PERCHLORATE IN GROUNDWATER: THE POTENTIAL SOURCE FROM PAST FARMING PRACTICES USING CHILEAN NITRATES IN FRANCE

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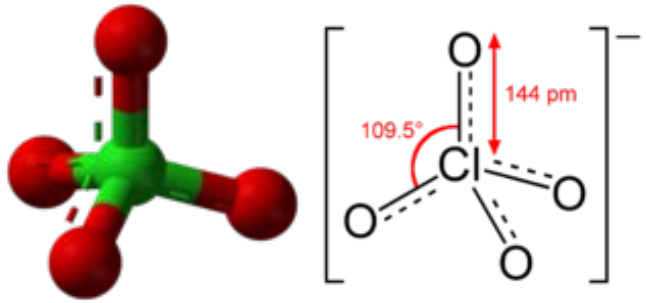
DEFINITION

What is perchlorate?

Classification (ClO_4^-)

- Inorganic chemical
- Oxyanion
- High oxidation level (+7)
- Weak reactivity



Toxicity

- Inhibits the absorption of iodine by thyroid glands

→ growth, metabolism and reproduction

→ leading to developmental and learning disabilities in children

Environmental fate

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

→ Biodegradation of perchlorate not occur in natural conditions in environments where anoxic conditions can develop

DEFINITION

Concern

Threshold value in drinking water

- EPA 2009 = adult 15 µg/L infants and pregnant = 4 µg/L
- **ANSES 2018 (French Health Agency) = 5 µg/L**

Treatment methods

- Reverse Osmosis
- Anion Exchange (Regenerable and non-regenerable)
- Distillation

→ **Perchlorate is not removed by most of the WWTP**

Concern in France

- Accidentally discovered in 2011 in a south-west French GW resource used as drinking water
- Monitored by the national health agency and some regional health agencies in supply waters in 2012-2013 and founded at concentrations above EPA threshold values
- Recommended to be included in the regular surveillance of French groundwater (French decree 15 August 2015 ; Lopez et al., 2015)

→ **Several GW resources used for drinking water are impacted by the presence of perchlorate**

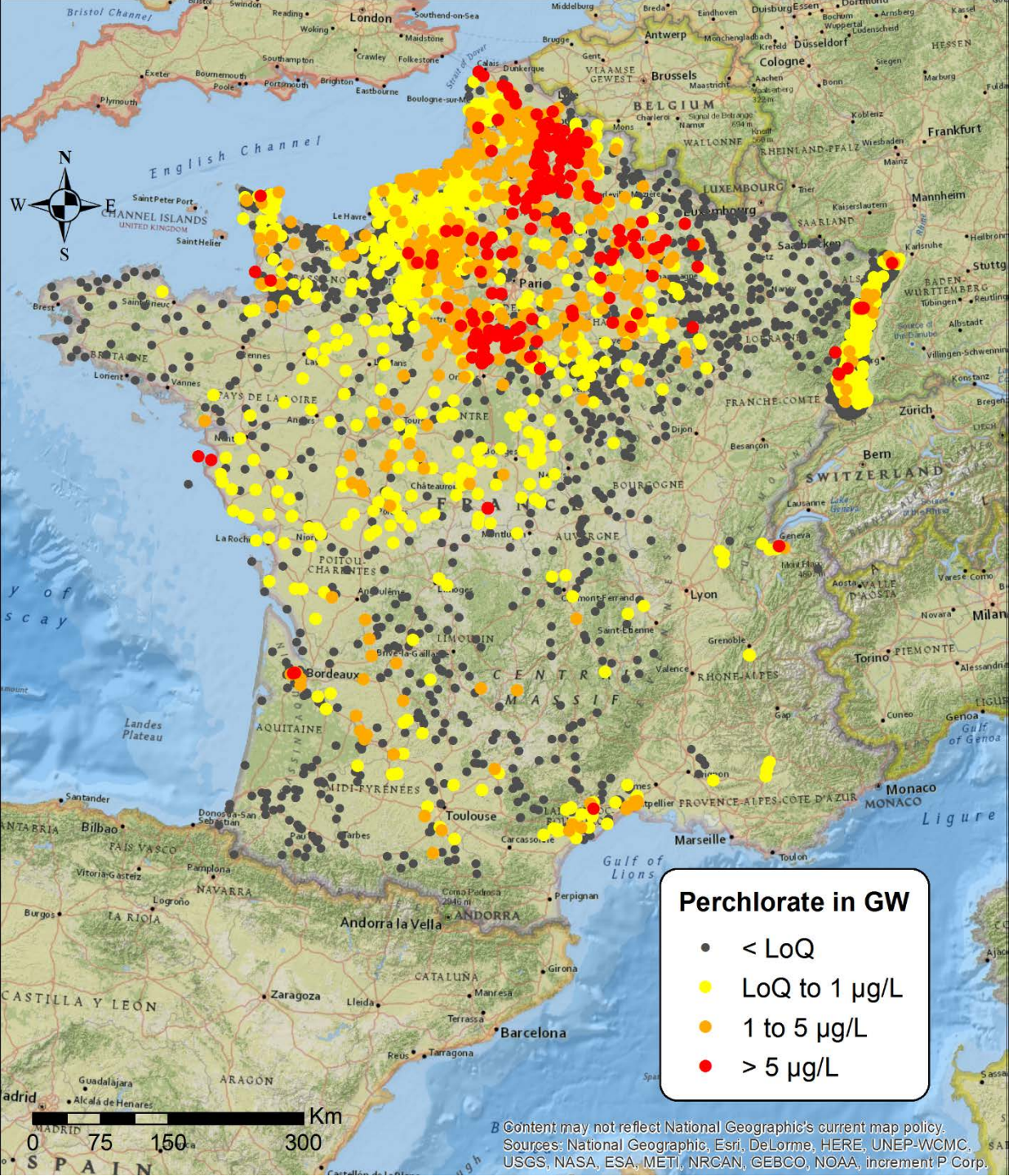
ClO_4^- occurrence in French GW

- Results from 2013 to June 2019
- 3323 sampling sites in GW
- 8825 analysis
- LoQ = from 0.1 to 1µg/L

1 site in 5
show [ClO_4] > 1µg/L

Results

	Quantification Frequency	Frequency of exceedance 5µg/L
Sites	**42%**	**5.4%**
Samples	**35.5%**	**6.2%**



- Perchlorates are frequently quantified in French Groundwater
- Centre, Northern and Eastern basins are the most impacted
- Concentrations can exceed the 5µg/L drinking value
- Some basins remain not-well investigated (not investigated or LoQ > 1µg/L)

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ISSUE

Perchlorate origin and uses

Natural perchlorate

- may occur **naturally**, particularly **in arid regions** (Chile Atacama desert, southwestern United States (Rao and others 2007))
- **natural impurity in nitrate salts from Chile**,

→ Which have been imported and used from 1840 to 1950 to produce:

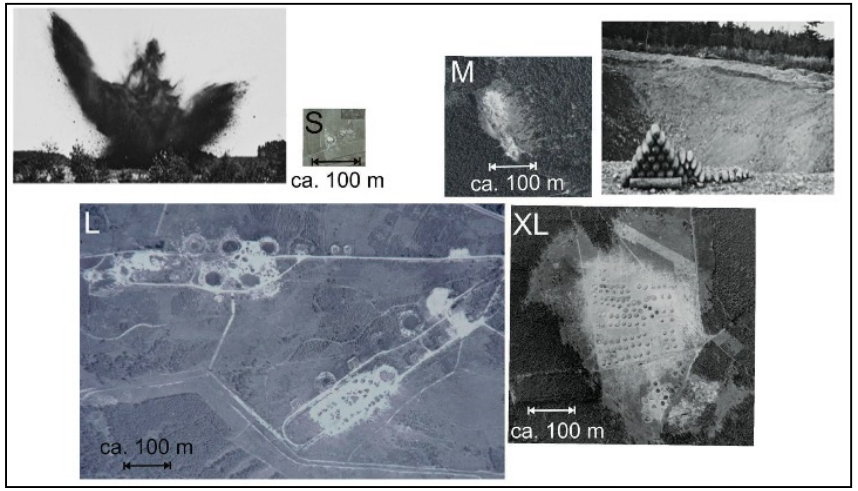
- Ammunitions, especially first world war bombs and shells
- Nitrate fertilizers and other products (Müntz, Achille 1846-1917; ITRC 2005)

San-miguel-island caliche

Synthetic perchlorate

- **manufactured** forms of perchlorate = perchloric acid and salts such as ammonium, sodium and potassium (EPA FFRRO 2005; ITRC 2005)
- used as an oxidizer in solid propellants, munitions, fireworks, airbag initiators for vehicles, matches and signal flares (EPA FFRRO 2005; ITRC 2005).

→ Of the domestically produced perchlorate, 90 percent is manufactured for use in the defense and aerospace industries, primarily in the form of ammonium perchlorate (GAO 2005)



Bombardment and unexploded bomb treatment

Perchlorate origin and uses

What is the source of perchlorate in French Groundwater?

3 hypothesis:

1) Punctual sources from industrial and military modern specific activities
2) First world war ammunition bombardments and breakdown interwar activities
3) Past farming Chilean nitrate fertilization

Groundwater specific vulnerability to perchlorate in France

Objectives

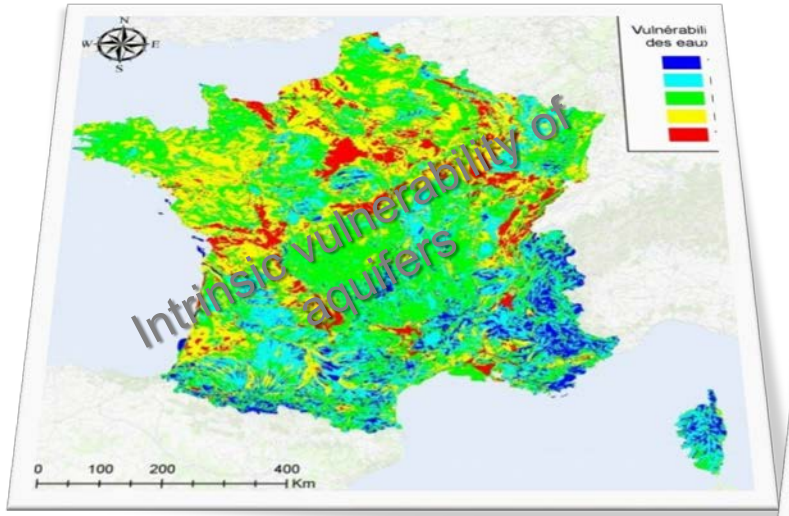
- Identify and locate aquifers that are vulnerable to perchlorate potentially emitted by anthropogenic activities
- Locate potential sources of perchlorate and verify their presence in vulnerable GW

⇒ **Test the hypothesis of potential sources of perchlorate in French GW**

Method

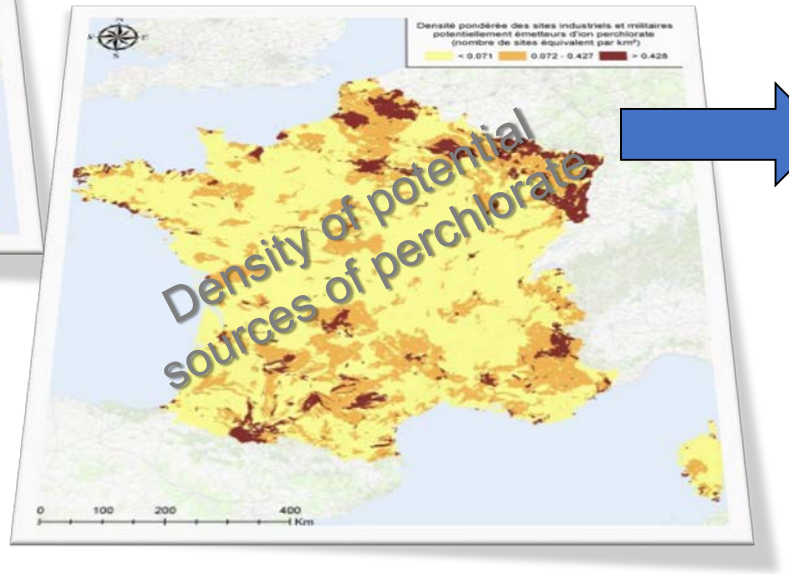
- 1) calculation of the GW specific vulnerability to perchlorate
- 2) estimation and location of the density of potential sources of perchlorate
- 3) validation and identification of the most impacting potential sources

Groundwater specific vulnerability to perchlorate in France

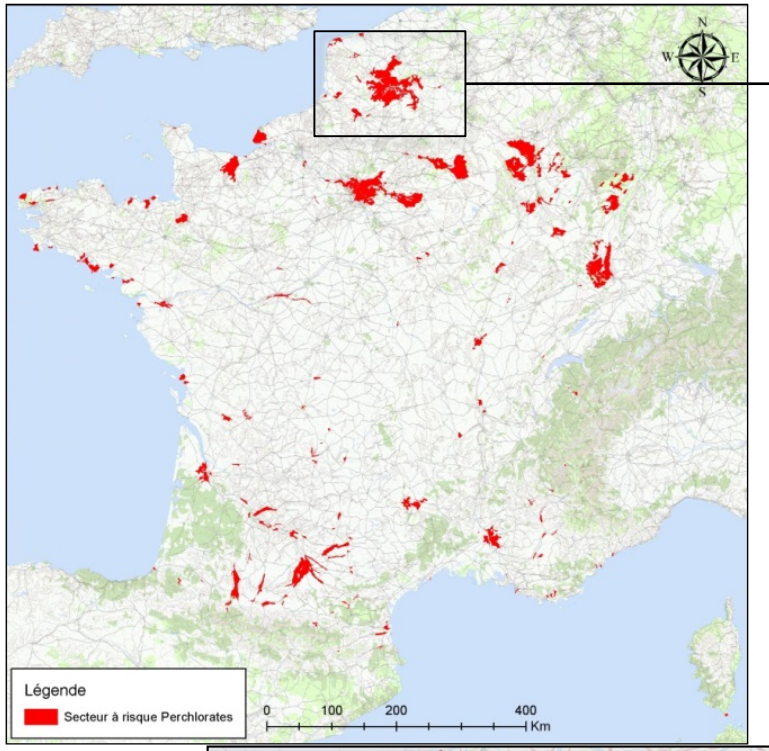


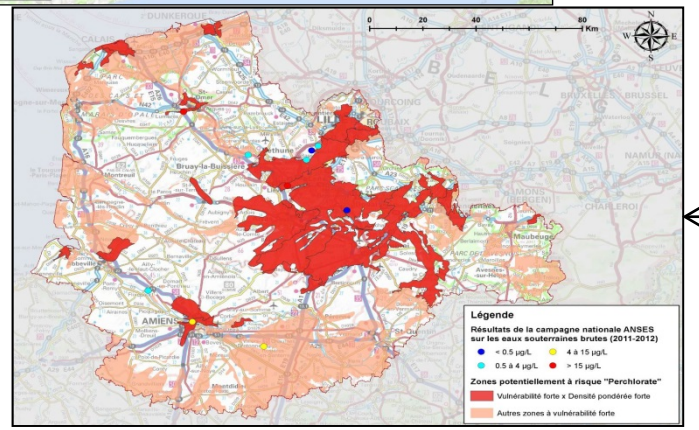
- Shallow Theoretical Groundwater Catchments mapping
- Network Persistent and Development Index (soil infiltration capacity)
- Thickness of Unsaturated zones

- Inventory and mapping of industrial and military potential sources
- Aggregation at GW catchment scale



National map of high risk to GW perchlorate contamination





> **Because perchlorate is conservative in groundwater**

Groundwater specific vulnerability to perchlorate

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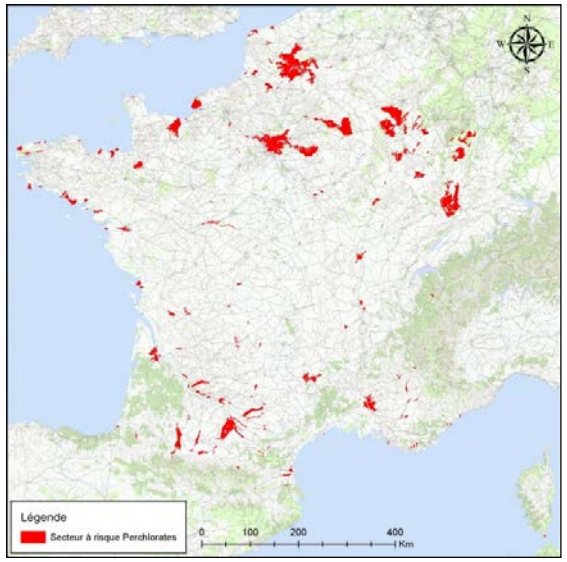
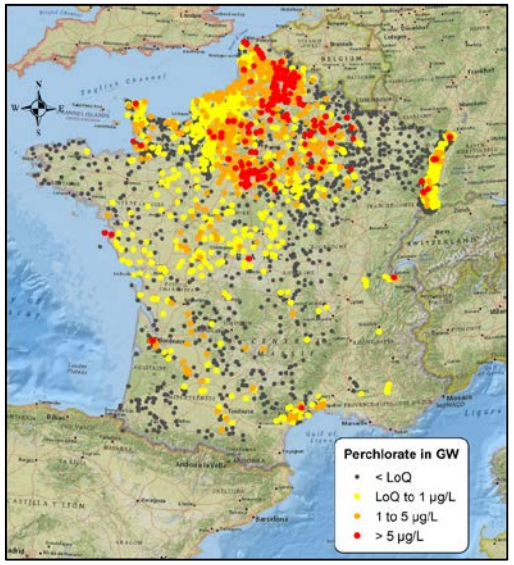
Intrinsic vulnerability X Density of potential sources of ClO_4

Validation and identification of the most impacting potential sources



Theoretical specific GW vulnerability to industrial and military sources' perchlorate



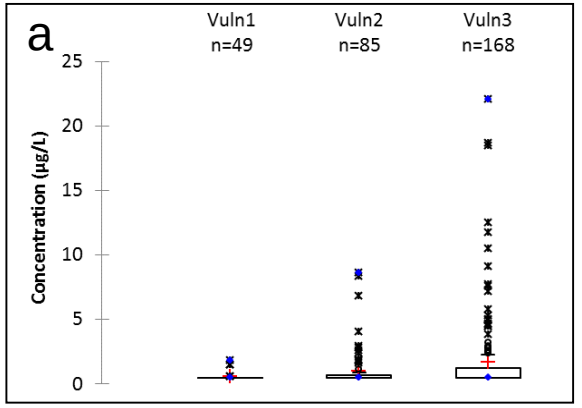
Perchlorate concentrations in GW

At national scale, industrial and military activities (including former military activities as first world war ammunition) can explain the majority of impacted sites

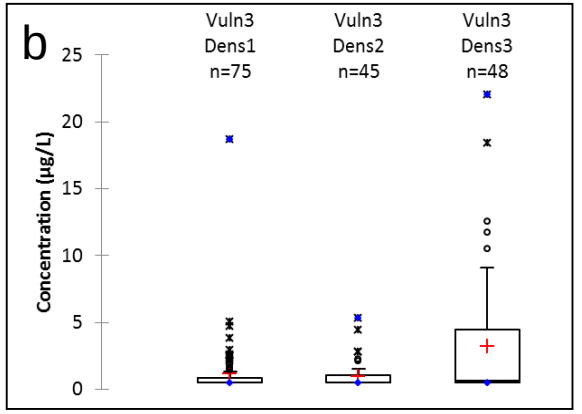
In some regions, perchlorate are observed in GW without any sources identified

Kruskall-Wallis test; p-value < 0.01

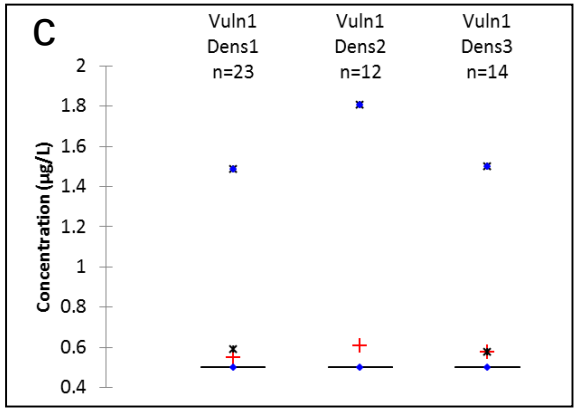
- (a) highest concentrations of perchlorate are find in high vulnerability aquifers



- (b) when intrinsic vulnerability is high, concentrations are significantly higher when density of sources is high



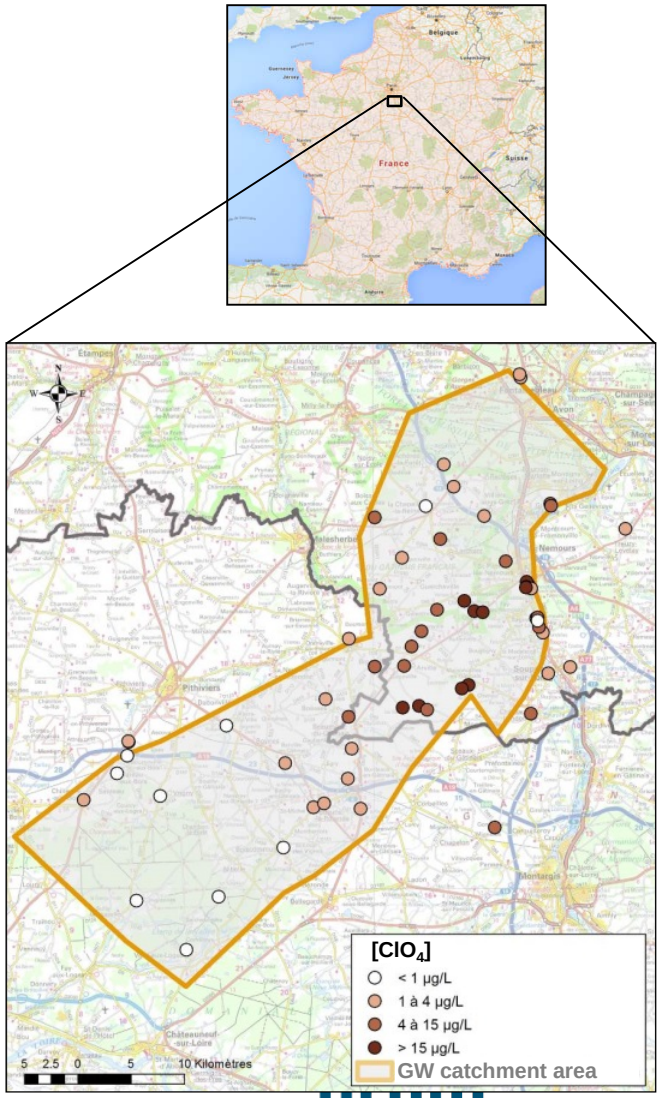
- (c) when intrinsic vulnerability is low, concentrations are low even if the density of sources is high



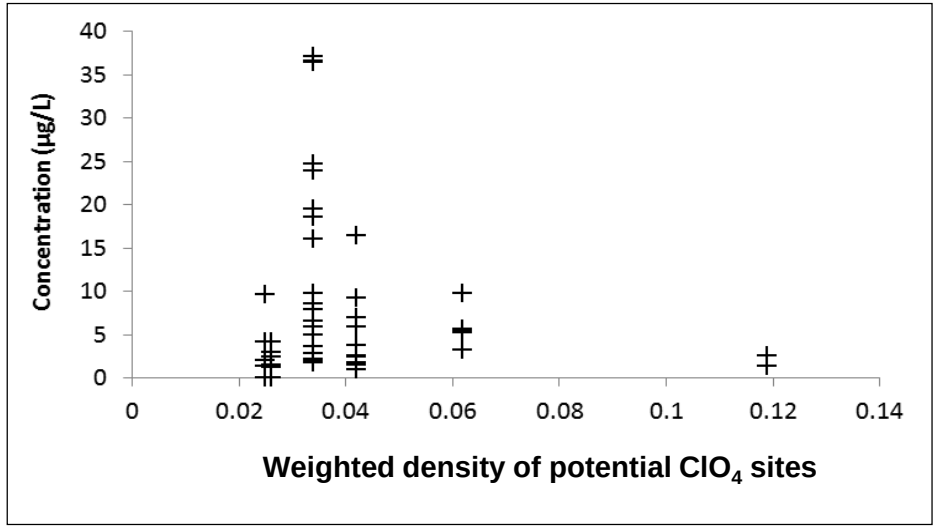
Source of perchlorate in agricultural land-use aquifer?

An example for which the known potential industrial and military activities don't explain ClO_4 in GW

- **Context**
  - Sedimentary multi-layer limestone aquifer - 100 km² catchment
  - Intensive agricultural land-use
  - In 2012, discovery of [ClO_4] up to 7 µg/L in GW used for water supply
  - 3 years study to identify potential source of perchlorate and predict evolution of the groundwater quality



No correlation between [ClO4] and density of potential sources despite high intrinsic vulnerability of the aquifer



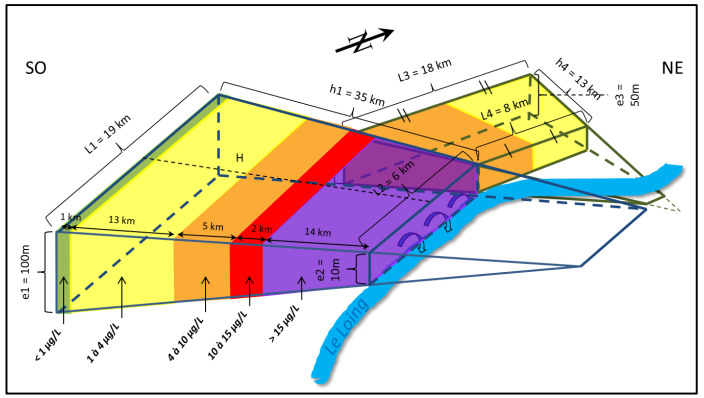
Source of perchlorate in agricultural land-use aquifer?

State of the art in agricultural landscapes

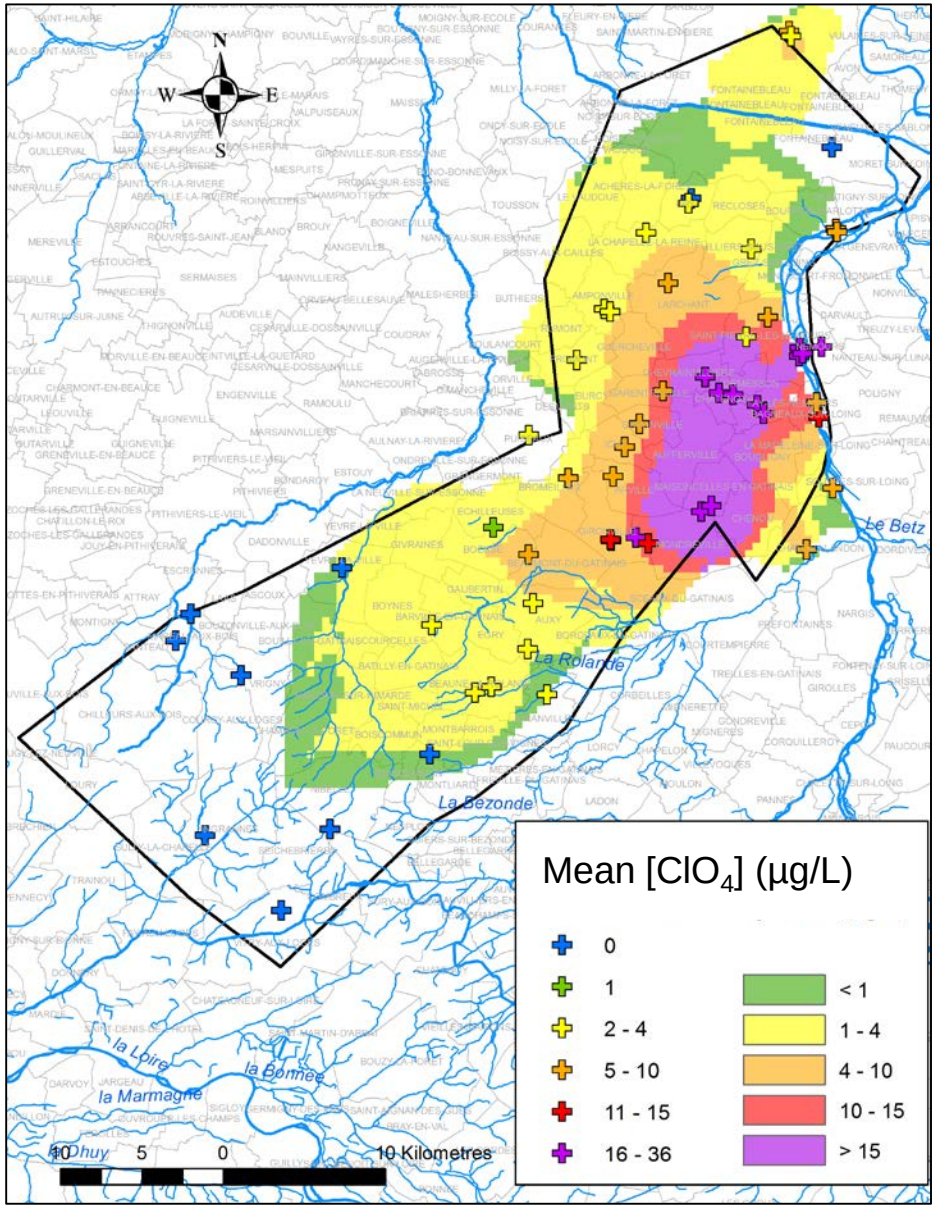
- *Sturchio et al. (2012) suggest that, in a California basin where much of the land was being used for agriculture, perchlorate in GW can derived from imported Chilean (Atacama) NO_3 fertilizer.*
- *Mastrocicco et al. (2017) link GW concentrations of chlorates in an Italian agricultural lowland landscapes (Po River plain) with the degradation of perchlorates originated from fertilizer leaking.*

Mutli-hypothesis testing strategy

- Literature revue of potential sources
- Geological and hydrogeological study
- 2 sampling campaigns (63 sites for chemical analyses)
- Plume mapping
- ClO_4 stock estimation
- Age-dating of groundwater (CFC/SF6 on 14 sites)
- GW quality data statistical analyses



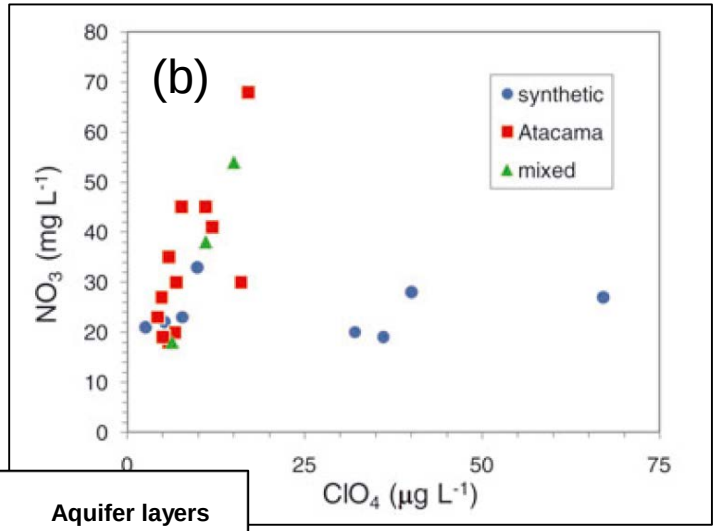
Estimate of ClO_4 stored in GW



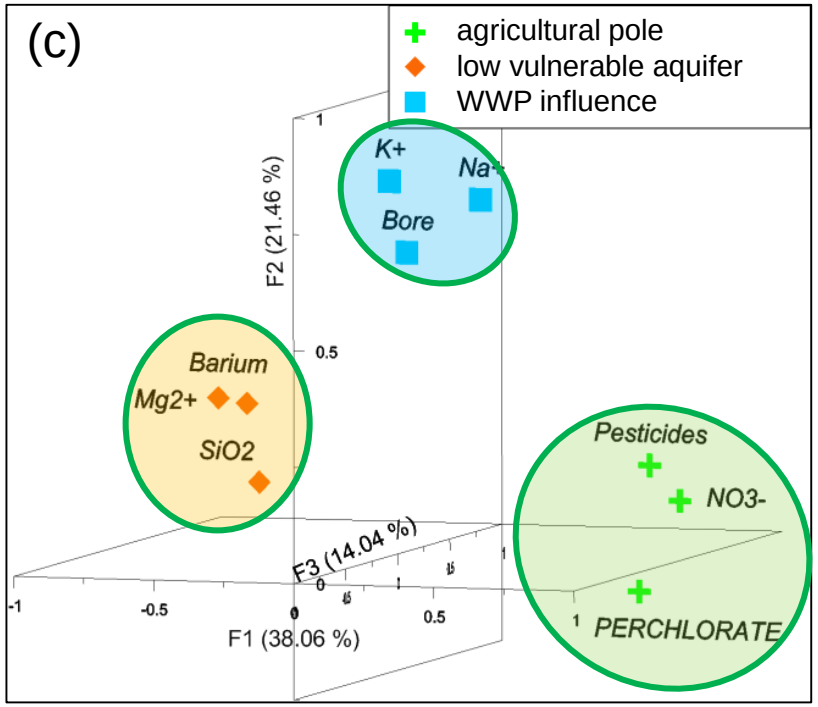
Source of perchlorate in agricultural land-use aquifer?

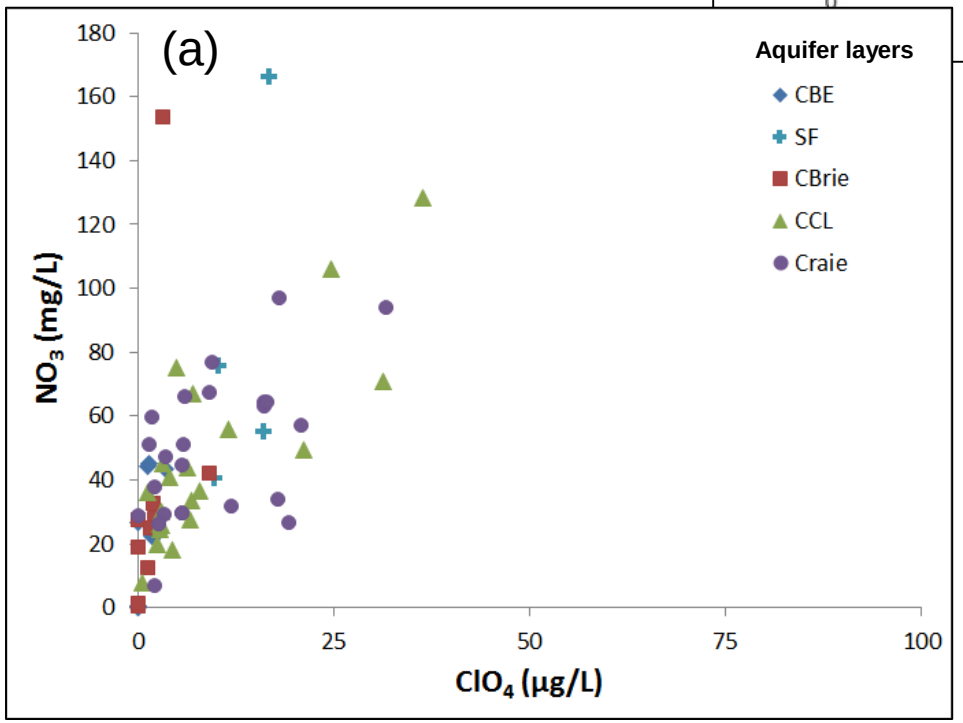
Chemical data analysis

- a) [ClO_4] and [NO_3] are quite well positively correlated in shallow vulnerable aquifer layers
- The average [NO_3] / [ClO_4] ratios range from 2000 to 5000, consistent with **Atacama nitrate signature** (Sturchio 2012 (b))
- c) PCA correlated perchlorate with NO_3 and pesticides agricultural source pollutants

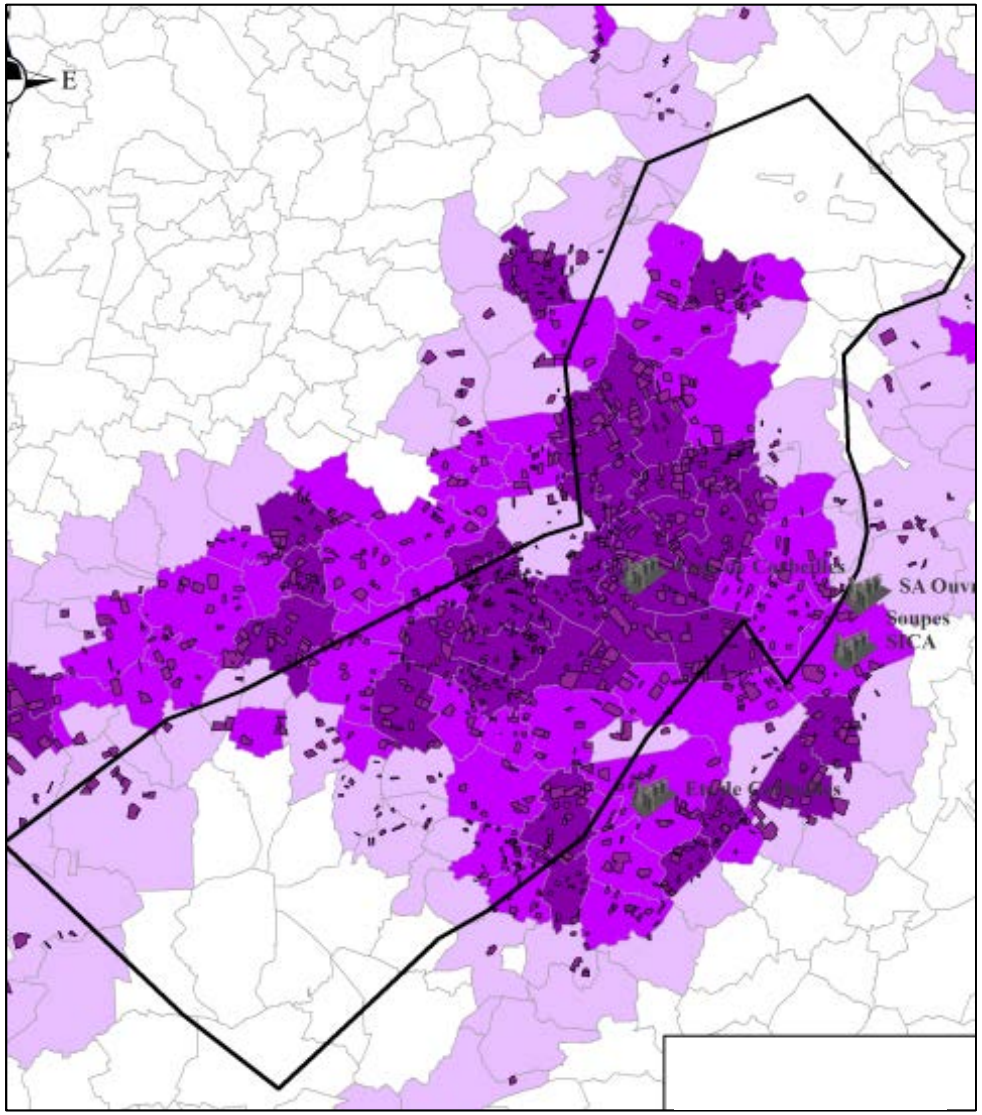


From Sturchio et al. 2012





Source of perchlorate in agricultural land-use aquifer?



- Beet root product is the main land-use activity in the studied area, since ages
- Chilean nitrate intensively used from 1850 to 1940 (800kg/ha on beet root)

Overlap of the ClO_4 plume and 2013 beet root mapping

- The most polluted zones correspond to the most densely cultivated zones with an offset of about 5 km downstream
- 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

Perchlorate in GW from former agricultural use of Chilean nitrates, A realistic hypothesis at national scale?

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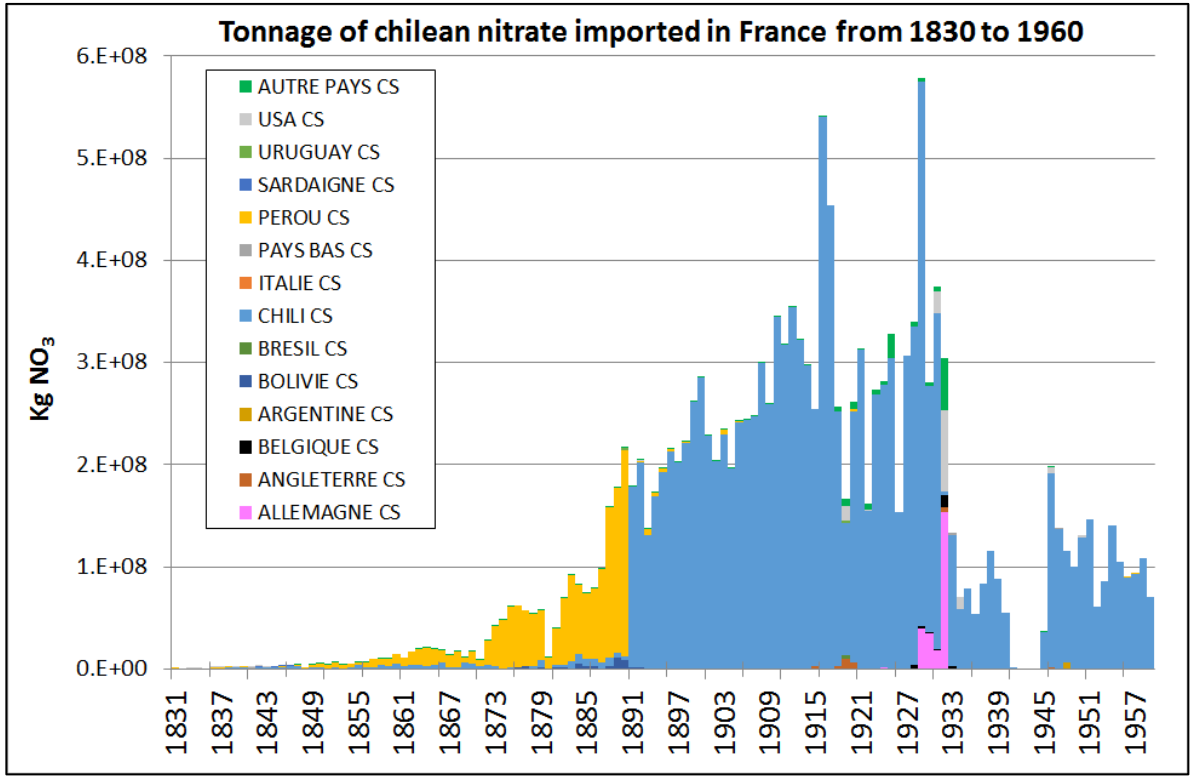
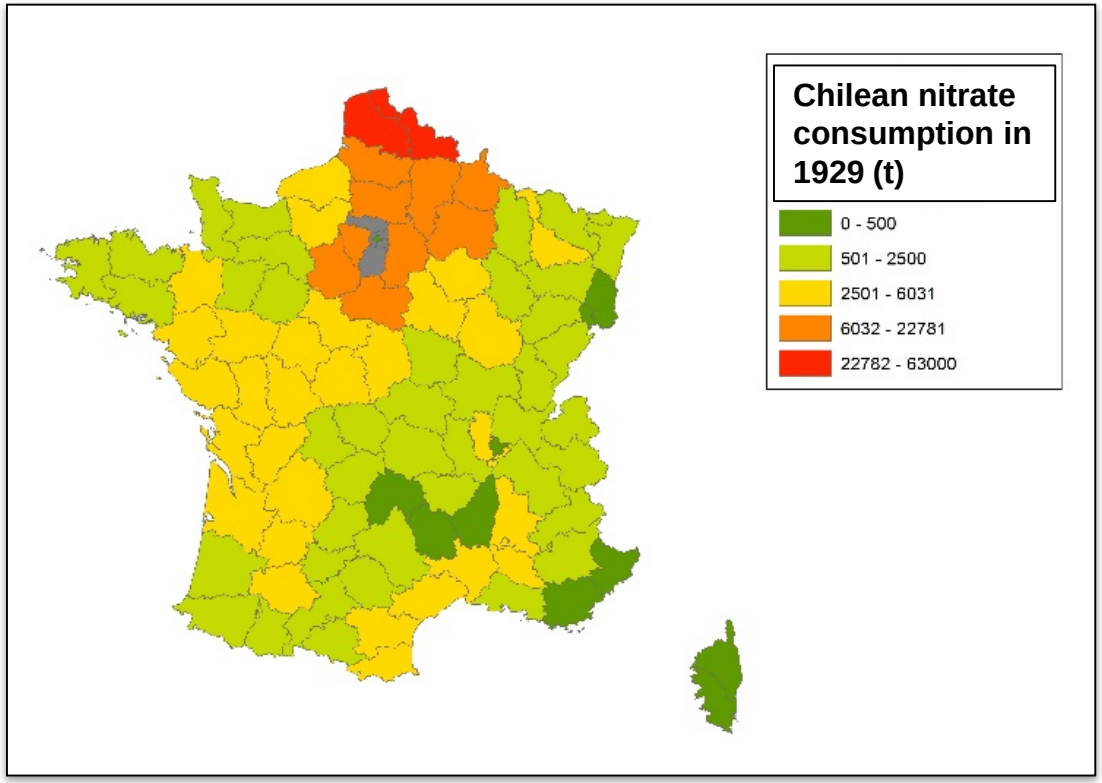
- Reconstitution of historical uses of Chilean nitrate



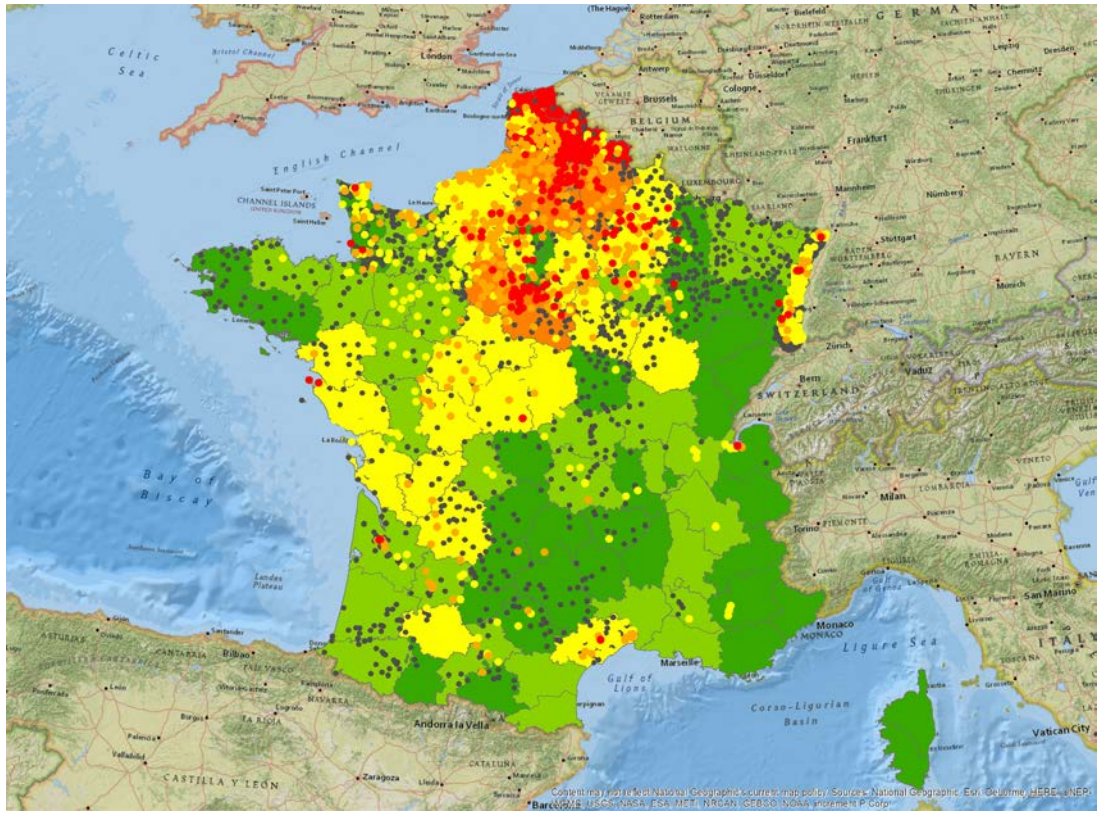
- Location of former agricultural uses



- Chilean nitrates have been heavily imported and used from 1870 to 1935 in France as
  - agricultural fertilizers especially on beet root (800 kg/ha) and wheat (400 kg/ha) during interwar periods
  - explosive material during war periods

- Centre and North are basins where Chilean nitrate have been hugely used
- Time transfers are slow in these chalk and multilayer sedimentary aquifers, GW are often > 50 years old

Perchlorate in GW from former agricultural use of Chilean nitrates, A realistic hypothesis at national scale?



At national scale, in region where time transfers to GW are slow, former use of Chilean nitrate should explain the contamination of groundwater by perchlorate

BRGM, 2015, national. archives, Washington

BUT

→ First WW battle fields and highly fertilized fields are often the same (center and northern France)

→ The same Chilean nitrates from Atacama have been used in war bombs and as fertilizers

→ Chilean nitrate contained in unexploded bombs have been re-used to fertilize fields

Search for tracers of perchlorate origin

In France, large plume of perchlorate in GW seem to be explained by Atacama Chilean nitrates

- Historical studies of former activities
- $[NO_3]/[ClO_4]$ ratios
- GW age dating

Research perspectives

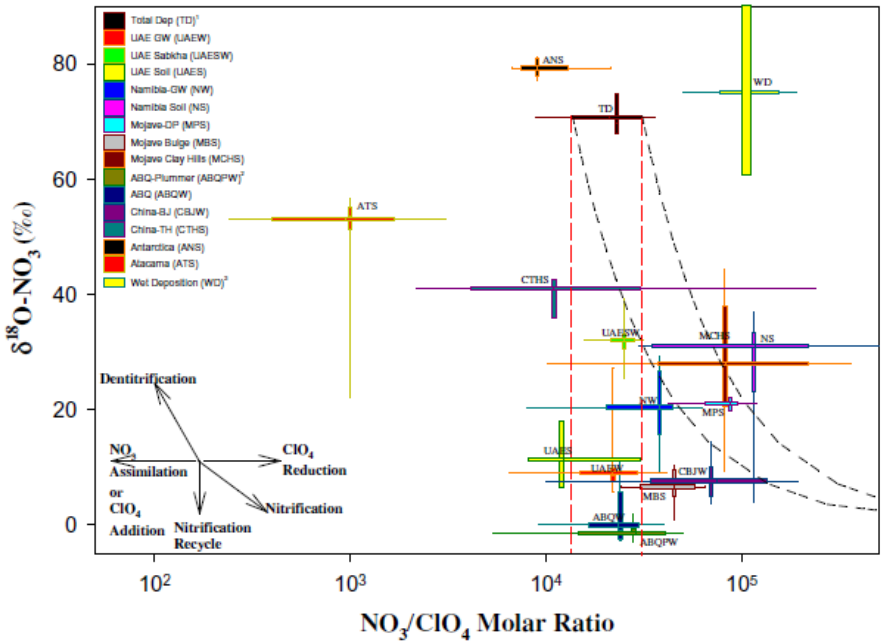
- Perchlorate, chlorate and nitrate ion isotopes ($\delta^{18}O$, $\delta^{15}N$, $\delta^{35/37}Cl$) and $[NO_3]/[ClO_4]$ ratios help to discriminate natural from synthetic sources of perchlorate

- But how to discriminate former agricultural from former military sources of perchlorate that have the same Atacama origin?

→ Co-occurring explosives compounds to trace former ammunition activities ?

→ Reconstitution and location of historical uses of Chilean nitrate

→ Military sources of perchlorate not yet well-investigated in France:
  - Former heavily shelled battlefields of First World War
  - Ammunition breaking down activities of interwar time



W.A. Jackson et al. / GCA 164 (2015) 502–522

Thank you for your attention

Calculation of the GW specific vulnerability to perchlorate

Shallow Theoretical Groundwater Catchments mapping

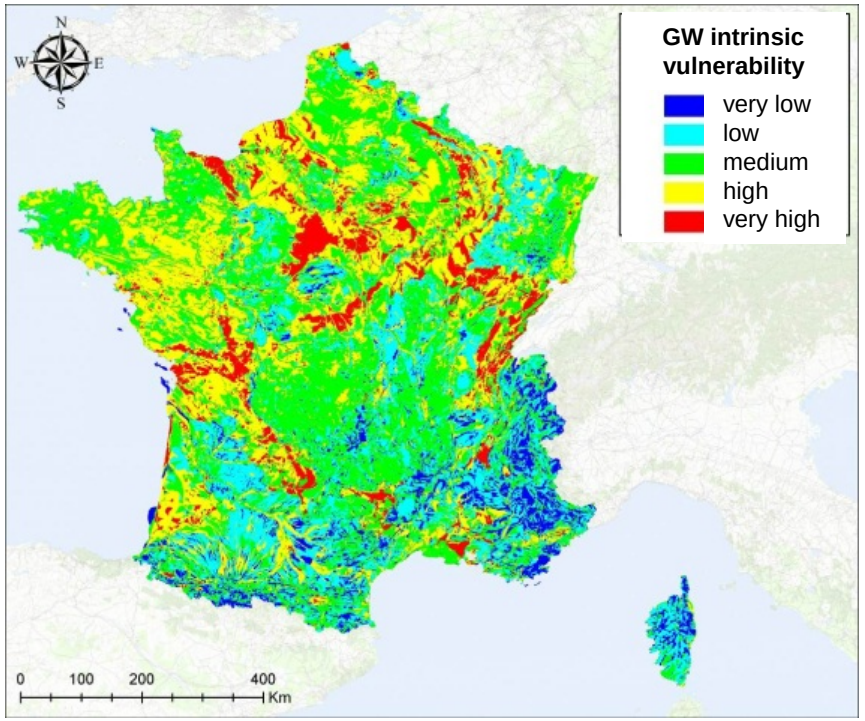
- Automatic mapping with ArcGIS 10.0 spatial analysis tools
- From
  - Field Numerical Model data
  - National elevation database
  - National grid of unsaturated zone thickness.

The Network Persistent and Development Index (IDPR)

- Analysis of the drainage patterns (calculated from a Digital Elevation Model) and the natural hydrological flow
- Reflects the influence of the underlying geological formations toward surface-water runoff or infiltration

Thickness of Unsaturated zones

- National grid of the difference in elevation between soil and water table level



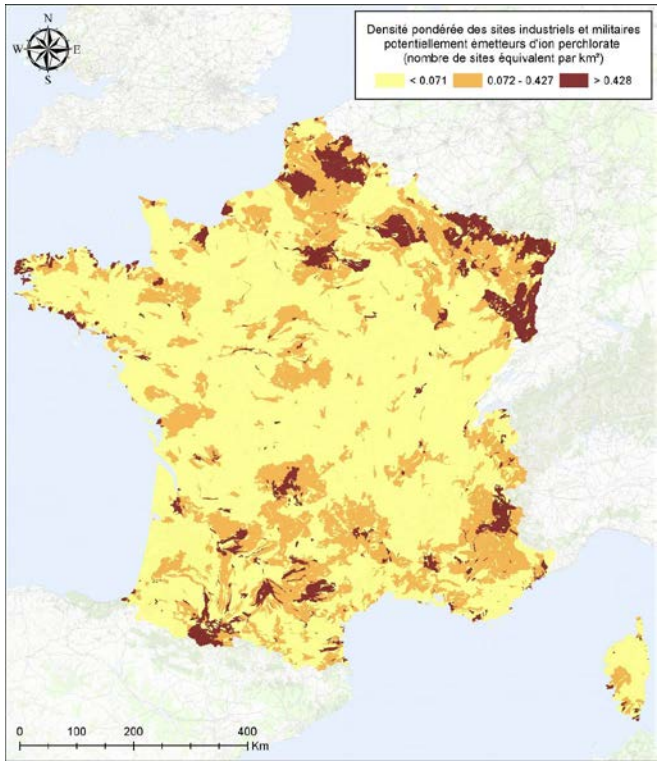
→ National simplified intrinsic vulnerability map of shallow aquifers

Density of potential sources of perchlorate at catchment scale

Method

- a) Inventory and mapping of industrial and military potential sources
- b) Aggregation at GW catchment scale

→ **Weighted density of potential ClO_4 sources mapping**

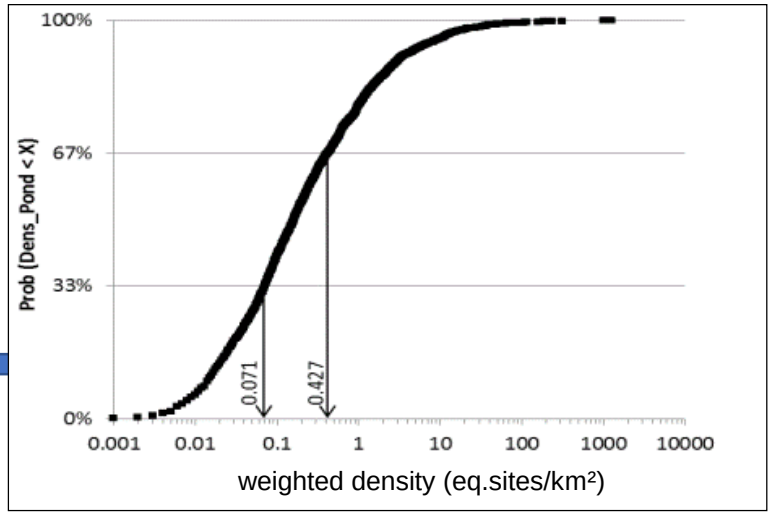


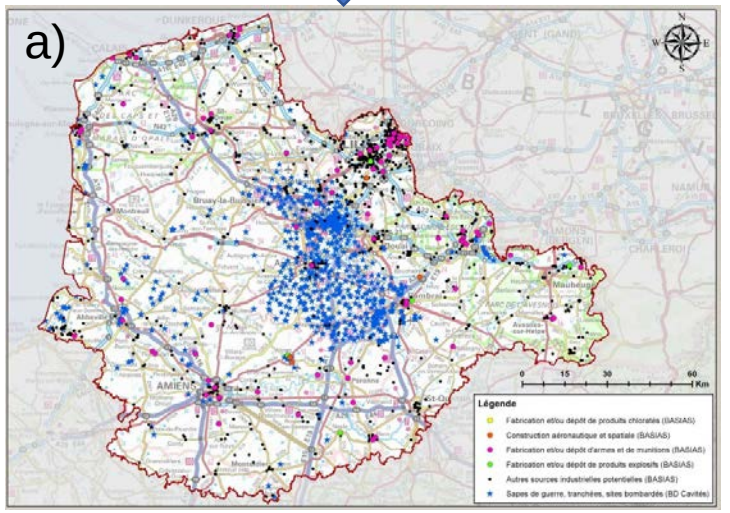
3 classes of density of potential sources

a)

Anthropogenic activities	Perchlorate salts	Sources of emission
Solid propellants for rockets and missiles	NH_4ClO_4; $Ba(ClO_4)_2$; $Ba(ClO_4)\bullet 3H_2O$; $LiClO_4\bullet 3H_2O$	Production sites, Aerospace industries
Explosives	$KClO_4$; $AgClO_4$; $NaClO_4$	Production sites, Military sites, war sites, mining sites
Fireworks and other pyrotechnics	NH_4ClO_4; $Ba(ClO_4)_2$; $Mg(ClO_4)_2$; $KClO_4$; $Sr(ClO_4)_2$	Production, use and storage sites
Chemical industries (drying agents, electroplating)	$Ca(ClO_4)_2$; $Mg(ClO_4)_2$; $HClO_4$; $KClO_4$; $NaClO_4$	Production sites
Metallurgy industries	$HClO_4$	Production sites
Plastic industries	NH_4ClO_4; $LiClO_4$	Production sites/Distribution network
Oxygen generators	$LiClO_4$; $KClO_4$	Production sites
Airbags	NH_4ClO_4; $KClO_4$; $NaClO_4$	Production sites, Scrapyard
Magnesium and lithium Batteries	$LiClO_4$; $Mg(ClO_4)_2$	Production sites, Scrapyard
Pharmaceutical activities	$KClO_4$; $RbClO_4$	Production sites
Herbicides (Impurities)	$NaClO_4$	Production sites, Agricultural farms
Paper mill, Tanneries (Impurities)	$HClO_4$; $NaClO_4$	Production sites
Fertilizers (Impurities)	$NaClO_4$	Production sites

b)





First World War ammunitions

In northern France, perchlorate should source from:

- 1915-1918 former heavily shelled battlefields of First World War

→ Large plume eastern from 1915-1948 battle line

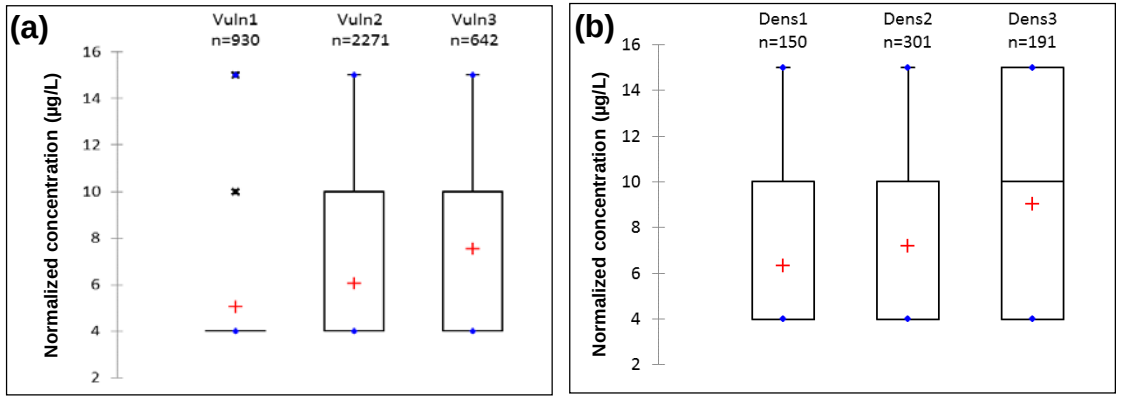
- Ammunitions breakdown interwar activities

→ Isolated hot spots western from 1915-1918 battle line

1915-1918 battle line

Isolated hot spots

High concentrations Estern 1915-1918 battle line



Kruskall-Wallis test; p-value < 0.01

p-value < 0.001