brabant Water
Altijd. Overal.

How to remove metals from groundwater for high quality drinking water production

principles, practices and drivers for research

Seattle, USA
Oktober 2017

Stephan van de Wetering
Manager Process Engineering
Brabant Water
The Netherlands

Where is the Netherlands

brabant Water
Altijd. Overal.

Drinking water in the Netherlands

Key figures

• Population	17 mio.
• Total production volume	1,126 mio. m^3
• Network length	119.000 km
• Investments	€431 mio.
• NRW	5,5 %
• Connected	99,9 %

Sources

Ground water	2/3
Surface water	1/3

Treatment

Ground water: Aeration, filtration, softening

Surface water: Extensive treatment

Distribution <u>No Chlorine</u>

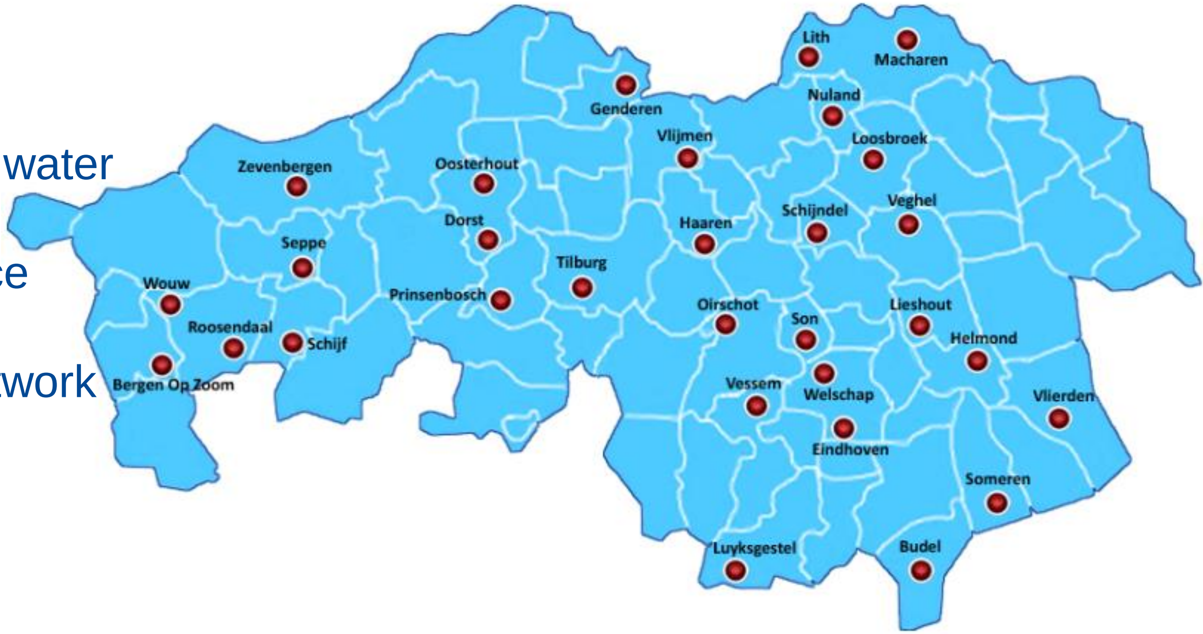
Introduction drinking water company Brabant Water

BRABANT WATER N.V.

- 2,5 mio. inhabitants
- 1,1 mio. connections
- 180,000 regional industries
- Annual production 176 mio. m^3 water
- 30 treatment plants
- Groundwater as the main source
- No chlorine
- 18,000 km main distribution network
- Non Revenue Water 2.5%
- 800 Staff
- Annual turnover €200 mio.

Water use 31,7 USgal (120 l) per person per day

Province North-Brabant



Design metals:
Iron and Manganese

Typical source groundwater

		Haaren	Oirschot	Vlierden	Lith
Abstraction depth	m-mV	142 - 200	175 - 205	135 - 210	19 - 60
pH	pH	7,73	7,99	6,87	7,15
Iron	µg/l	505	325	4300	7475
Manganese	µg/l	40	20	200	1152
Ammonium	mg/l	0,49	0,6	1,33	1,58
Calcium	mg/l	42	31	62	101
Magnesium	mg/l	3,5	6,1	11,8	8,1
Total hardness	mmol/l	1,19	1,02	2,03	2,86
Bicarbonate	mg/l	181	173	319	330
Nitrate	mg/l	<0,2	<0,2	<0,2	<0,2
Sulfate	mg/l	<1	<1	<1	42
Methane	mg/l	0,49	280	4,2	0,70
Conductivity	mS/m	26,15	25,25	51,65	57,5
Temperature	ºC	12,6	12,9	13,8	11,2

Iron and Manganese in drinking water

- Basic design parameters
  - m² filtration surface?
  - One ore two step treatment?
- Maintenance distribution network
- Discolouration

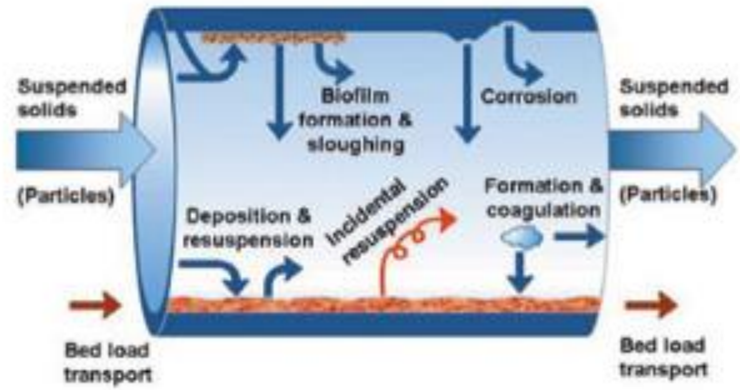
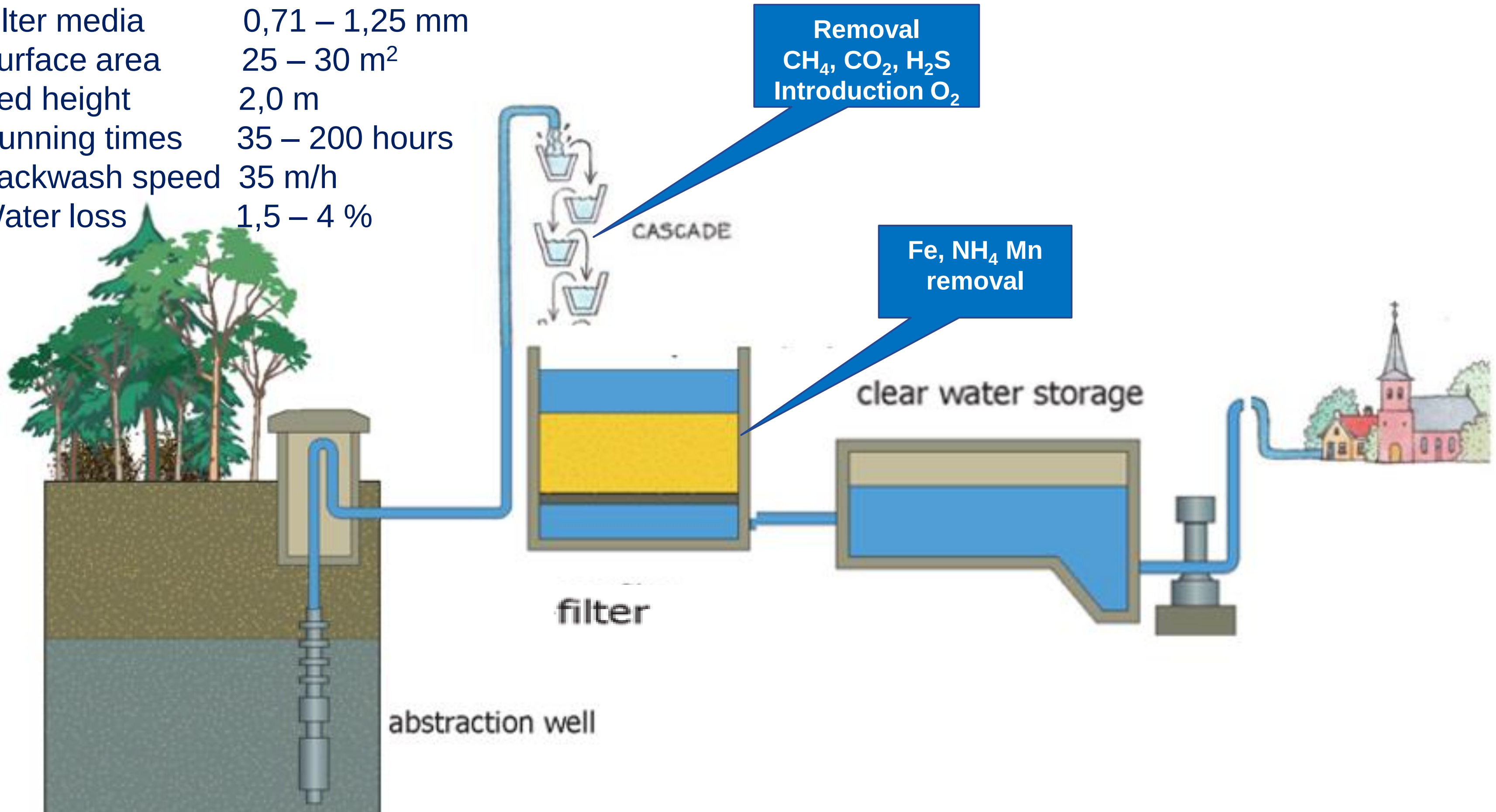


Figure 1
Physical processes resulting in discolouration (Vreeburg, 2007)

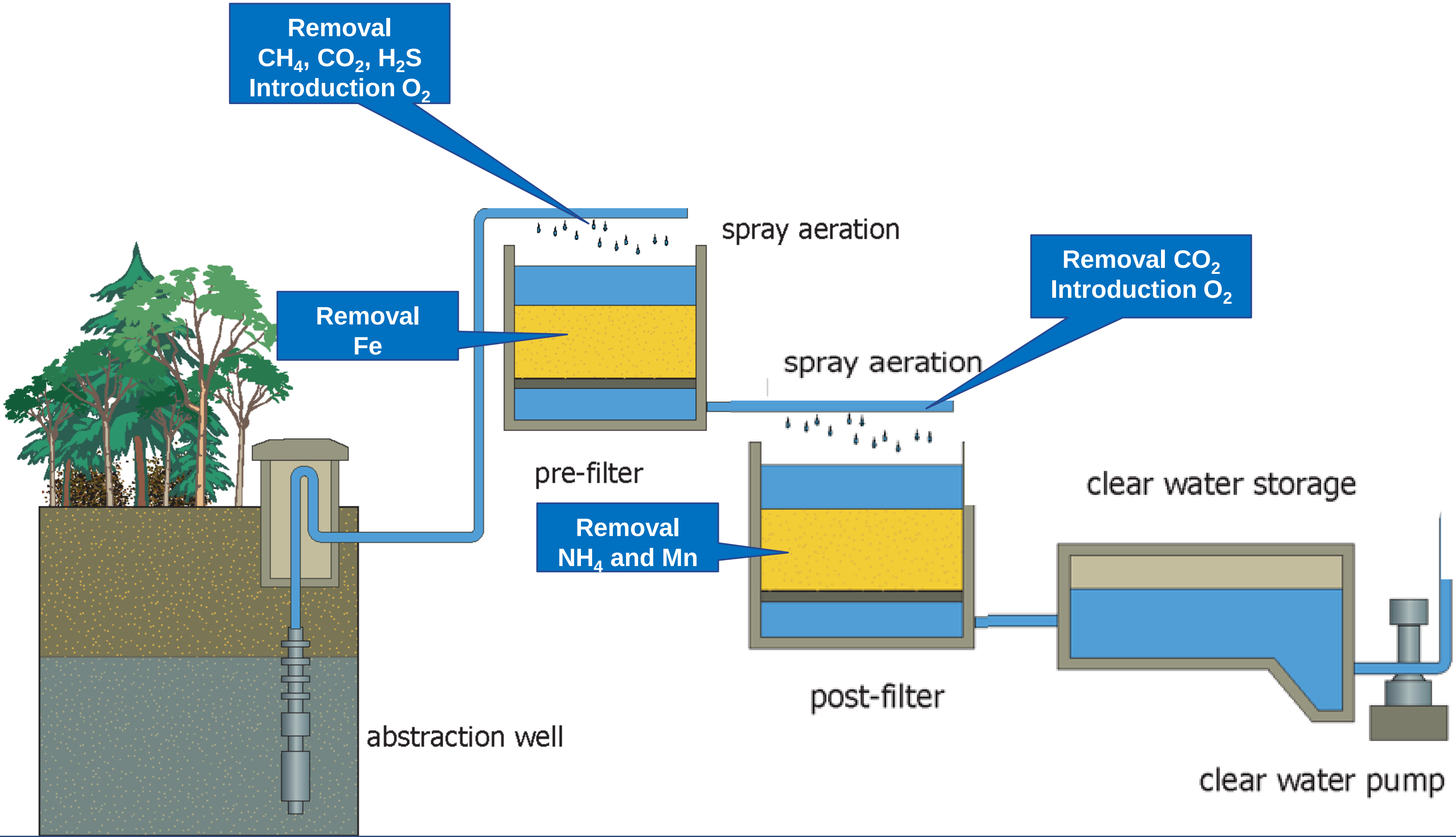
Typical treatment scheme 1

General design rapid sand filtration

- Filtration rate 3 – 14 m/h
- Filter media 0,71 – 1,25 mm
- Surface area 25 – 30 m²
- Bed height 2,0 m
- Running times 35 – 200 hours
- Backwash speed 35 m/h
- Water loss 1,5 – 4 %



Typical treatment scheme 2



Iron and manganese removal

Depending on the water quality and treatment:

Fe(II) removal:

- Homogeneously $Fe^{2+} + ¼O_2 + 2½H_2O \rightarrow Fe(OH)_3(s) + 2H^+$
- Heterogeneously $S\text{-}OH^0(s) + Fe^{2+} + ¼O_2 + 1½H_2O \rightarrow S\text{-}OFe(III)(OH)_2^0(s) + 2H^+$
- Biologically $Fe^{2+} + ¼O_2 + 2½H_2O$ + Gallionella *spp* $\rightarrow Fe(OH)_3(s) + 2H^+$ + biomass
- Or combined mechanism

Mn(II) removal

- Autocataltic $2Mn^{2+} + O_2 + 2H_2O \rightarrow MnO_2(s) + 4H^+$

  $Mn^{2+} + MnO_2(s) \rightarrow Mn^{2+}MnO_2(s)$

Treatment plant at Vlierden

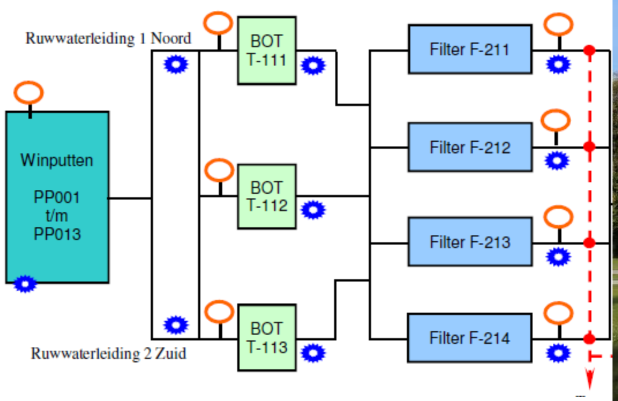
Build 2016

Abstraction Permit 4,5 mio. m^3 / year

Capacity 900 m^3/h

Storage 5000 m^3

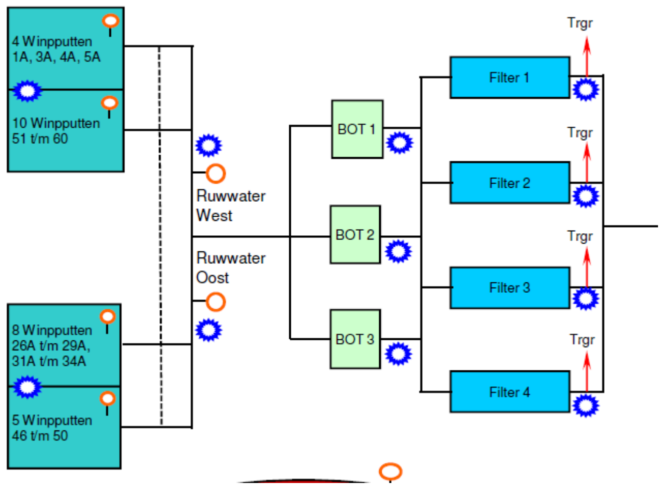
Process scheme



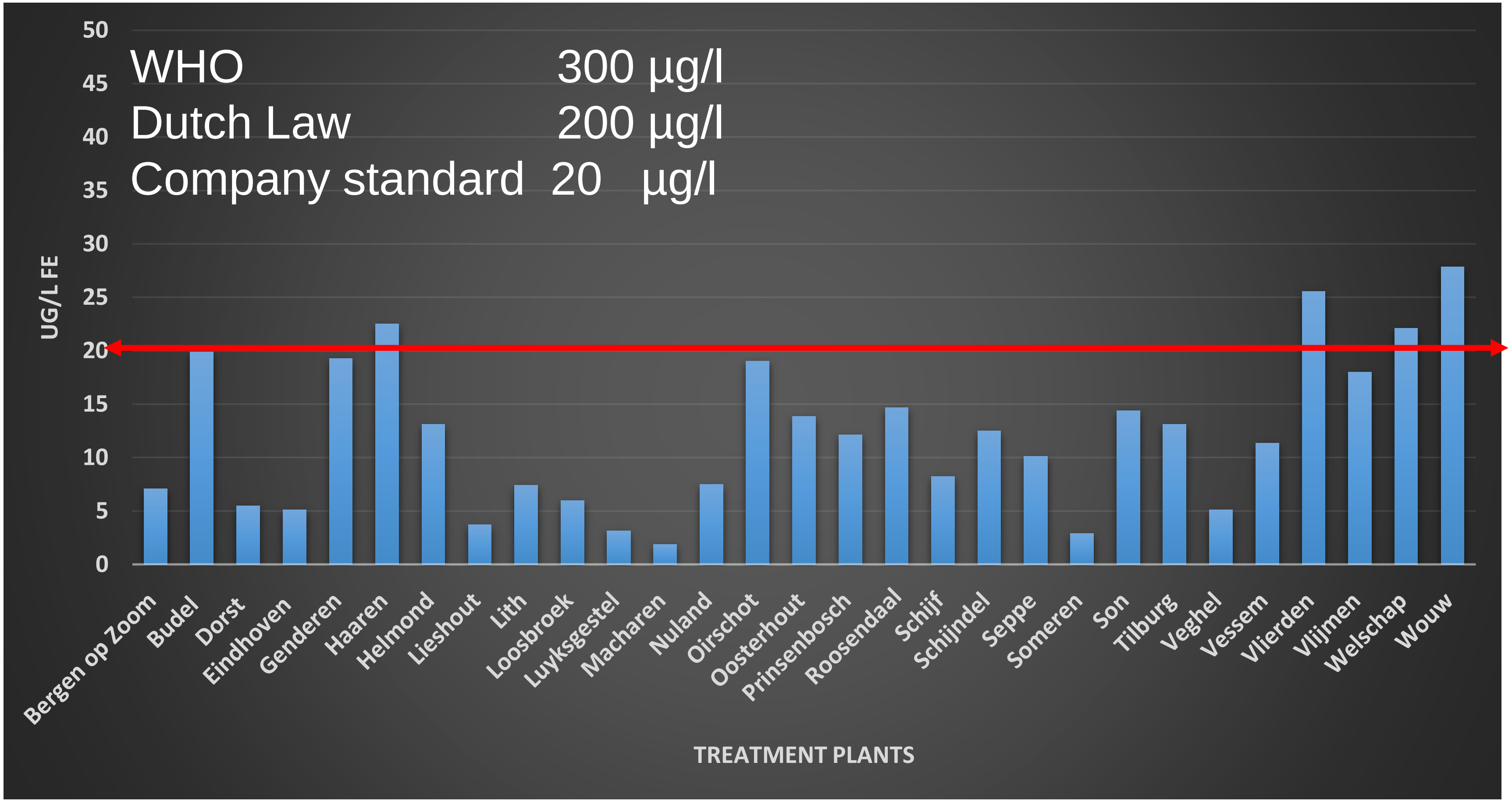
Treatment plant at Haaren

Build	2011
Abstraction Permit	8 mio. m^3 / year
Capacity	2000 m^3/h
Storage	11.000 m^3

Process scheme

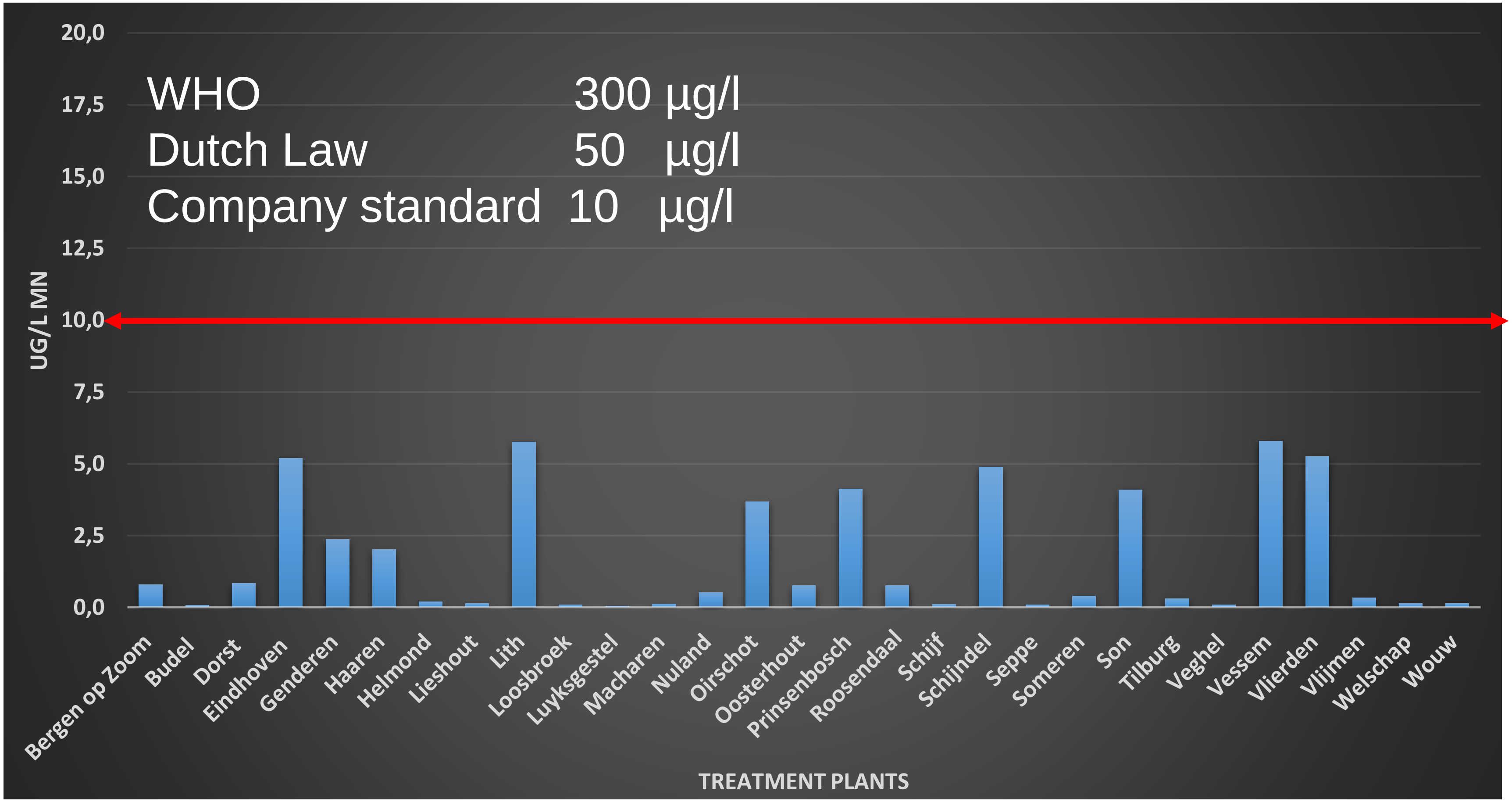


Iron in produced drinking water



brabant Water
Altijd. Overal.

Manganese in produced drinking water



Comfort metal: Calcium

Central softening program of Brabant Water

Reasons for softening

- Environmental Benefits
- Financial benefits €20 or $ 25 /yr/ conn
- Aesthetics and Comfort

Softening policy

- WTP with hardness > 2,0 mmol/l must be softened
- If we soften, lower the hardness to 1,40 mmol/l
- Existing WTB with softening we lower the hardness to 1,4 mmol/l

Deltaplan softening

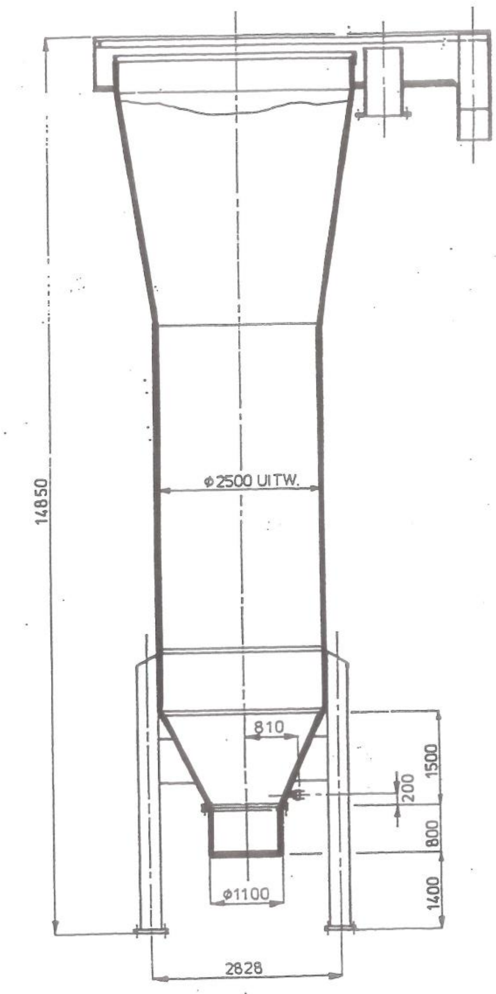
- 6 new central softening plants
- Combined with renovation
- Investment: €110 million ($130 million)
- Start engineering 2011
- In operation 2018

Objective soft water for the customers

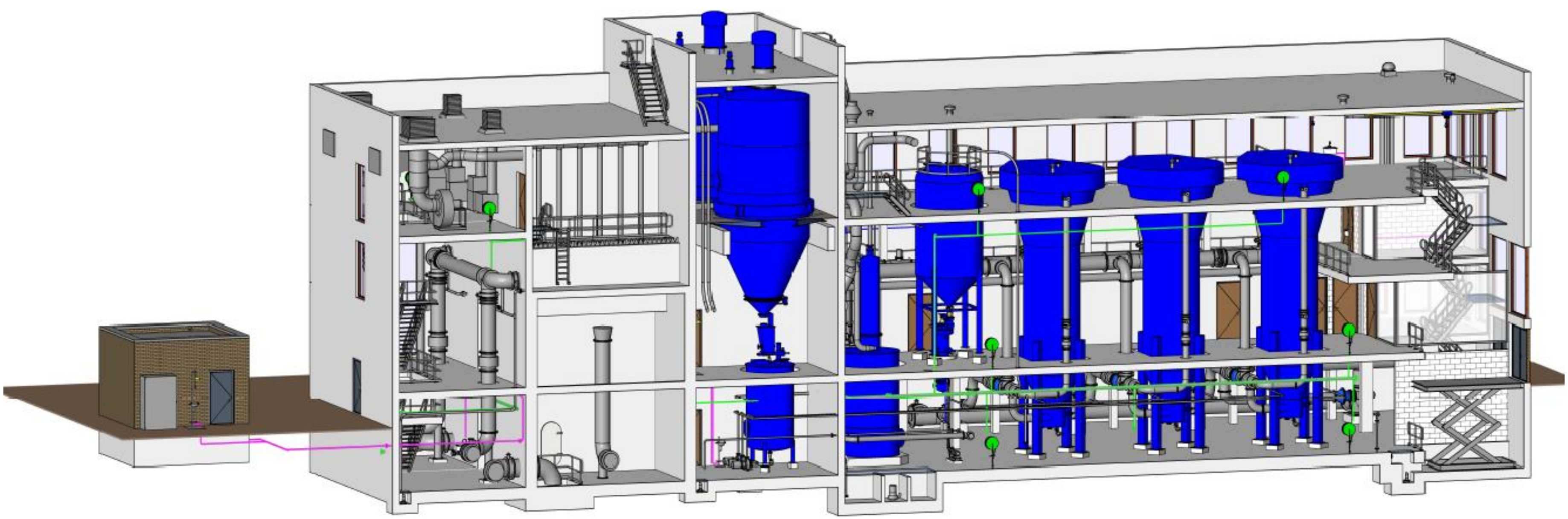
Softening principle

Pellet softening

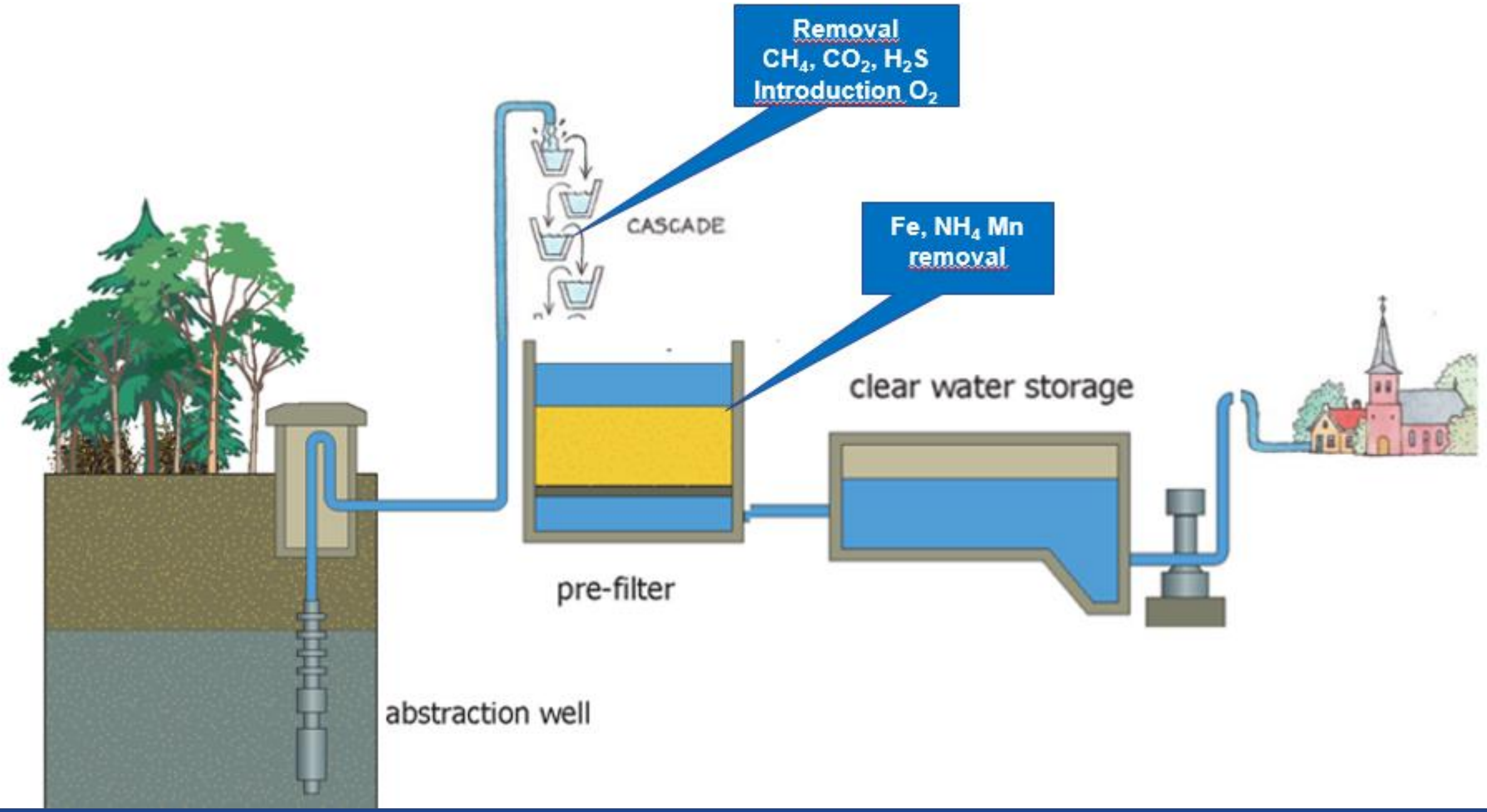
- Use of calcite as crystallization seed
- Fluidized bed (60 – 100 m/h)
- Cautic soda or milk of lime to drive crystallization
- Small footprint (but tall building)
- Easily usable sollid $CaCO_3$ waste (pellets)
- Fully automated operation



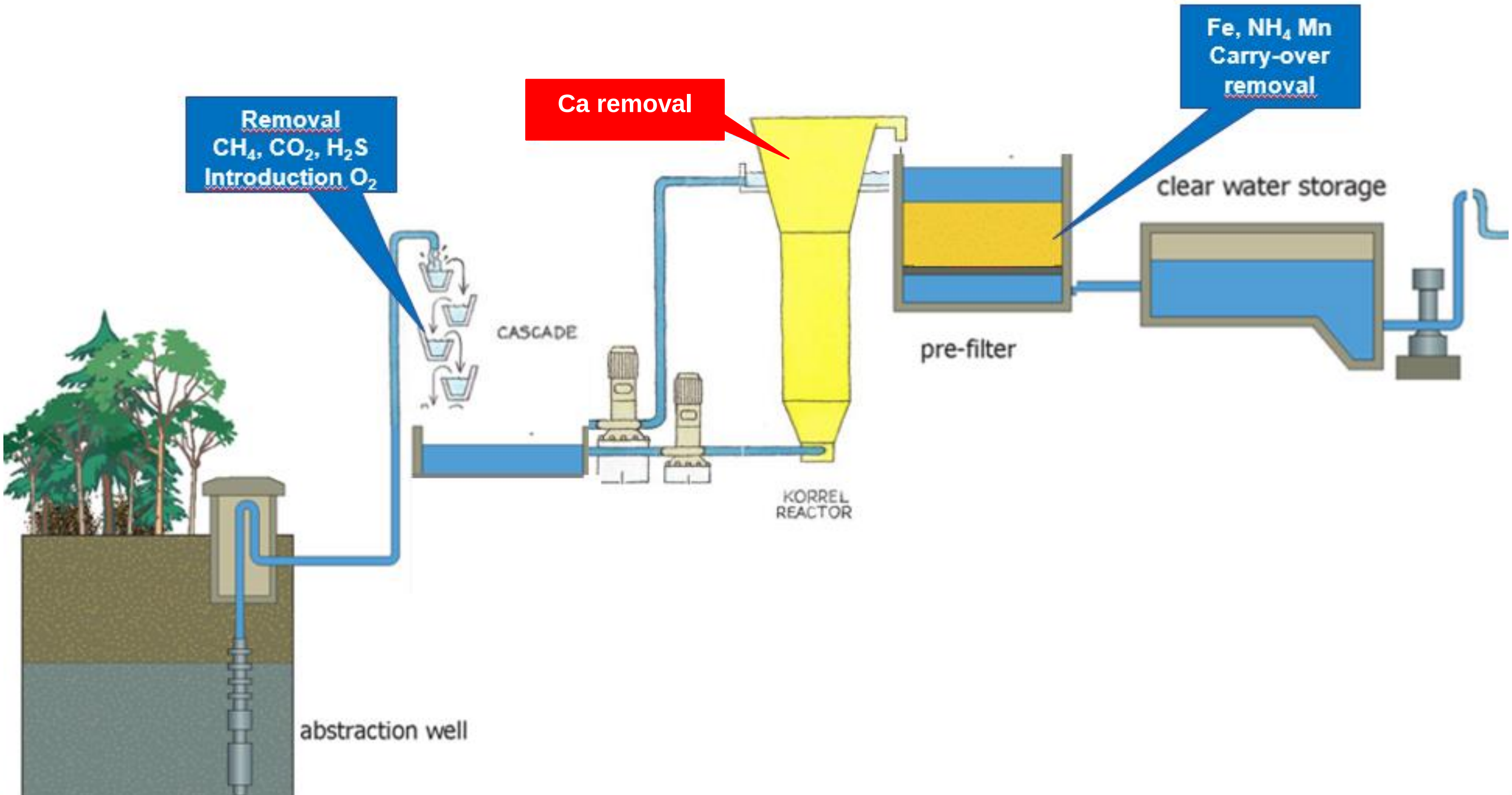
Softening building



Typical treatment scheme



Treatment with pellet softening



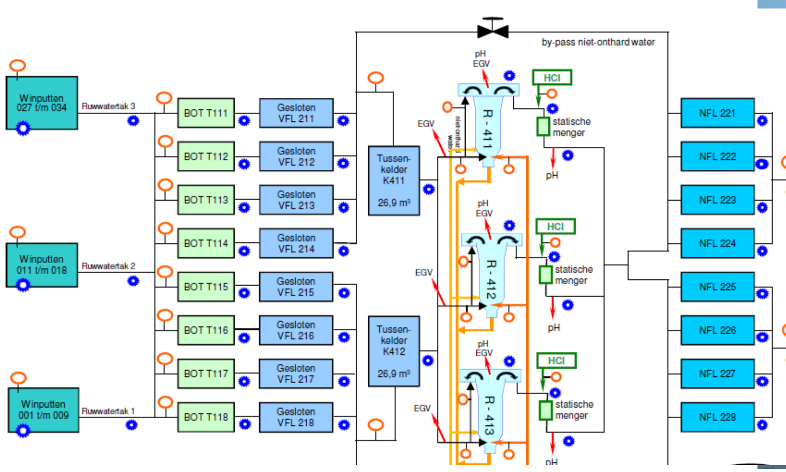
Pellet reactor

brabant Water
Altijd. Overal.

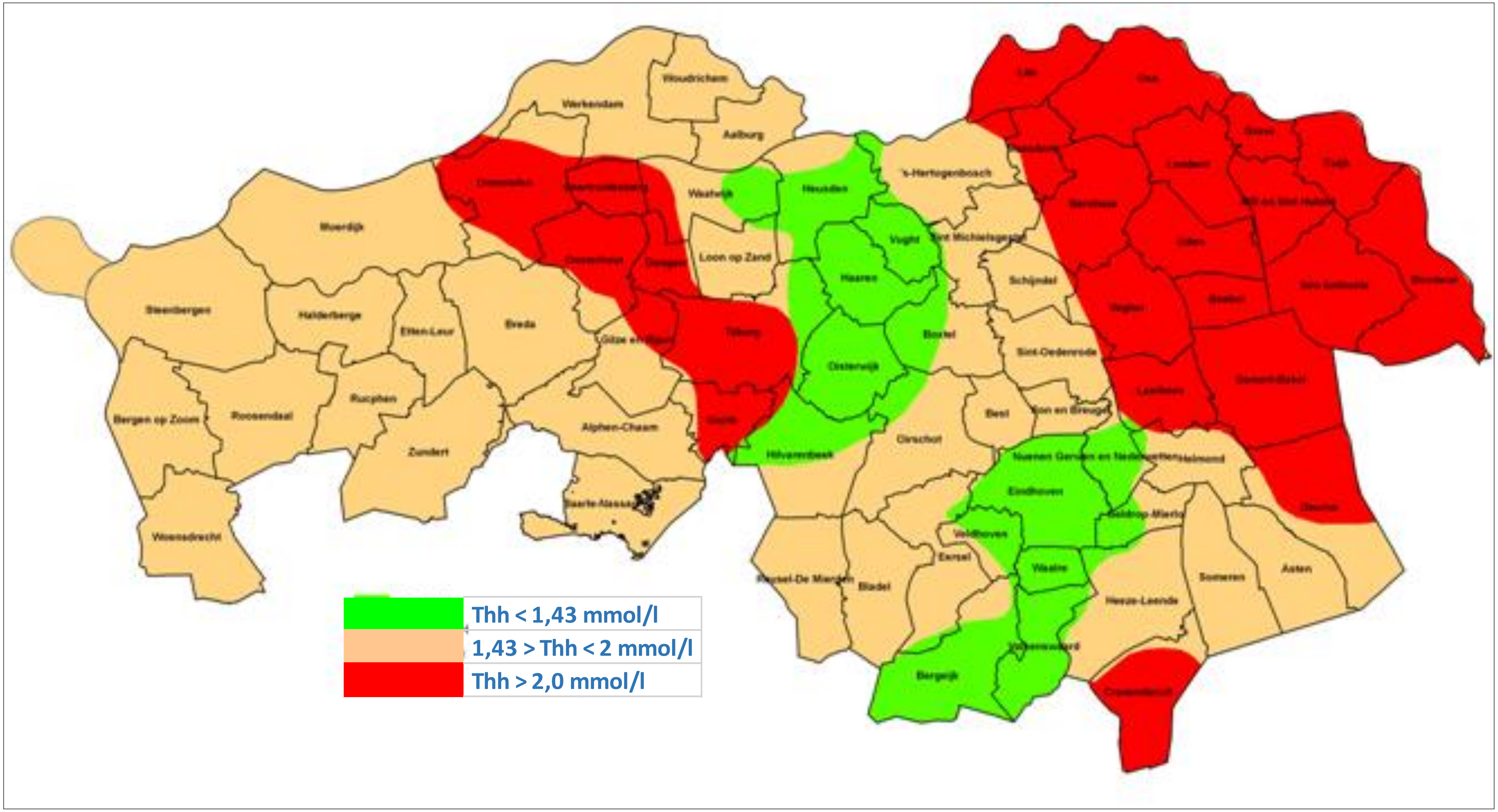
Treatment plant at Loosbroek

Build	1969, 2014 introduction softening
Abstraction Permit	8 mio. m^3 year
Capacity	1750 m^3/h
Storage	12.000 m^3

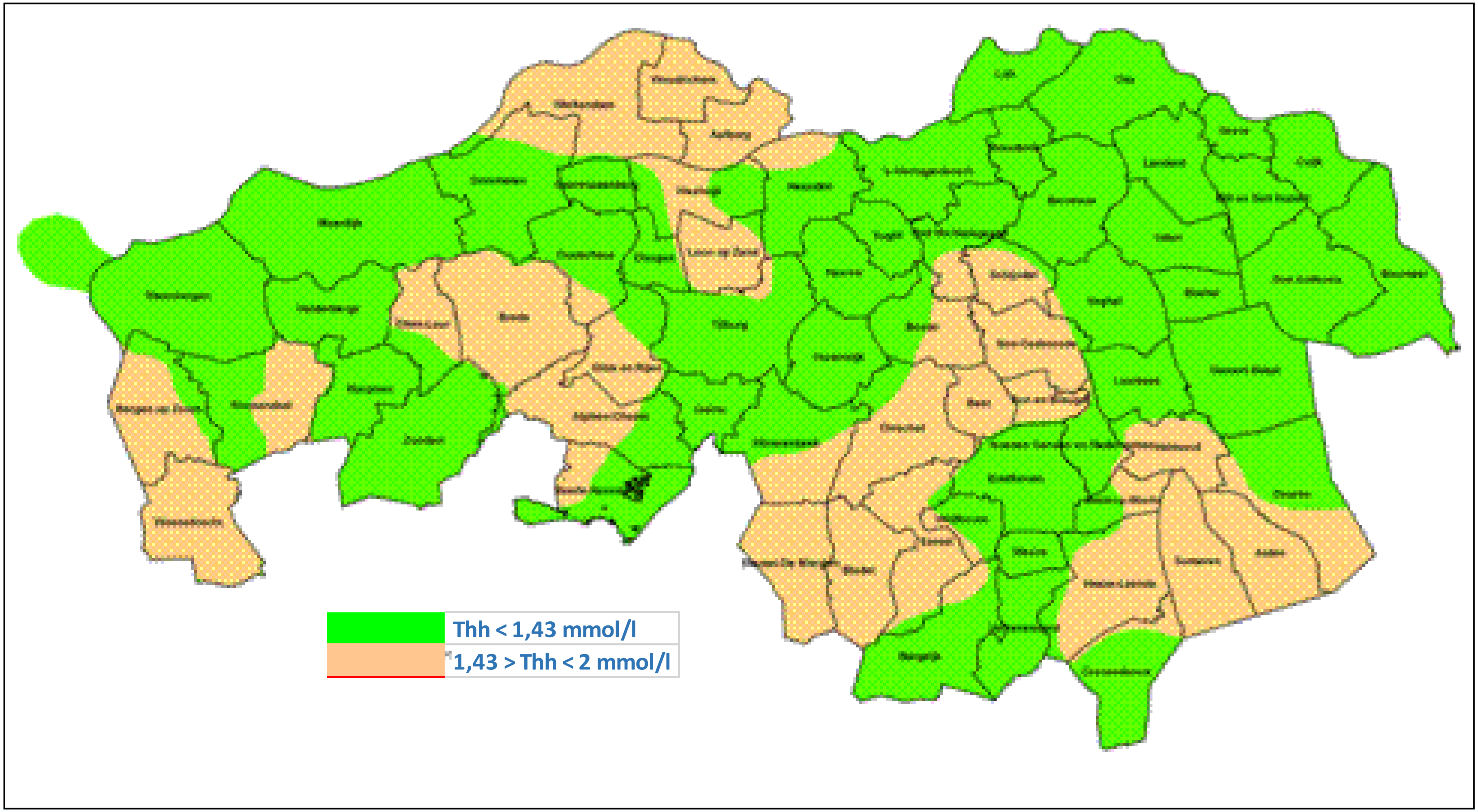
Process scheme



Total hardness 2010



Totale hardness 2018



brabant Water
Altijd. Overal.

Threat Chromium (VI)?

Health risk based “recommendations” for Cr(VI)

California Environmental Protection Agency
Office of Environmental Health Hazard Assessment

Public health goal: *0.02 µg/L* Cr(VI)

State of New Jersey
Department of Environmental Protection
Division of Water Supply and Geoscience

Estimated MCL: *0.07 µg/L* Cr(VI)

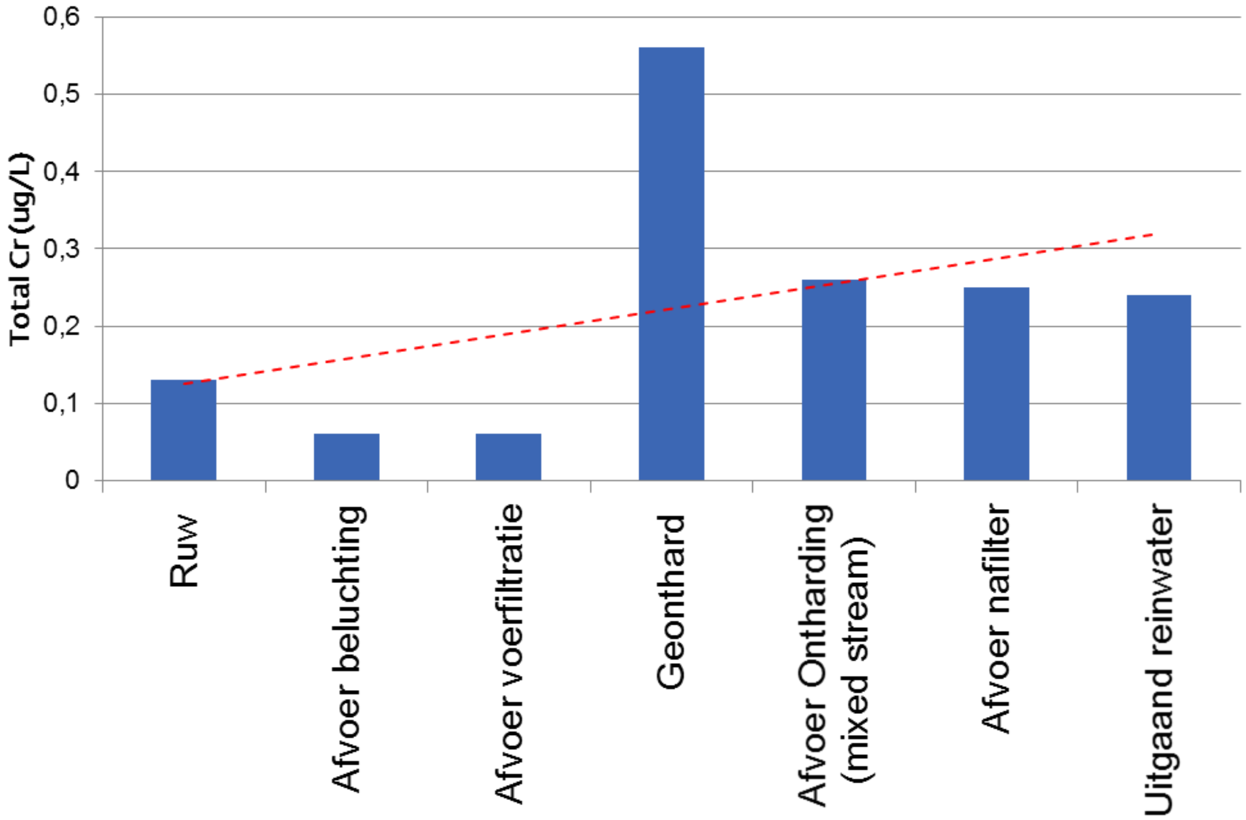
Federal Ministry of Health

Target level: *0.3 µg/L* Cr(VI)

Provisional Guideline: *0.2µg/L* Cr(VI)

Threat Chromium (VI)?

There's is an increase Cr^{VI} by dosing lime for softening



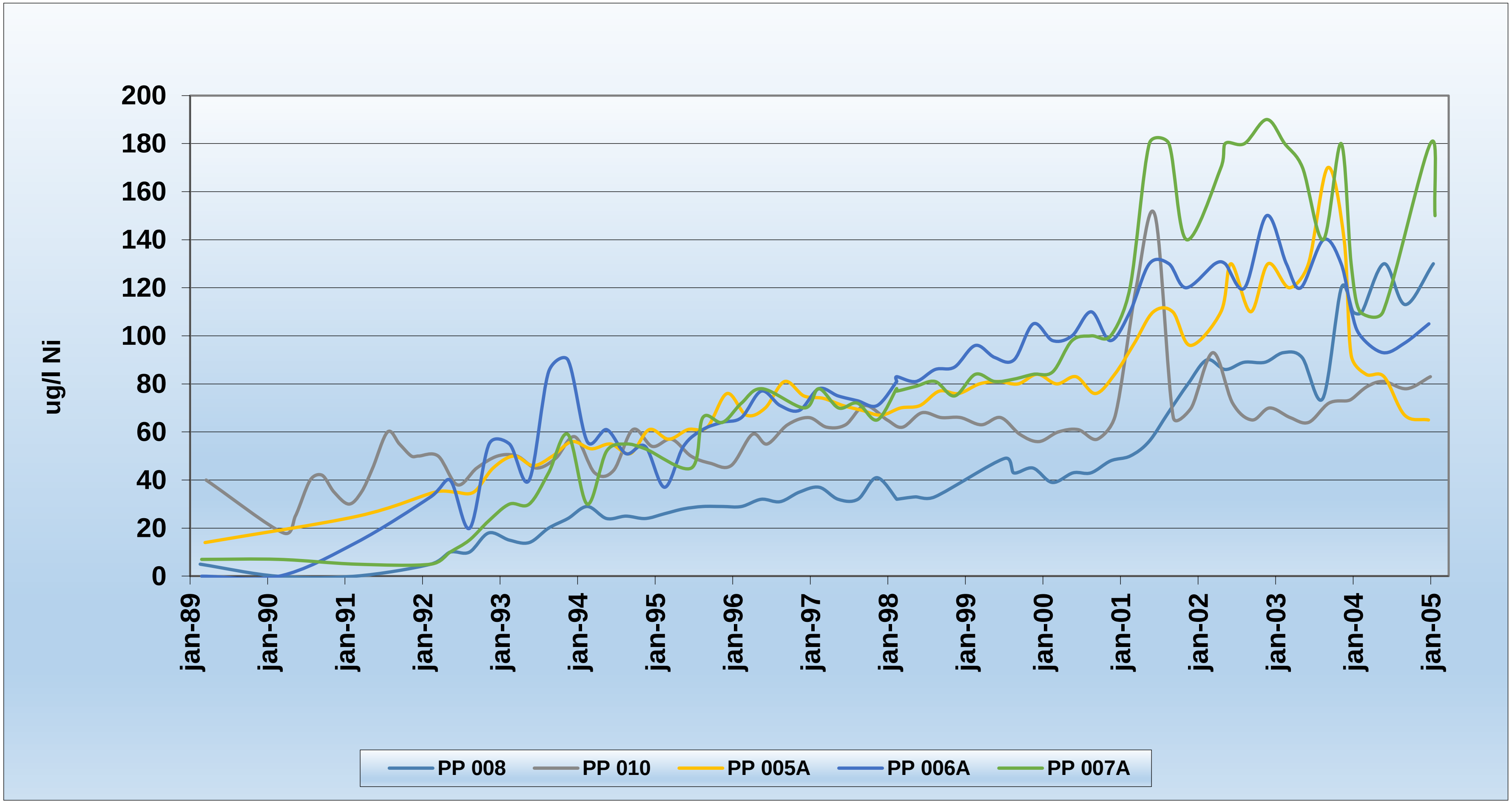
Health related metals

- Nickel
- Arsenic

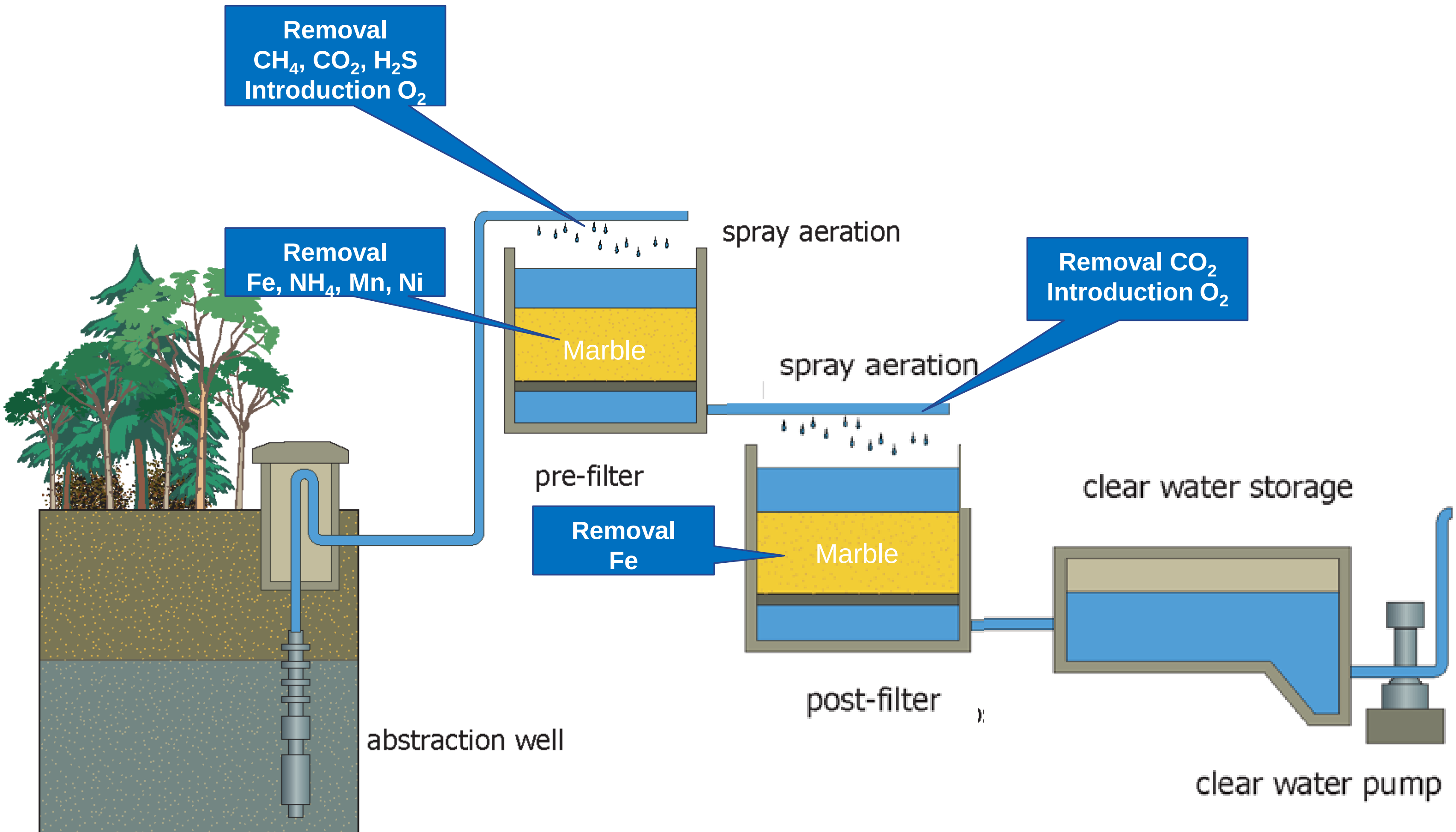
Nickel problems caused by Over-fertilization

- Decreased pH leads to geochemical processes
- Quality of groundwater changes. Acidification releases bounded nickel
- Nickel concentration at treatment plant Vierlingsbeek was increased

Nickel in groundwater wells

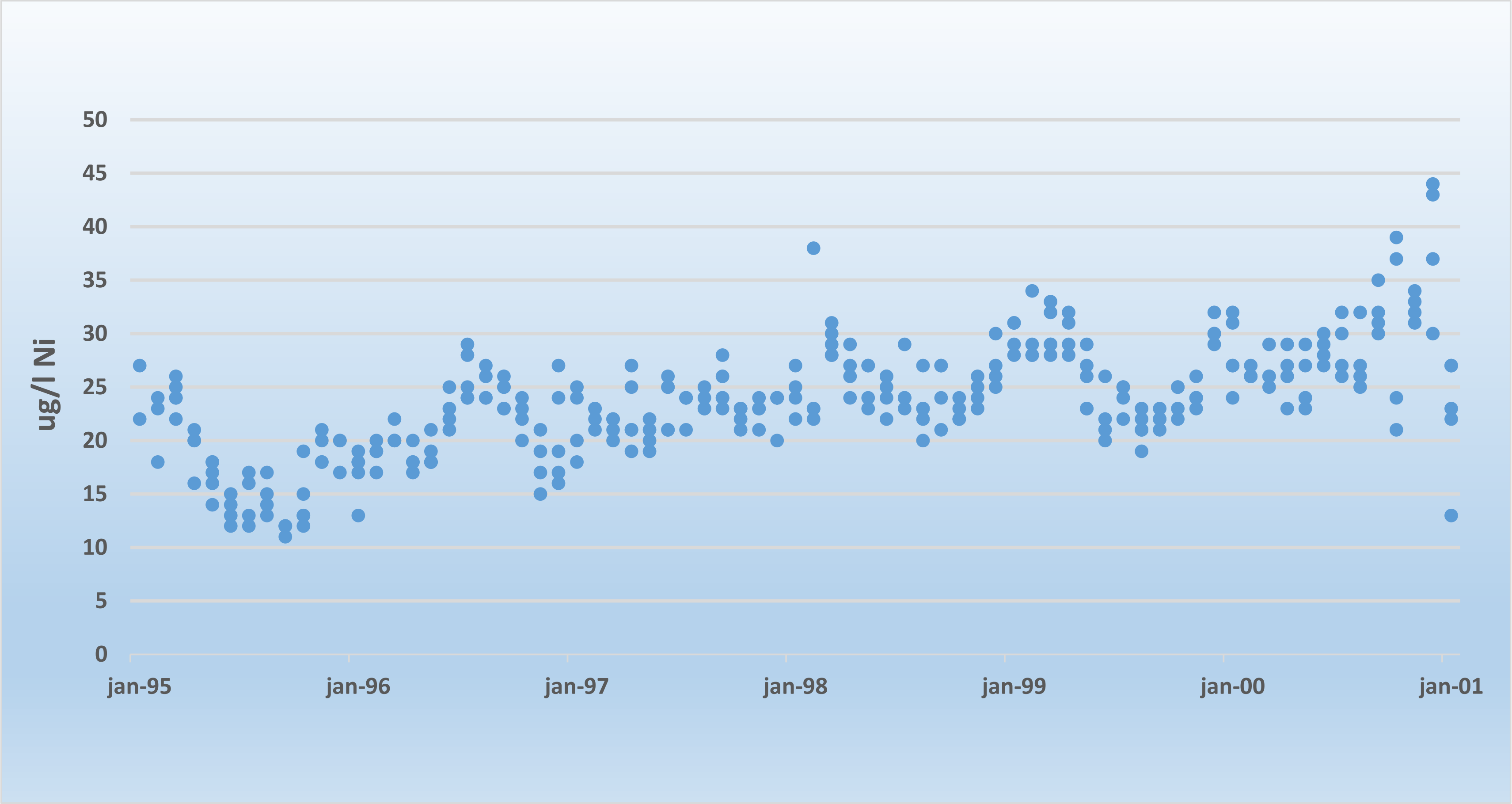


Treatment plant at Vierlingsbeek



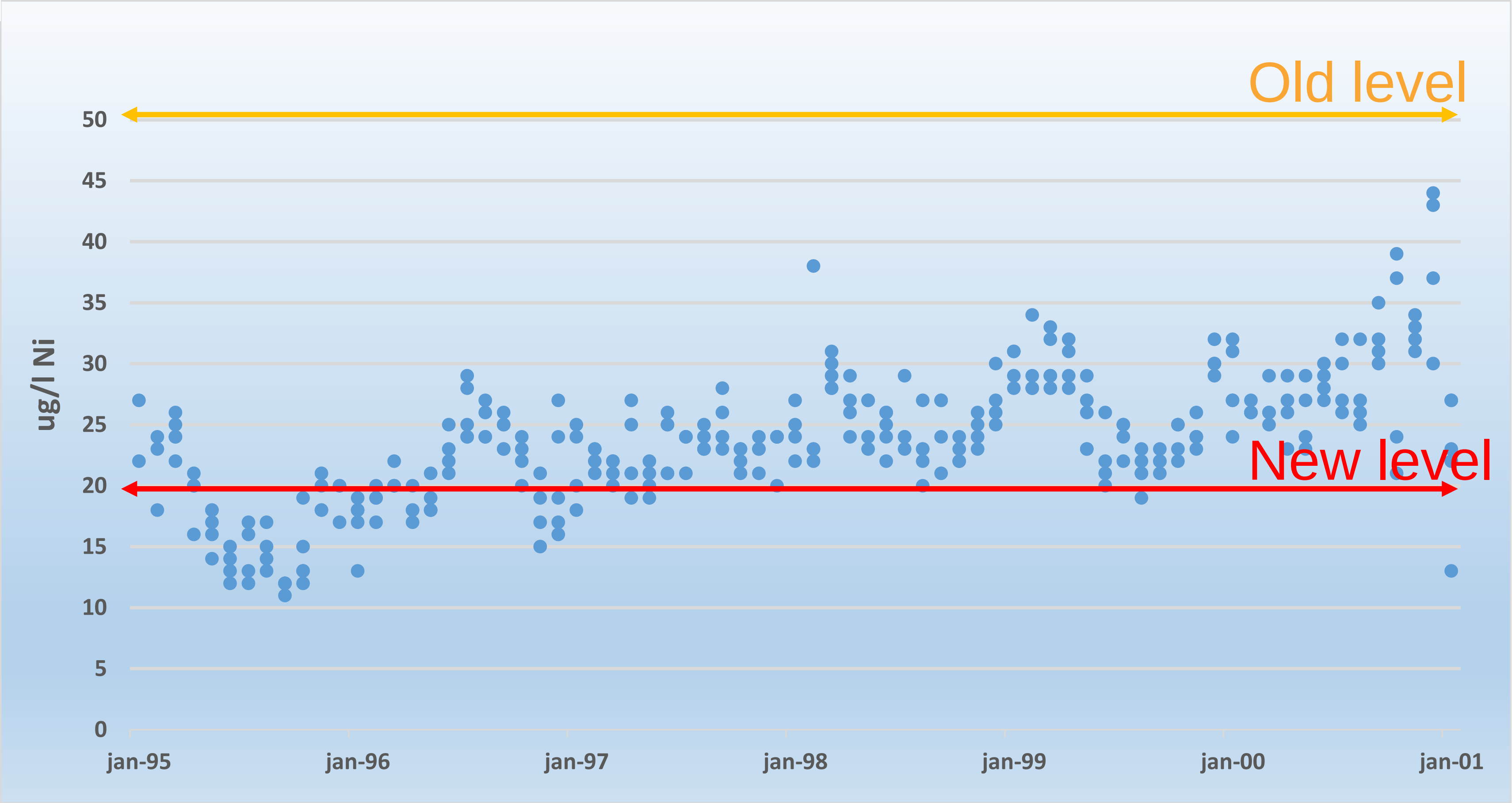
brabant Water
Altijd. Overal.

Nickel in drinking water (1)



Nickel in drinking water (2)

- Legal level nickel decreased from 50 to 20 ug/l (2002)
- Nickel in clear water would rise above the new legal level

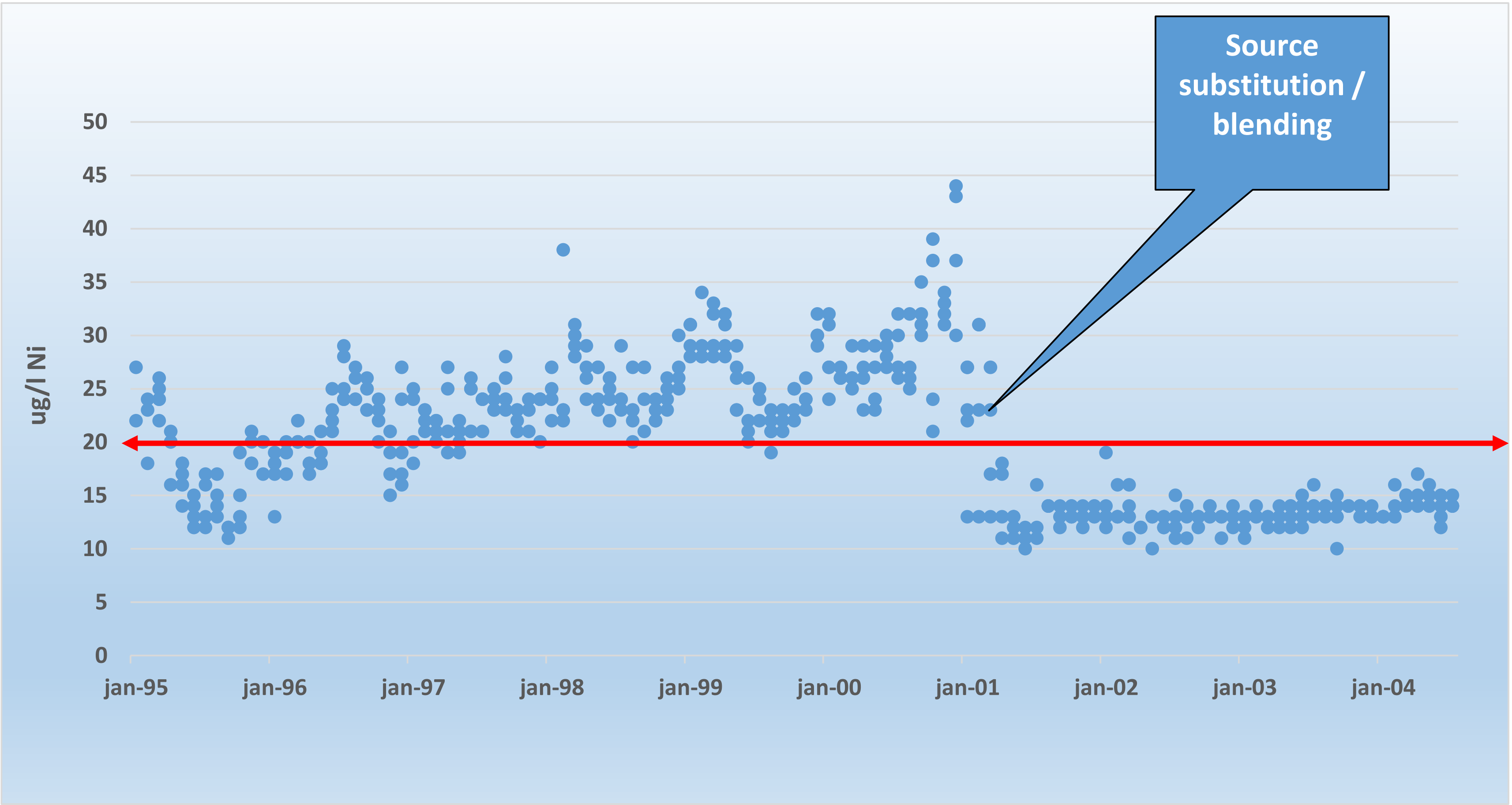


Managing the problem

Source substitution and/or blending

- Usage of groundwater wells with relative low nickel concentration
- Mixing clear water of WTP Vierlingsbeek with clear water having low nickel concentration from WTP Son

Source substitution and/or blending



brabant Water
Altijd. Overal.

Managing the problem

Research for a robuust Ni removal process

***Phase 1** literature*

- Nickel precipitates as $Ni(OH)_2$ at pH 9 – 10,- useful in case of pellet reactor.

***Phase 2** laboratory tests*

- Caustic soda to raise the pH. At pH > 8,2, than nickel removed to < 20 ug/l.
- Nickel adsorbes to formed manganese oxide.
- Conditioning of groundwater with NaOH, to pH >8,2, is not useful for Vierlingsbeek because of a reduced removal of **aluminium.**

Conclusion phase 2:

The <u>adsorption</u> of nickel to the manganese oxide formed by demanganization is promising for nickel removal.

Nickel removal from water

Demanganization?

Naturally in the first filtration step.

Could we introduce an extra de-manganization in the second filtration step?

Yes, we can !

It is possible to produce the extra manganese oxides by adding $MnCl_2$.

Theory

Morgan en Stumm (1964)

Graveland (1971)

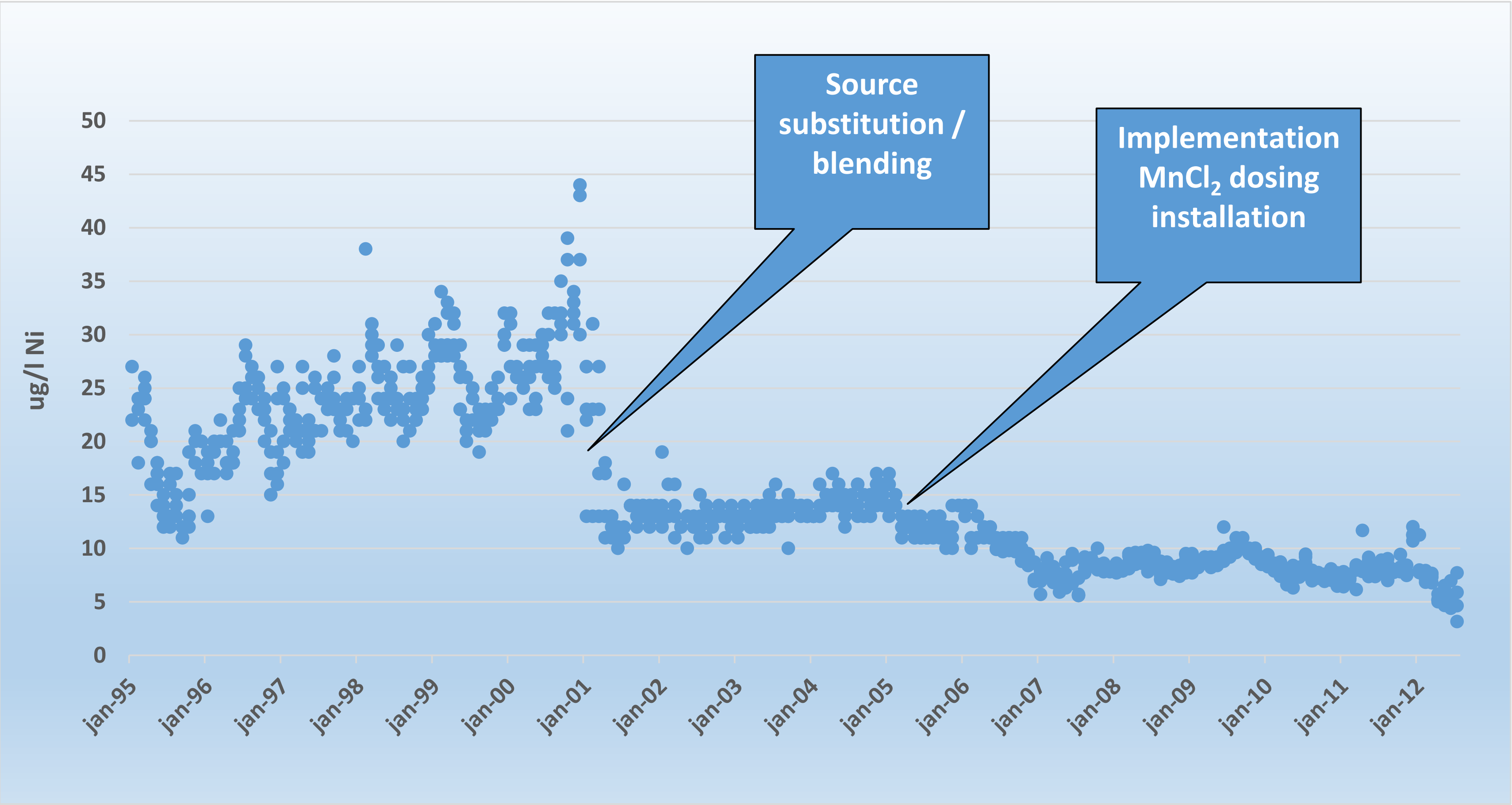
Adsorption of manganese to manganese oxide

$$-Mn-OH^0 + Mn^{2+} = -Mn_2O-Mn^{+} + H^{+}$$

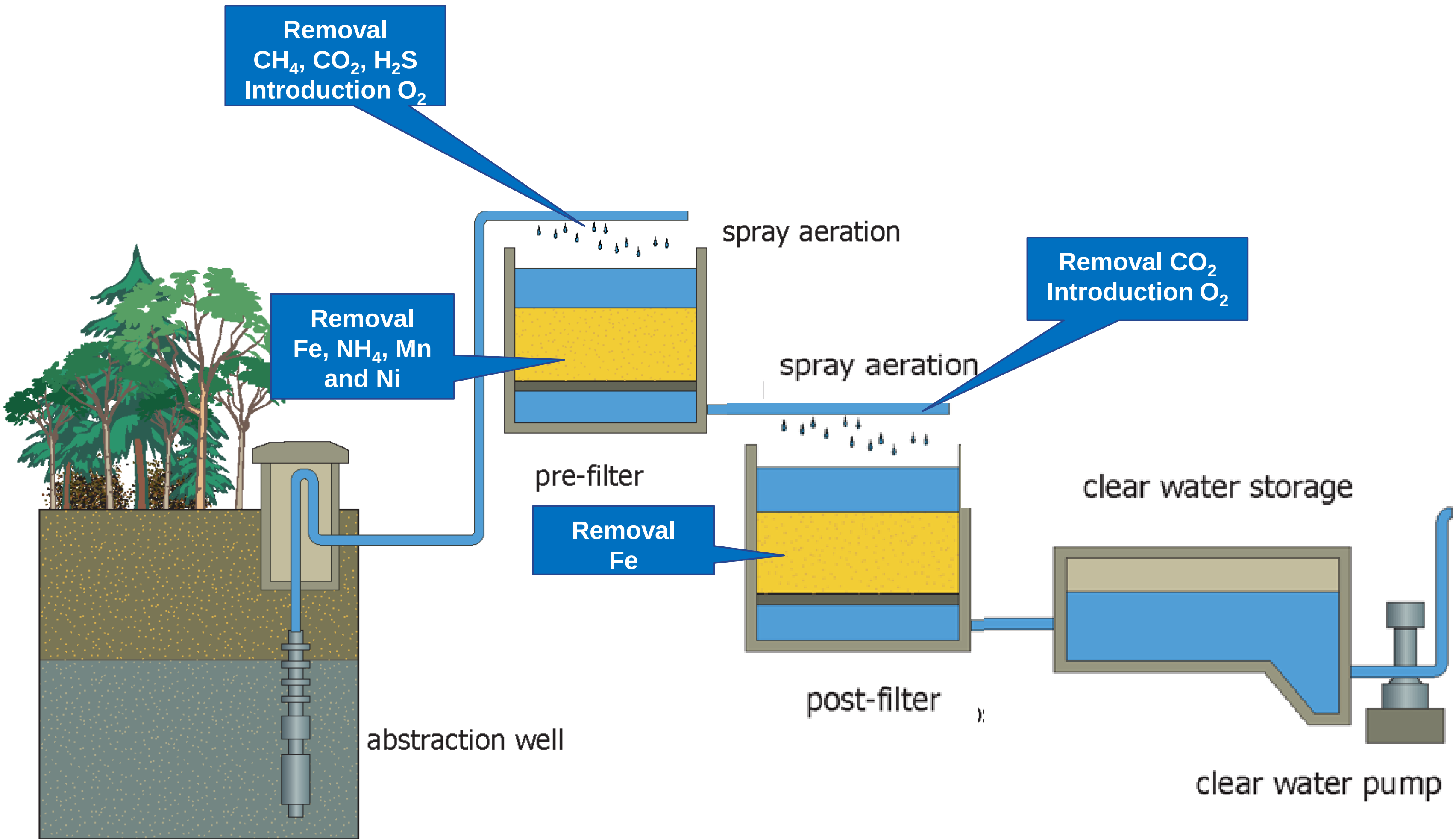
Contemporary: co-preciptation of nickel

$$-Mn-OH^0 + Ni^{2+} = -Mn_2O-Ni^{+} + H^{+}$$

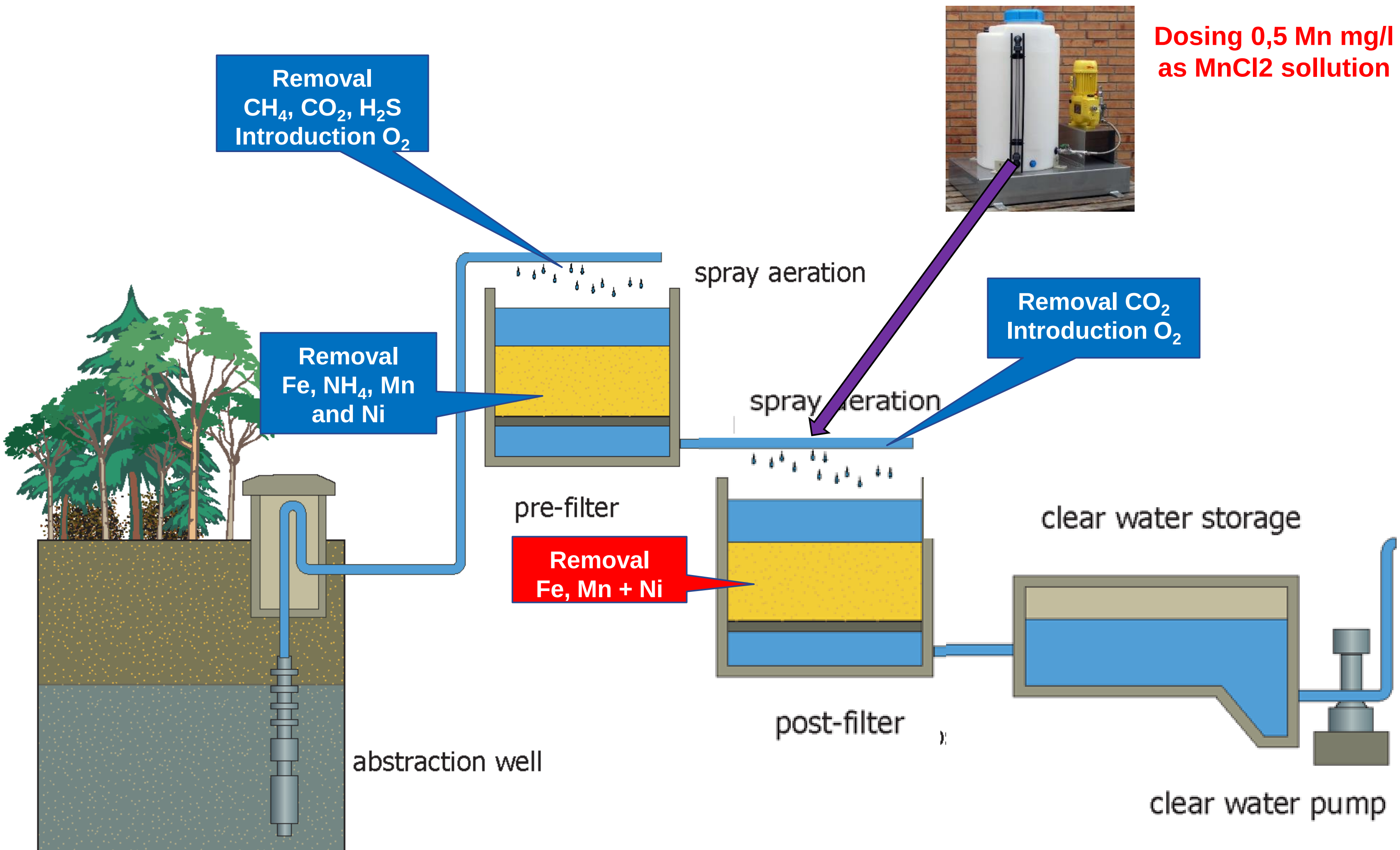
Results dosing $MnCl_2$



WTP Vierlingsbeek



WTP Vierlingsbeek



Treatmentplant at Vierlingsbeek

Build	1965 (Closed 2015)
Abstraction Permit	8 mio. m^3 year
Capacity	1200 m^3/h
Storage	3,600 m^3

brabant Water
Altijd. Overal.

Summary

- Source protection is essential to prevent metal pollution
- Aeration- rapid sand filtration is the simplest and robuust method for ground water treatment
- Pellet-softening is a Dutch innovation to remove calcium with small footprint
- Chemical preciptation with $MnCl_2$ is a smart technique to remove nickel
- Follow research and developments drinking water standards water quality parameters
    - Chromium VI
    - Borium
    - Arsenic
    - Nickel

brabant Water
Altijd. Overal.

Arsenic

GROUNDWATER TREATMENT FOR ARSENIC REMOVAL

Paper No. 35-2

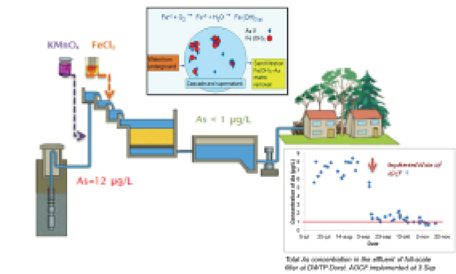
Arslan Ahmad

NOMINATIE BTO IMPLEMENTATIEPRIJS

AOCF voor verlaging arseen tot <1 µg/l

Indieners: Stephan van de Wetering (Brabant Water), Tim van Dijk (Brabant Water), Arslan Ahmad (KWR)

Juryoordeel: "De technologie in dit project is uniek. Het is een schoolvoorbeeld van een Speerpuntproject, waarbij een issue dat speelt bij één bedrijf wordt verdiept en versneld en vervolgens verder in de bedrijfstak wordt uitgezet."



Het AOCF-proces bij de drinkwaterproductieplant Dorst.

AOCF voor verlaging arseen tot <1 µg/l

Brabant Water onderzocht met KWR in het Speerpuntonderzoek hoe arseen uit grondwater kan worden verwijderd op locaties waar de gevonden concentraties hoger zijn dan 1 µg/l. Dat bleek mogelijk te zijn door Advanced Oxidation Coagulation Filtration (AOCF) toe te passen. Met behulp van $K/NaMnO_4$ wordt As(III) geoxideerd naar As(V), vervolgens hecht arseen zich aan de ijzervlokken en worden deze vlokken afgevangen in het zandfilter. Brabant Water heeft inmiddels het AOCF-concept geïmplementeerd op Waterproductiebedrijf Dorst om het arseen te verlagen van 5,5 naar <1 µg/l. Ook Waterproductiebedrijf Prinsenbosch voldoet met 2,7 µg/l arseen niet aan bedrijfsnorm van <1 µg/l arseen. Samen met KWR zijn op basis van bench-scale experimenten en pilotonderzoek de technologische uitgangspunten vastgesteld voor verlaging van het arseen op Waterproductiebedrijf Prinsenbosch met het AOCF concept. Het programma van eisen voor de arseenverwijdering voor WPB Prinsenbosch is inmiddels gereed. Voor Waterproductiebedrijf Oosterhout loopt een pilotonderzoek naar de implementie van AOCF voor eenzuivering inclusief pelletontharding.

Andere waterbedrijven

Het AOCF-concept is ook toepasbaar bij andere (water)bedrijven. Het DPWE-project voor implementatie van het AOCF-concept op Waterproductiebedrijf Katwijk, Ouddorp en Leiduin is in de basis een spin-off van de bevindingen van het Brabant Water-onderzoek. Op 18 februari jl. heeft Brabant Water een miniworkshop gehouden om kennis over het AOCF-concept te delen met Dunea en Waternet.

Internationale belangstelling en toepassing

Het technologisch AOCF-basisconcept kan breed ingezet worden op de arseen probleemgebieden in de wereld. Het is robuust en kan ook hogere concentraties arseen verwijderen. De ontwikkelde AOCF-technologie is gepubliceerd in Water21 (oktober 2014) en heeft een hoofdstuk gekregen in de IWA Best Practice Guide on Control of Arsenic. Het Turkse waterbedrijf MASKI bezoekt in juni KWR en Brabant Water om te bespreken of AOCF geschikt is om hun arseenproblemen aan te pakken. Er is ook belangstelling uit India en Bangladesh.

In juni 2016 presenteert Brabant Water een keynote speech over de AOCF technologie op het 6th International Congres on Arsenic in the Environment (As2016) in Stockholm (Zweden). Toepassing van de techniek laat zien dat de Nederlandse watersector vooruitloopt op de tot op heden praktische onderbouw de WHO-arseennorm van 10 µg/l.

V.l.n.r. Stephan van de Wetering (Brabant Water), Tim van Dijk (Brabant Water), Arslan Ahmad (KWR)

KWR Watercycle Research Institute

Thank you for your attention

Any question?

More information:

Stephan.van.de.wetering@brabantwater.nl