Perchlorates in French groundwater: Former uses and emerging concerns

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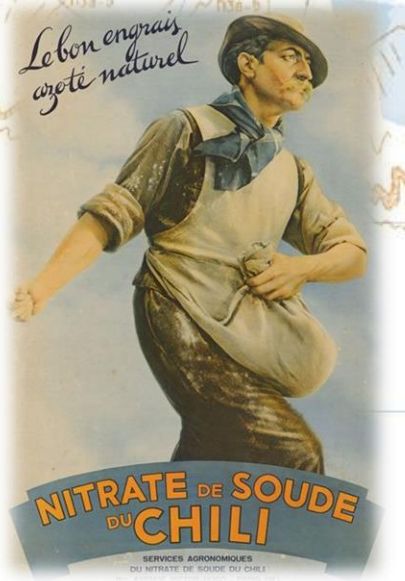

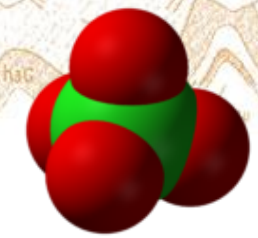

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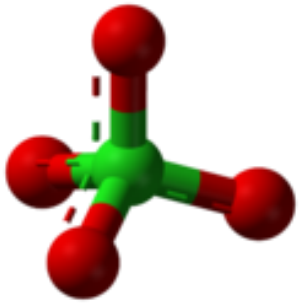
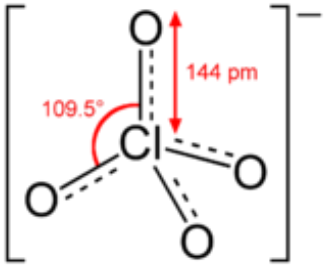
Definition - What are perchlorates?

> Classification (ClO_4^-)

- Organic compound
- Oxyanion
- High oxidation level (+7)
- Weak reactivity





> Toxicity

- Physiological troubles in animals and humans
- Inhibitor of iodine fixation => growth, metabolism and reproduction (infants and children)
- Hemophilic anemia due to reduction of ClO_4^- ions in ClO_3^- and Cl^-
- Decrease in immune cells (T3 et T4)

> Threshold values in raw water = 15 µg/l and 4 µg/L

- Advice ANSES 2011-SA-0024 et 2012-SA-0119 (infants and pregnant)

> Transfer properties in groundwater

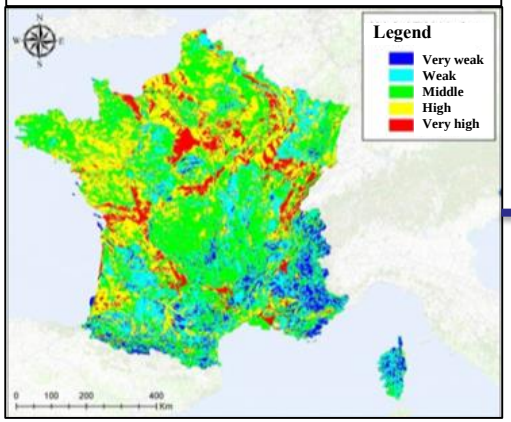
- Extremely water-soluble and stable
- Not adsorbed on subsurface minerals
- Biodegradation of perchlorate in groundwater not occur in natural conditions

$\Rightarrow$ **Persistent in natural conditions**

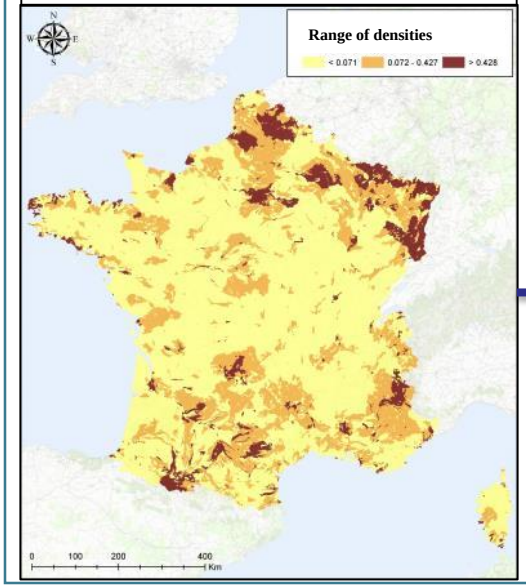
GW specific vulnerability to perchlorate

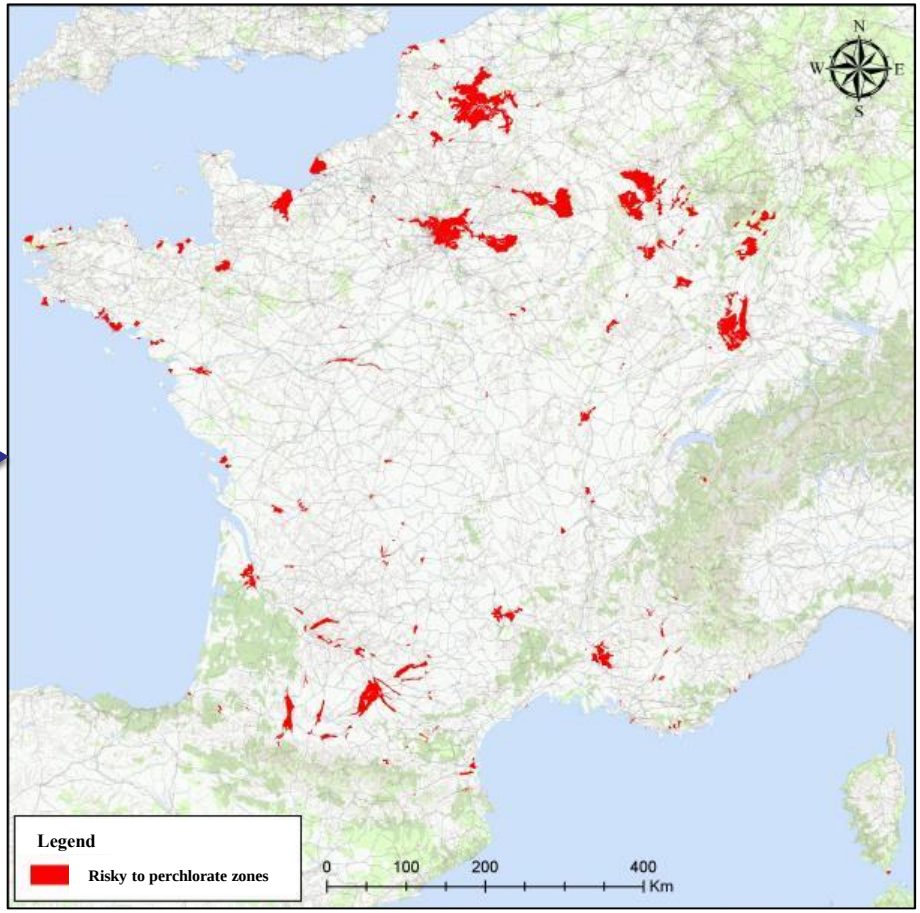
- Specific vulnerability = Intrinsic vulnerability X Density of sources of ClO_4

Aquifer intrinsic vulnerability



Density of potential sources of ClO_4^-





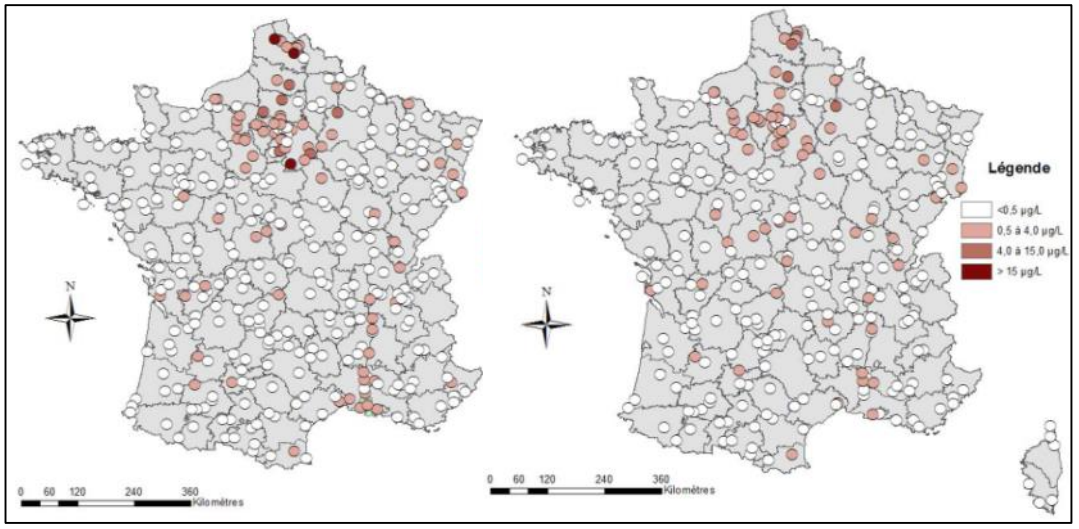
Identification of aquifers vulnerable to industrial and military perchlorates

(Lopez et al., 2014 – BRGM/RP-63270-FR)

Discovery of the ClO_4 GW pollution in France

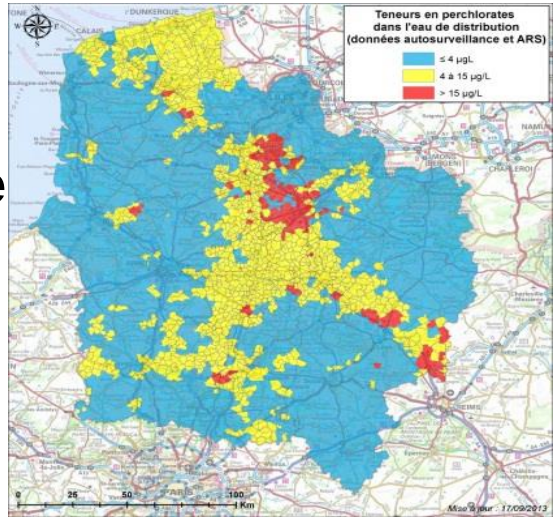
2011-2012

- **National campaigns in GW for human consumption**
  - 302 GW sampling sites



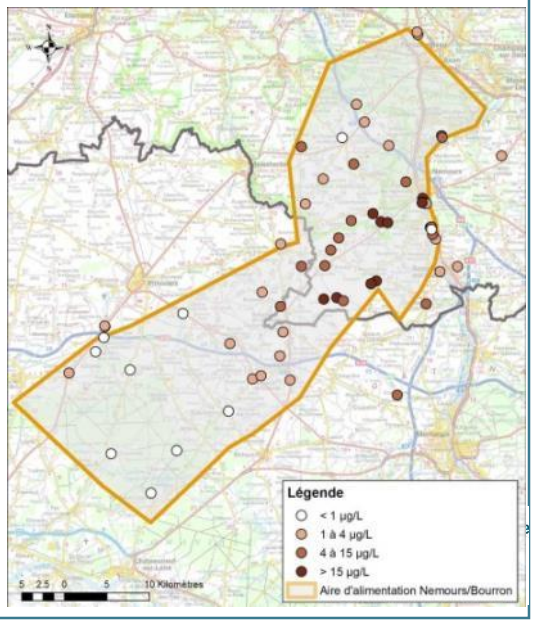
2012

- **Regional data from health Agencies of the Northern France**
  - Supply water of 3483 cities



2013

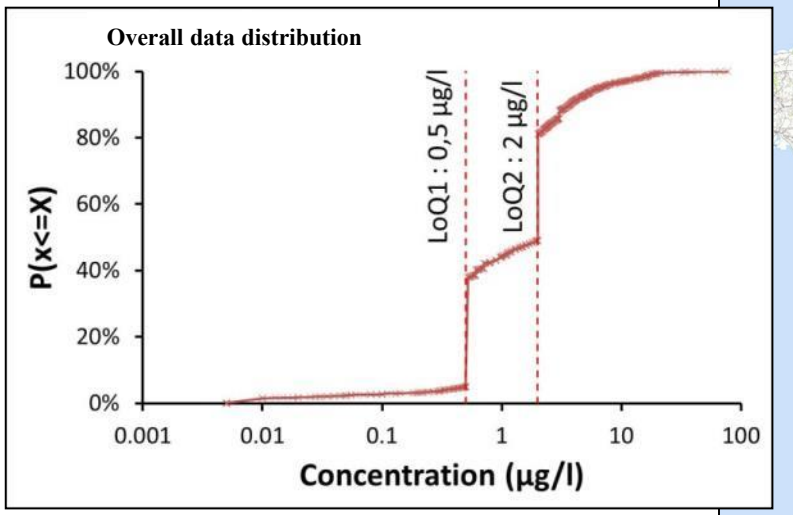
- **Local data (BRGM/Supplier project)**
  - Agricultural Catchment scale; 62 sampling sites in GW

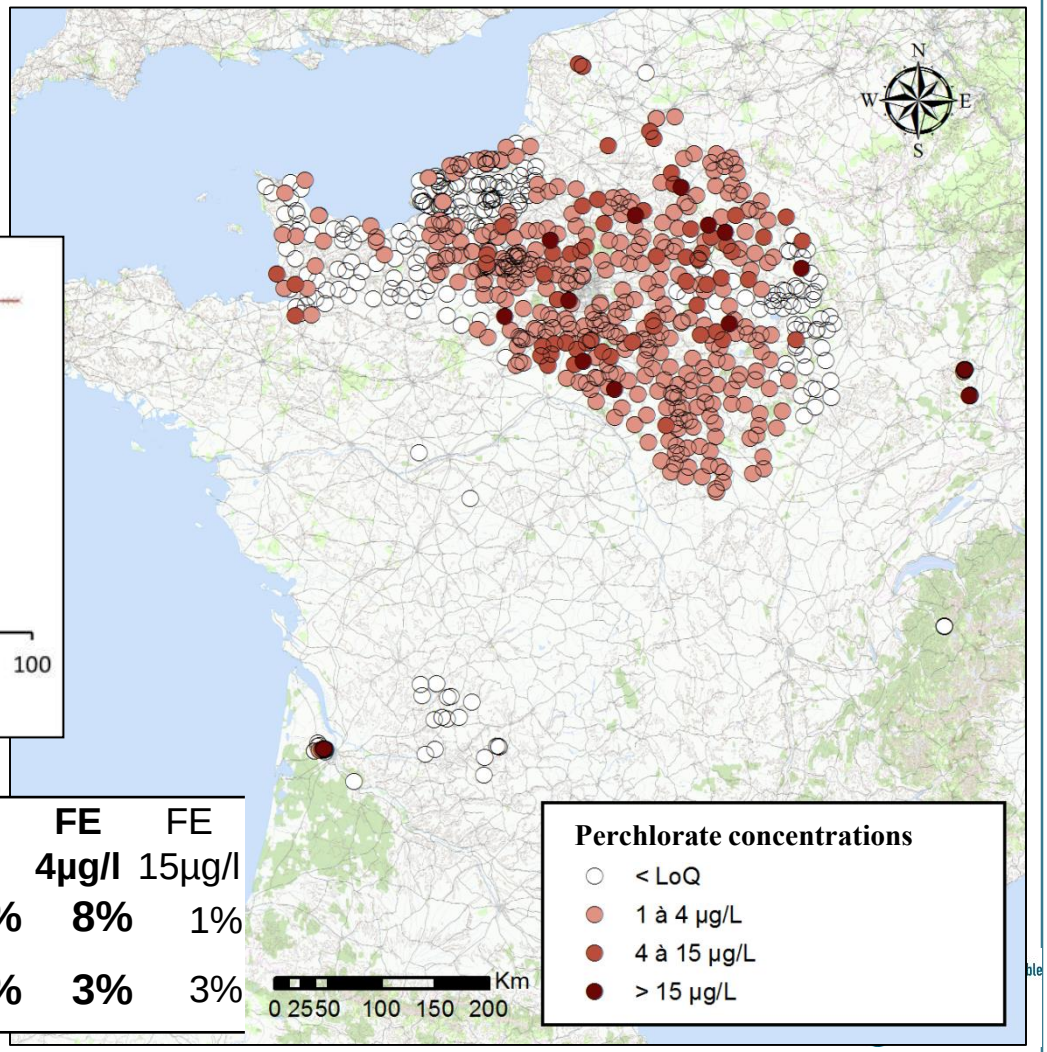


Today GW ClO_4 contamination knowledge

> **Current data in the GW national database ADES** (> 2300 analyses)

- New regulatory survey (SN Basin, 527 sites)
- DRIRE RHA (3 sites)
- SGR GUY (13 sites)
- Drinking water (230 sites)





	Date min	Date max	N anal.	QF	FE 4µg/l	FE 15µg/l
SN Basin	apr.-13	dec.-14	1849	**24%**	**8%**	1%
Drinking water	agu.-11	nov.-14	448	**61%**	**3%**	3%

Case study: Source of perchlorates in agricultural land-use aquifer (Beauce region)

> Context

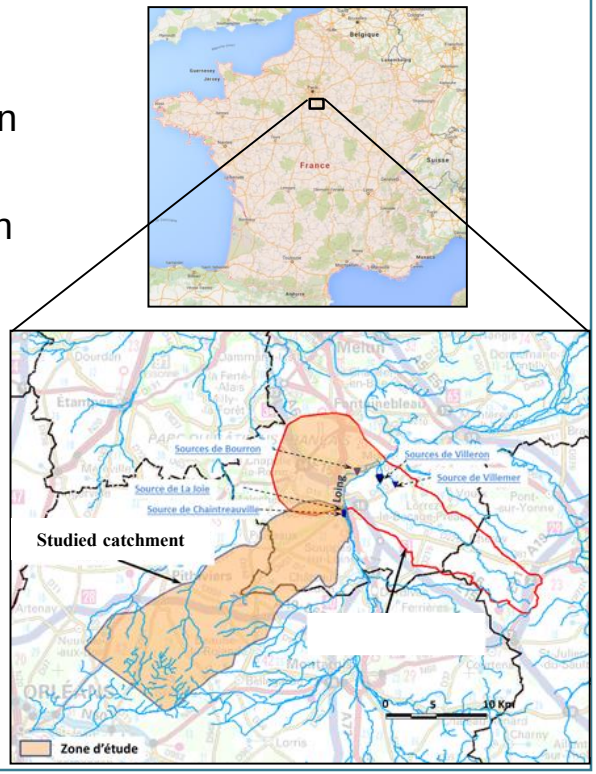
- In 2012, discovery of ClO_4 concentration > 7 µg/l in GW used to supply 2 sectors of Paris
- In France, first studies have shown that sources of perchlorate could be of different types: former history of intensive cultivation, former heavily shelled battlefields of First World War, ammunition breaking down activities of interwar time, some current industrial activities
- Consortium : BRGM, Seine-Normandy Basin Agency, Health Agency, *Eau de Paris* (supplier)

> Goals of the study

- To identify and to locate the origin of the perchlorate pollution
- To assess the spatio-temporal evolution of the pollution
- To estimate extend of plumes, stocks and speed of migration

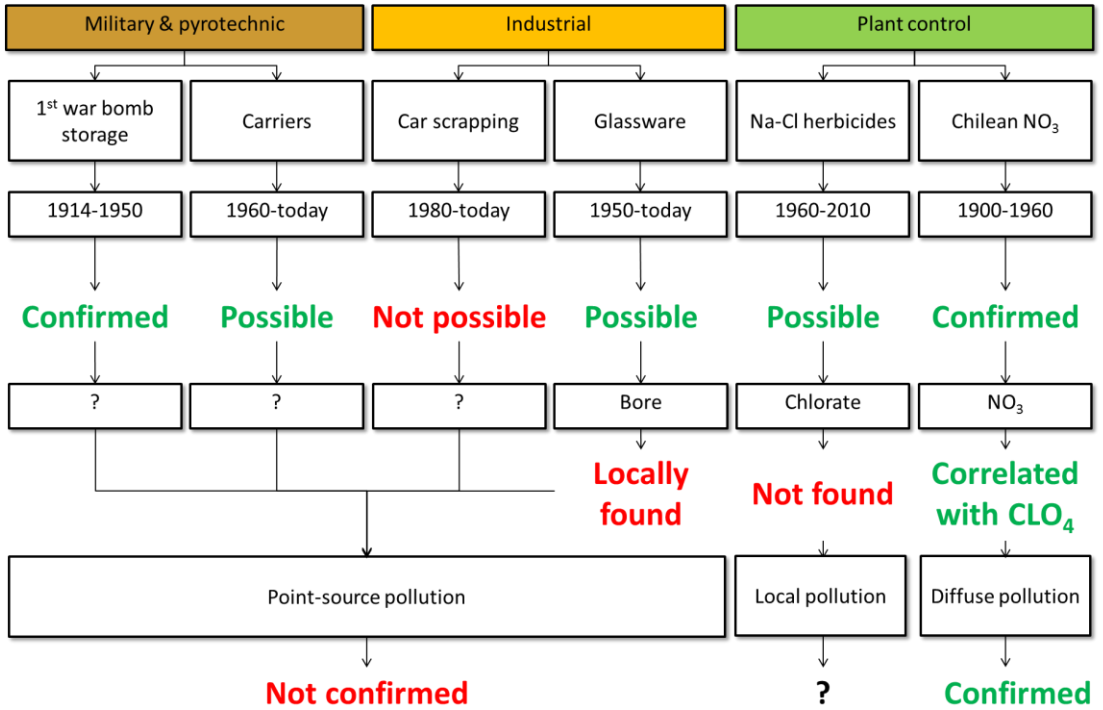
> Material and method

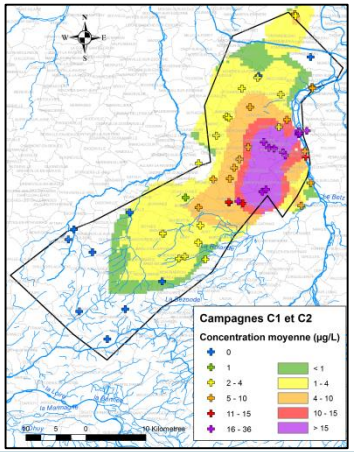
- Literature revue of potential sources
- Geological and hydrogeological study
- 2 sampling campaigns (63 sites for chemical analyses)
- Age-dating of groundwater (CFC/SF6 on 14 sites)
- Chemical well logging
- Statistical multicriteria analyses

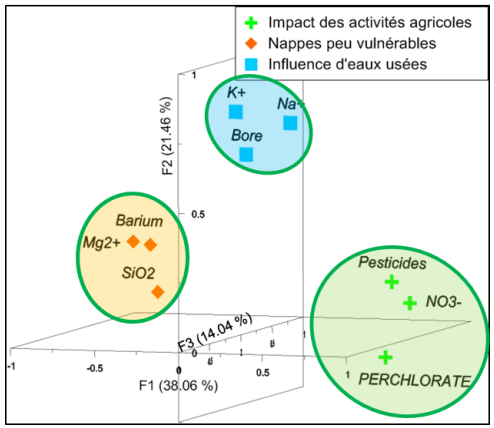


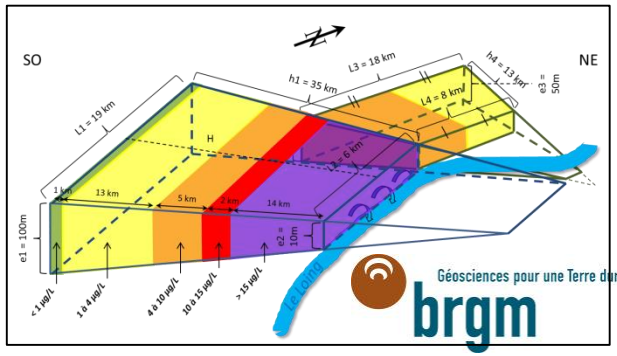
Hypothesis testing strategy

- ***Potential sources***
  - On the catchment area
- ***Emission period***
  - CFC/SF6 age dating
- ***Tracers of ClO_4 origin***
  - Chemical analysis
- ***Expected pollution***
  - **Plume mapping**

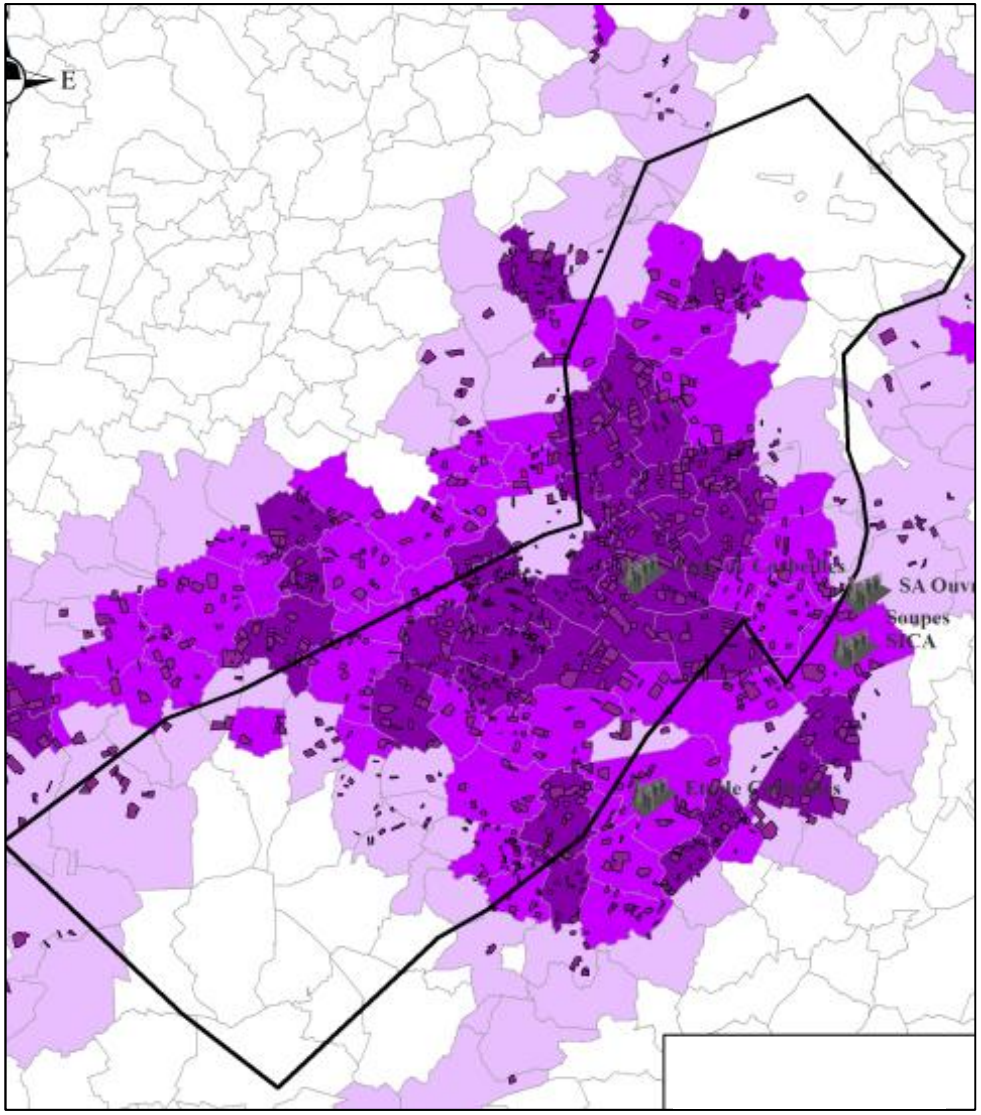






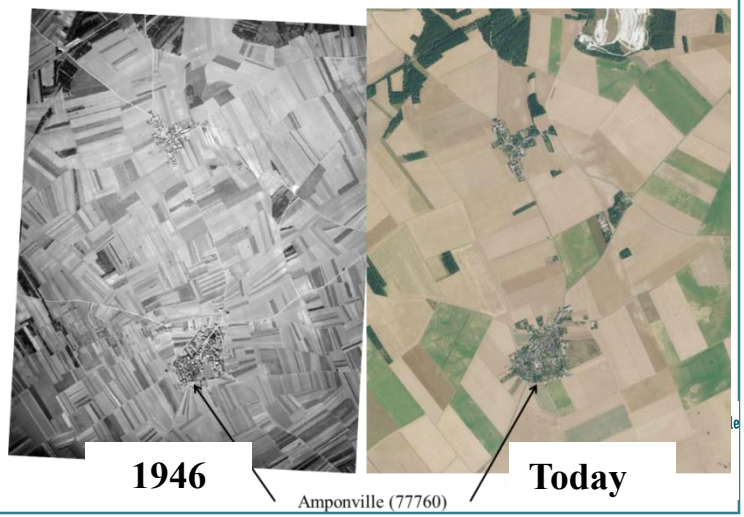


Chilean nitrate hypothesis



Overlap of the ClO_4 plume and 2013 beet root density mapping

- The most polluted zones correspond to the most densely cultivated zones with an offset of about 5 km downstream
- Chilean nitrate intensively used from 1850 to 1940 (800kg/ha)
- Contains 0.05 to 0.2% of ClO_4 = 30 to 60 tons emitted
- Consistent with the calculated 7.5 tons stock into the aquifer



Other issues

2011→ former heavily shelled battlefields of First World War

Probable origin but non-unique and non-demonstrated

Perchlorate in northern France drinking water

Forefronts of the First World War

Ammunitions breakdown interwar activities => point source ClO_4 pollution

Perspectives

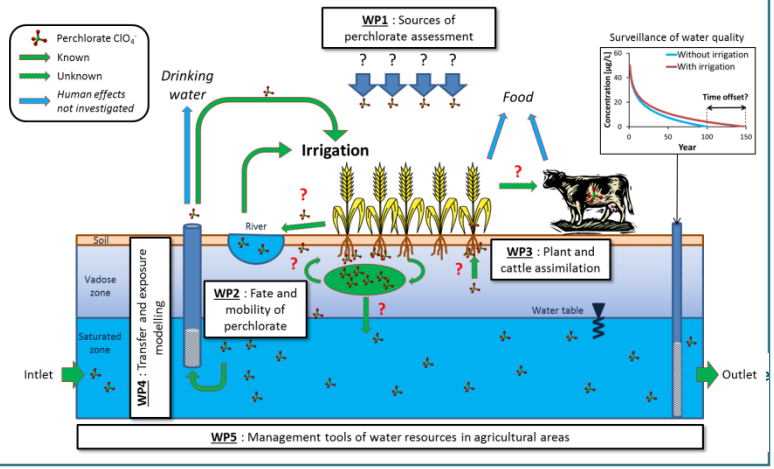
- Need for tracers of perchlorate sources:
  - Perchlorate, chlorate and nitrate ion isotopes,
  - Explosives compounds,
  - Boron, pesticides and metabolites associated with sodium chlorate …
- Need to know and to locate historical uses of Chilean nitrate
- Military sources of perchlorate not yet investigated in France:
  - Former heavily shelled battlefields of First World War
  - Ammunition breaking down activities of interwar time

- *Perchlorate: one explosive among many, more toxics.*

=> *Could it be "the tree that hides the forest"?*

- *What about the fate of perchlorate in irrigated agricultural context ?*

⇒ ***PRESAGE*** *Project Proposal at WaterWorks2015 Cofunded JPI Call*



Many thanks for your attention

"They would ask for natural Chilean nitrate"

"If beet root could talk"

1920 Poster

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