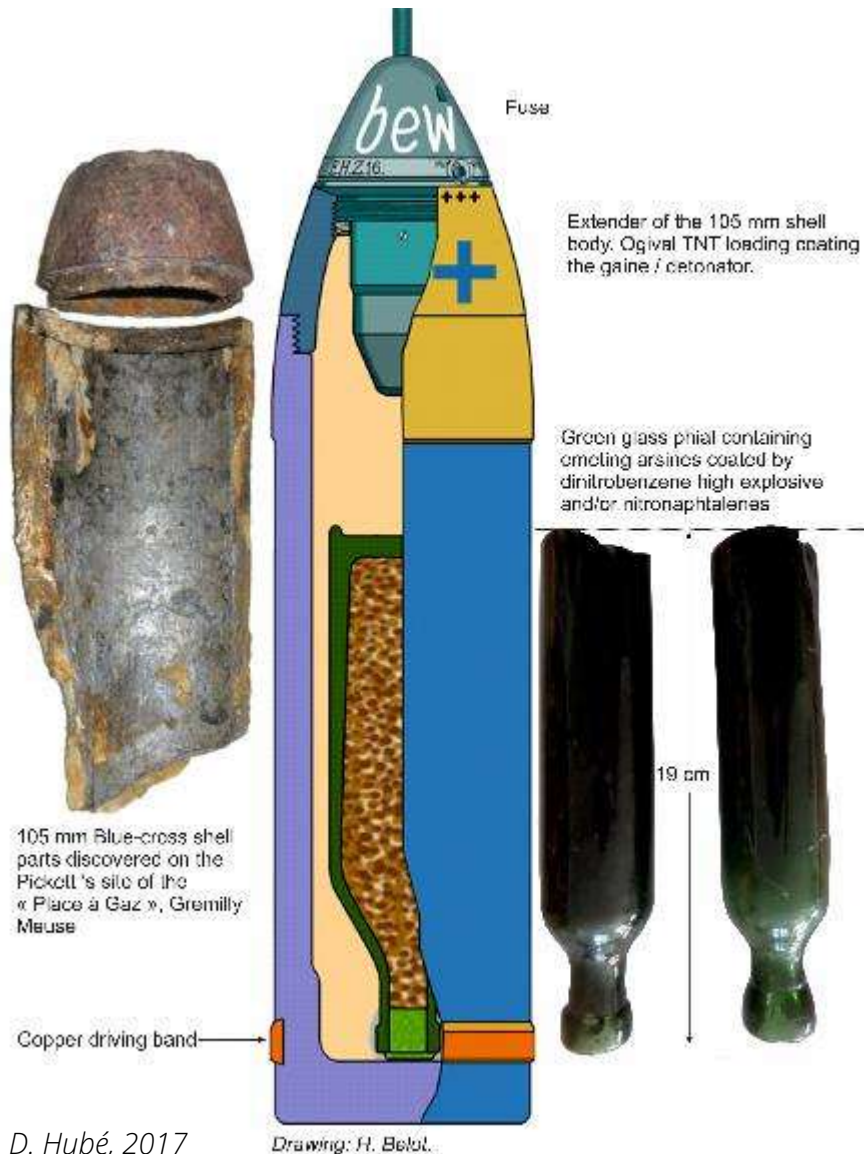
New processes had been developed to dispose all type of projectiles to recover valuable material (lead, copper, scrap, ammonium nitrate....).

Open-burning, washing out

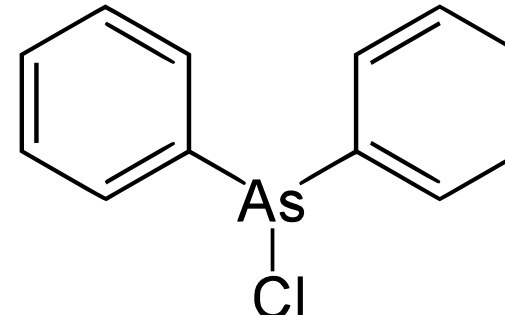
“There is no proper methods to eliminate Ammunition” F.N. Pickett, 1921



Arsenic in warfare during WWI



German 77 mm, 105 mm, 155 mm and 210 mm “**Blue Cross**” shell loaded with solid diphenylchlorarsine (Clark 1), diphenylcyanoarsine (Clark 2) appeared on the battlefield in September 1917.



Emetic and irritant properties made masks wearing unbearable and forced soldiers to pull them up thus making them vulnerable to more aggressive gas.

Low solubility (3 to 2 000 mg/L).

No arsine in chemical projectiles of the allies.

- AsCl₃ in french and german rounds used as smoke producing agent

The AgriAs site

Former German backlines,
20 km northeast of Verdun,
France. Former German
ammunition dump



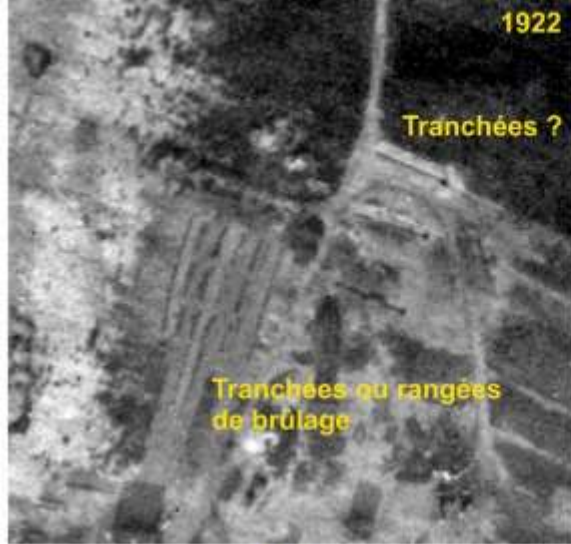
The AgriAs site in the past: Clere & Schwander factory

- A former chemical ammunition breaking-down facility of the interwar period converted into agricultural land near Verdun, France,
- One of the most important historical area of chemical ammunition destruction of WW I, containing arsenical chemical warfare agents, located in a sensitive zone for agriculture and groundwater uses,
- The site will be used to assess the impacts of agricultural practices on As speciation, bioavailability and mobility through groundwater.

An historical view of the ammunition destruction facility near Verdun, near 1921. Preparation of an open-burning operation of shells (source Private archives, D. Hube, BRGM)



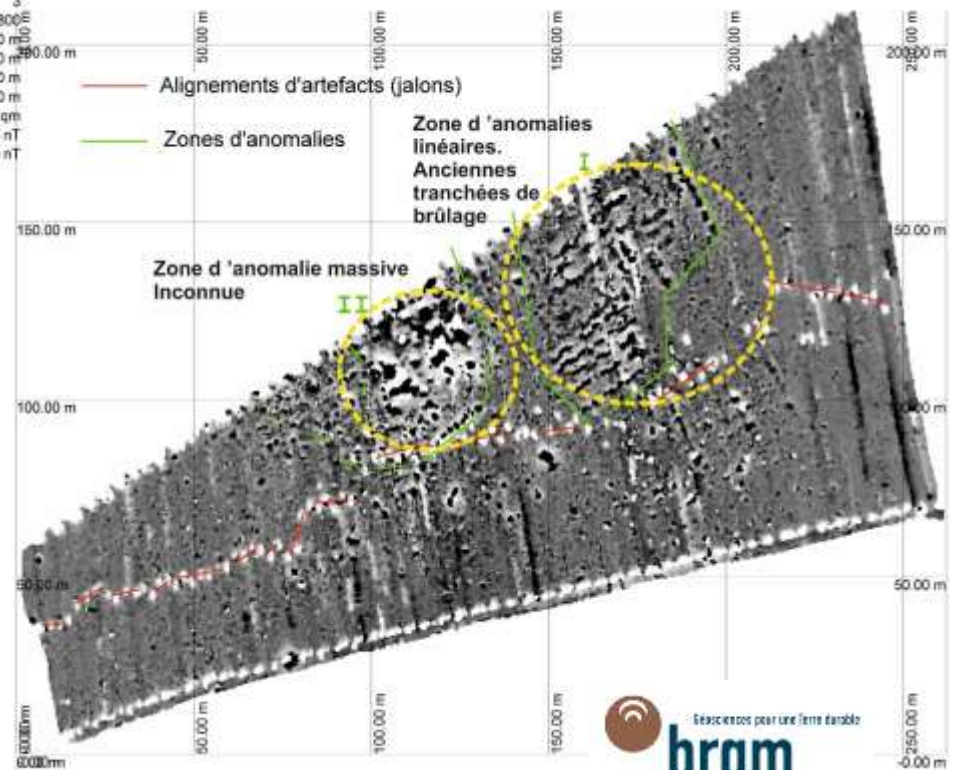
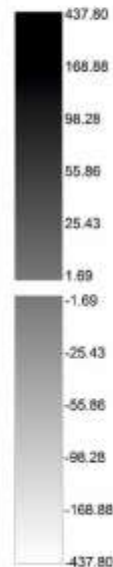
Mayfair, 1921; preparation of an open-buring operation in trenches. Burning ground Poelkapellen (Belgium).



Areal photograph of 1922 and geomagnetic measurement showing systems of burning trenches and industrial facilities near the former open-detonation destruction ground (BRGM, 2016).



Nom: Carte couleur...
 ID: 3
 Echelle: 1:800
 Longueur du terrain: 260.00 m
 Longueur Couloir: 206.00 m
 Largeur Couloir: 0.50 m
 Intervalle entre points: 0.50 m
 Surface: 25535.63 qm
 Minimum: -2289.35 nT
 Maximum: 2293.69 nT



The AgriAs site today



The site as a barley field

Severe pollution was identified with inhibition of the growth of the crops → resulting in crops destruction and temporary impoundment of the agricultural uses.

> 21



Clark vials some of them showing Clark and Clark oxidation by-products.

Blackened bare soils



Meuse : 14-18 tue la récolte 2015

EXCLUSIF

POLÉMIQUE Les productions de sept exploitations du canton de Spincourt sont détruites depuis le mois de juillet à cause d'une pollution du sol qui résulterait de la destruction d'obus chimiques après la première guerre mondiale. En Région

Meuse : la terre empoisonnée ?

La récolte 2015 de sept exploitations agricoles du Nord-meusien a dû être détruite à cause d'une potentielle pollution du sol qui surviendrait à la fin de la guerre de 14-18.

Dans le canton de Spincourt, tout le monde le sait, mais personne n'en parle. Et l'omerté a sensiblement gagné toute la Meuse puisqu'il a été très souvent conseillé de ne pas ébruiter l'affaire. Sept exploitations seraient concernées à Vandœuvre, Muzeray et Lison. Les agriculteurs ont reçu la nouvelle comme un coup de massue au début du mois de juillet, en pleine saison. La direction départementale de la culture sociale et de la protection des populations (DDCSPP) s'est présentée sur leurs exploitations pour leur expliquer que leurs productions ne pourraient plus être commercialisées, jusqu'à nouvel ordre. Par mesure de précaution, le temps que des analyses soient effectuées. En cause ? Une pollution qui remonterait à près d'un siècle.

Dans un arrêté pris le 4 juillet 2015,

la préfecture de la Meuse rapporte que « des activités polluantes de déconstruction et destruction de munitions chimiques et explosives » ont été réalisées dans cette zone située à une trentaine de kilomètres au nord-est de Verdun, à deux pas de la Meuse et Moselle. Des études et prélèvements menés par le Bureau de recherches géologiques et minières (BRGM) démontrent que plusieurs parcelles situées sur le territoire des communes de Muzeray, Vandœuvre et Lison affichent la « présence de métaux et de composés organiques toxiques dans le sol ». La DDCSPP et la préfecture de la Meuse ont donc décidé de procéder à des « restrictions sanitaires d'utilisation et de mise sur le marché de productions agricoles végétales issues des parcelles contaminées par des résidus chimiques sur le site Clerc & Schwander », le note dans un permis de construire concerné par la contamination potentielle.

« L'État se réveille cent ans après »

Les céréales cultivées cette année dans cette zone ont été détruites, le lait produit par les vaches potentiellement alimentées par ces céréales, collecté tous les deux jours est jeté depuis le mois de juillet, et celles destinées à l'alimentation restent dans



La Bureau de recherches géologiques et minières (BRGM) survole le mardi un champ situé entre Muzeray et Vandœuvre. Photo: FLORENCE LALLEMAND

l'attable. Depuis que ces mesures ont été prises, l'équivalent de 150.000 litres de lait aurait déjà été jeté. « Tout ce qu'on produit part à la poubelle », révèle sous couvert d'anonymat l'un des agriculteurs concernés. « L'État se réveille cent ans après », déplore-t-il, désemparé. « Il faut arrêter les nerfs volés pour supporter ça, surtout en pleine crise agricole ». Les agriculteurs cultivent ces terres depuis plusieurs générations, et s'étonnent de

la réaction tardive des autorités et de ce qu'il y a.

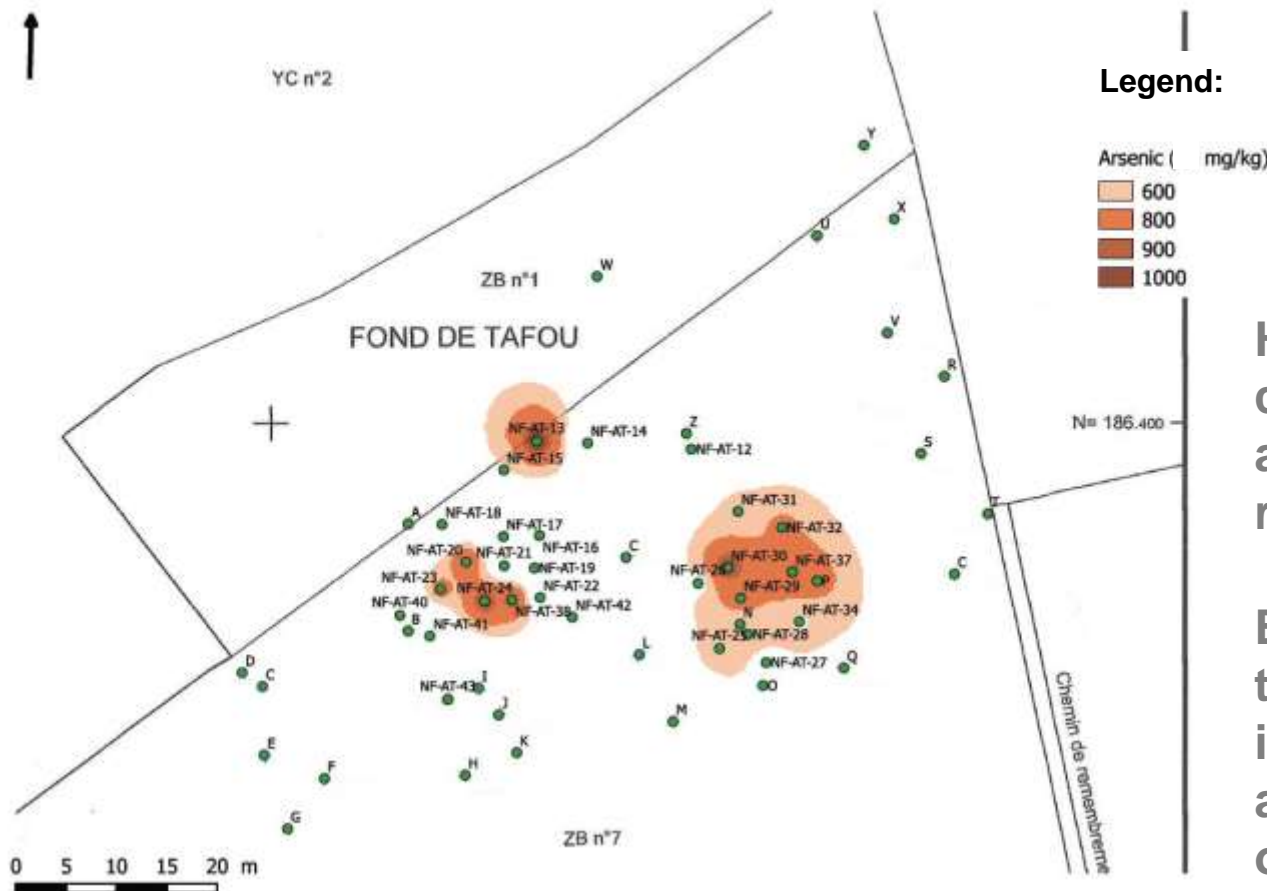
Ce qui étonne également, c'est que cette affaire a été mise sous embargo total depuis plusieurs mois. Il suffit d'évoquer le sujet pour voir ses interlocuteurs se débarrasser. Le préfet de la Meuse, contacté à deux reprises via son cabinet n'a pas donné suite à nos sollicitations.

Le BONCHERON



How to communicate about a hundred year old forgotten contamination ?

The AgriAs site today : As top-soil contamination



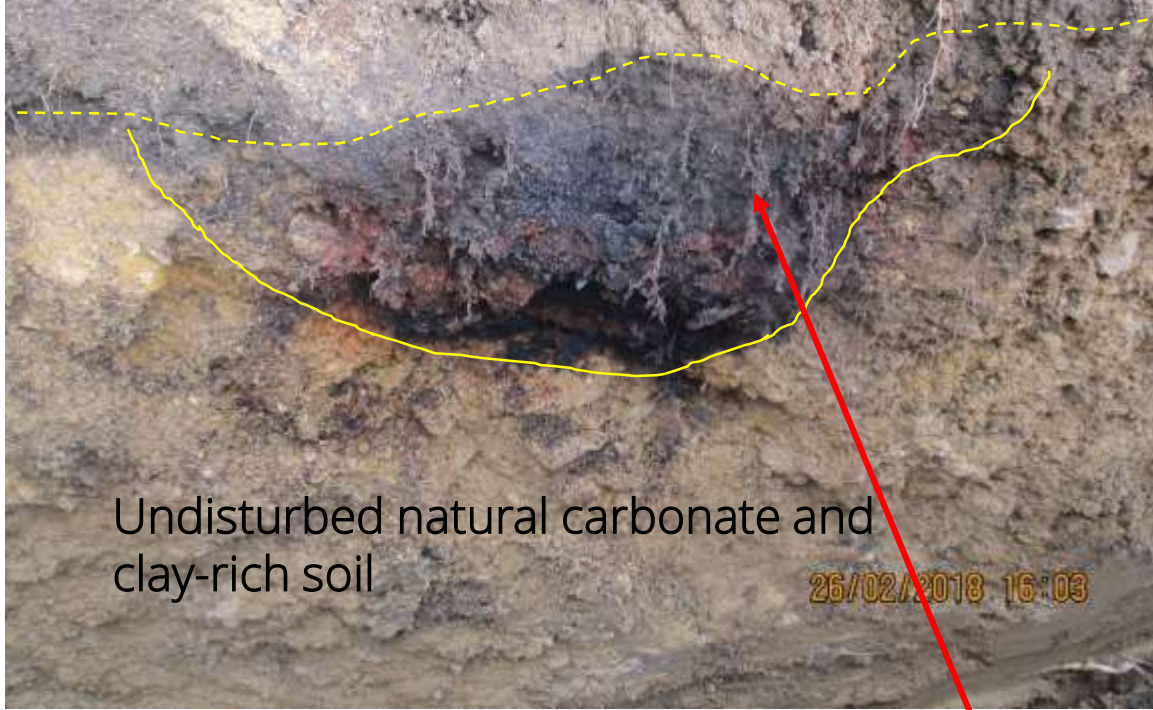
Hot spots of As concentration + availability of reference zones



Excellent model site to study the influence of agricultural practices on arsenic behaviour and transfer

source D. Hube, BRGM

(0,4 m layer of through ploughing
homogenized top-soils



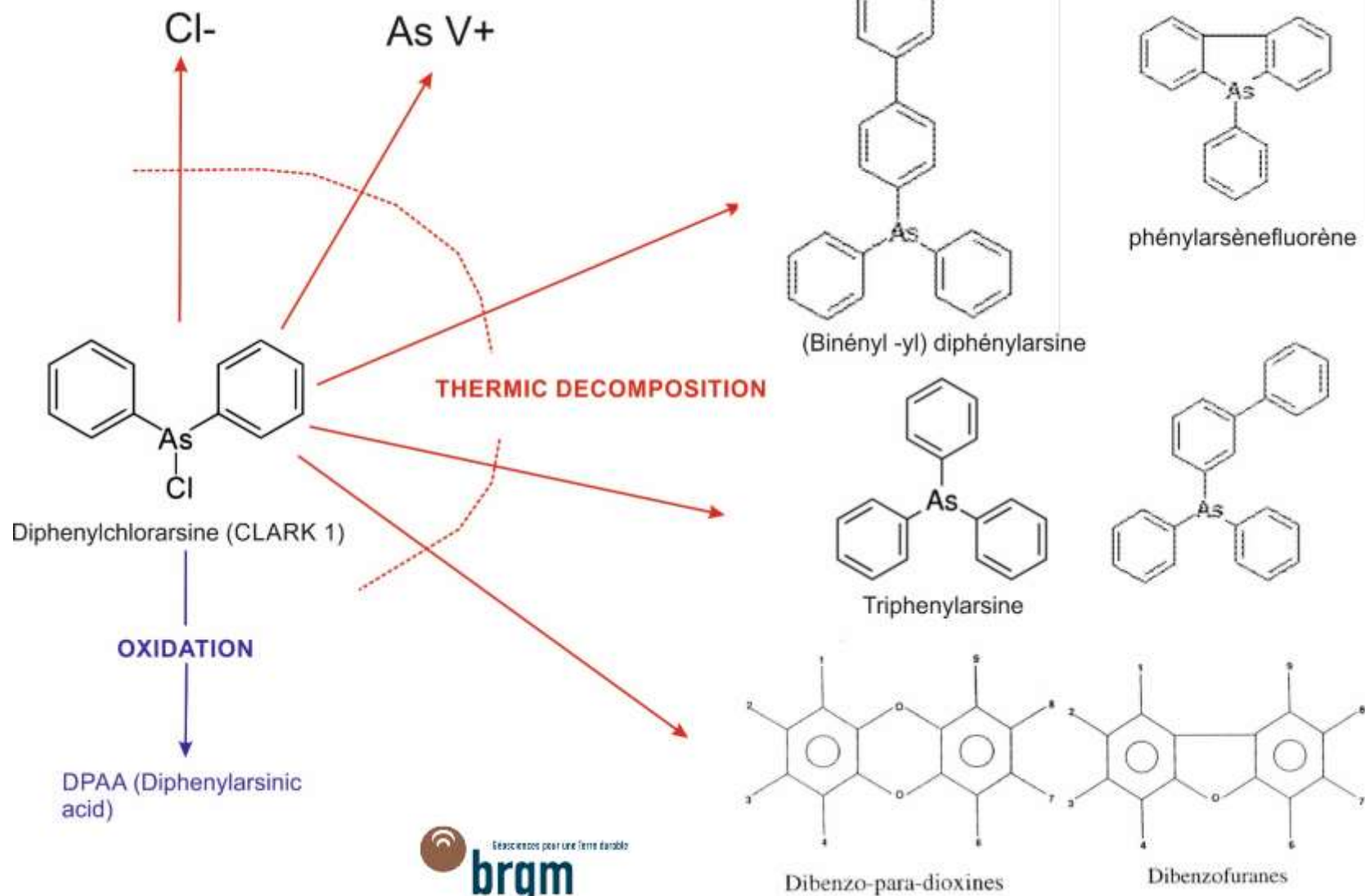
Undisturbed natural carbonate and
clay-rich soil



**Cross section of a burning trench showing
As rich-burning residus (100 to 12 000
mg/kg) associated with Zn, Sn, dioxins,
nitroaromatic compounds and high toxic
DPAA (200 – 800 µg/kg).**



The AgriAs site: fate of phenylchlorarsines





Similar situations in Belgium (potatoes) and Germany (Wheat, Colza). Anonymous sites.



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Geosciences pour une terre durable

Arsenic near Verdun site: first step of the risk assessment. Learning to measure pollutant in the crops.

Science of the Total Environment 589-600 (2017) 314-323



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Analyzed samples:

- maize silage, barley and wheat
- foodstuffs of animal origin (meat and milk)

Human health risks related to the consumption of foodstuffs of plant and animal origin produced on a site polluted by chemical munitions of the First World War



Sébastien Gorecki ^a, Fabrice Nesslany ^b, Daniel Hubé ^c, Jean-Ulrich Mullot ^d, Paule Vasseur ^e, Eric Marchioni ^f, Valérie Camel ^g, Laurent Noël ^h, Bruno Le Bizec ⁱ, Thierry Guérin ^a, Cyril Feidt ^j, Xavier Archer ^k, Aurélie Mahe ^a, Gilles Rivière ^{a,*}

Exposure to different contaminants (including As) through the consumption of foodstuffs produced locally on the considered site was unlikely to be a health concern. However, as for inorganic arsenic, given the presence of highly contaminated zones, it was suggested that cereals should not be grown on certain plots



Arsenic near Verdun site: risk based remediation

Risk assessment goes on, including groundwater sampling

The last results show that some parts of the site could be remediated by excavating the top soils contaminations but the thin layer of partially contaminated clay-rich soil on the rock (lime) may limit the possibilities of the re-used of the ground for a productive agricultural use.

Furthermore, the crops rotation has been broken since 2015 on impounded grounds yielding to a lost of the agricultural productivity.

The best long term future for the site will result in a balance between risk based assessment, geoscientific experts evaluation, socio-politic acceptance and remediation cost for community.

Comparison

Criteria	Tampere (FI)	Freiberg (GER)	Verdun (FRA)
As source	Geogenic (bedrock)	Geogenic (bedrock) Anthropogenic (mining)	Anthropogenic (Destruction of ammunition)
Extent	7400 km ² (5 - 30 mg/kg)	288 km ² (>50 mg/kg)	Hot spots (100 – 10000 m ²)
As: Baseline concentration	30 mg/kg	20 – 40 mg/kg	18 mg/kg
High As concentration in soil	Top 1050 mg/kg, Subsoil 9280 mg/kg	5000 mg/kg	12000 mg/kg
Agricultural land use	Yes, not affected by arsenic	Yes, still ongoing	No, stopped in 2015



Conclusions

- Arsenic can be either geogenic or anthropogenic element and human activities can spread also geogenic arsenic to larger extent.
- Baseline concentrations were in the same level in all studied regions
- Maximum concentrations were much higher than the baselines
- In addition to the total arsenic concentration in soil, bioavailability and potential leaching to water bodies should be studied

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