National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Sulphate, a new potential threat to the quality of surface water and groundwater

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Sub-title

DO WE CREATE A NEW PROBLEM

BY SOLVING AN EXISTING ONE

OR

REGULATE

OR LEAVE IT TO THE MARKET

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Contents

1. Introduction

Acidification of the environment

Important causes: atmospheric emissions of
SULPHUR and NITROGEN

Reduction of S-emissions successful:

In NL: deposition of S dropped from 80 kg ha^{-1} yr^{-1} (1980)
to les than 10 kg ha^{-1} yr^{-1}

Crop requirement of sulphur: 20 – 40 kg ha^{-1} yr^{-1}

Result: sulphur soil-deficiency for some crops

1. Introduction

Reduction of N-emissions less successful

In NL agricultural sector important source (40%) of acidifying emissions

Important sources of ammonia:

- Volatilisation of ammonia from manure (in storage and applied on land)
- Ammonia emission from stables in industrial livestock farming

2. Recent developments

Reduction of ammonia emissions by:

- Lower pH in manure; stabilisation of ammonia
- Treatment of air from stables, in air scrubbers

Common process: Mix ammonia with sulphuric acid:

$$2NH_3 + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4$$

When applied as fertiliser:

$$(NH_4)_2SO_4 + 4O_2 \rightleftharpoons 2NO_3^- + SO_4^{2-} + 4H^+ + 2H_2O$$

- New resource to compensate for sulphur deficiency in soils!
- Increased N-efficiency

3. Methodology

Subject of study:

Impacts on water quality of the large scale use of sulphur-enriched fertiliser / waste products

Methodology

assessment of:

- water quality base line conditions
- scenarios for using sulphur enriched fertiliser (waste products)
- impacts on water quality

4 Sulphate in water leaching from root zone: status 2009-2011

Peat and clay; rich in sulphate due to presence marine deposits

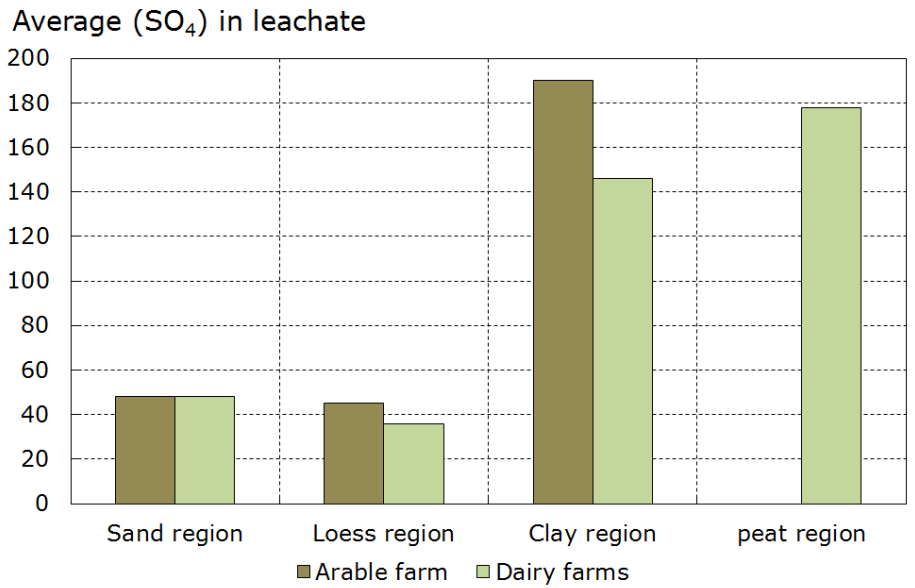
Water quality on farms:

(SO_4) -leachate **sand**: 48 – 62 mg/l
ditches sand: 43 – 87 mg/l

-leachate **clay**: 111 – 190 mg/l
ditches clay: 76 – 156 mg/l

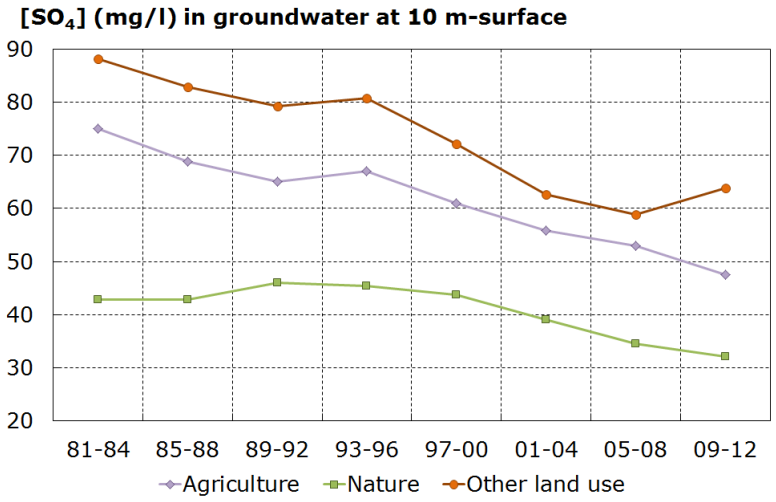
-leachate **peat**: 178 mg/l
ditches peat: 104 mg/l

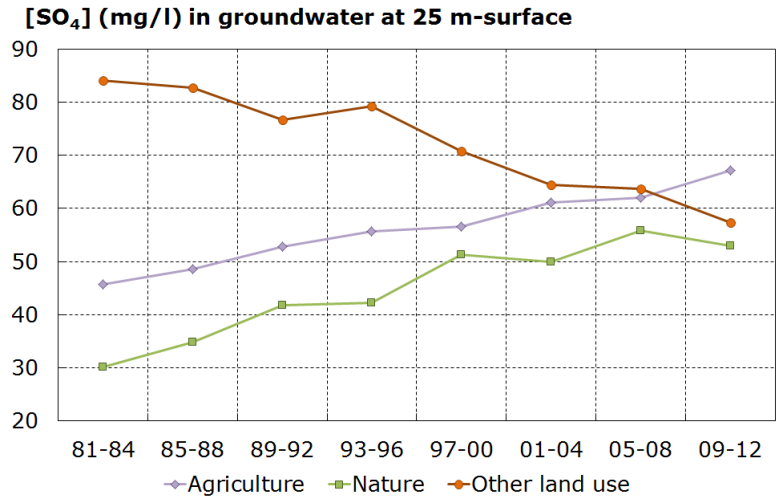
-leachate **loess**: 36 – 45 mg/l

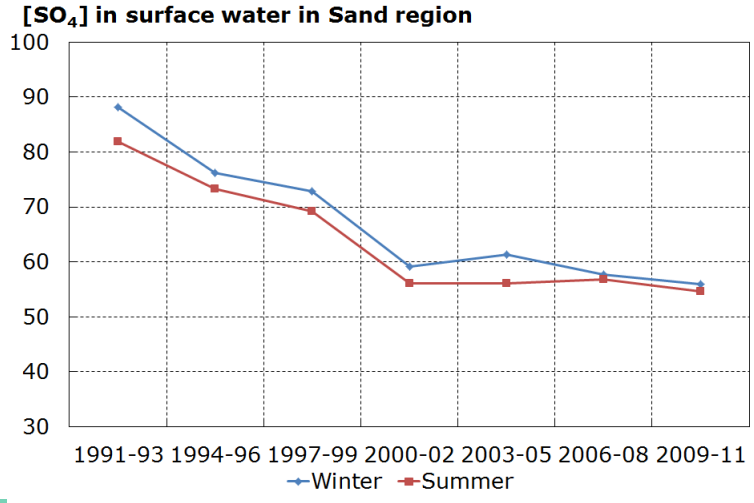


On sand and loess impacts of reduced deposition most clearly visible

4 Sulphate in groundwater and surface water: evolution.







5 Scenarios and impacts - General

Assuming a rainfall surplus of 300 mm/year,

Deposition of 1 kg S ha^{-1} yr^{-1}will ultimately result in $[SO_4]$ increase in ground water and surface water of 1 mg/l

<u>Considerations</u>:
In Dutch regulations:

- No standards for $[SO_4]$ in soil
- Guideline for groundwater: maximum $[SO_4]$ 150 mg l^{-1}
- Target value $[SO_4]$ (max.) in surface water: 100 mg l^{-1}

- Water Framework Directive: no ceiling, but general guideline to limit or avoid input of polluting substances.

5 Scenarios and impacts

Acidification of manure with sulphuric acid

N application maximised by EU- Nitrate Directive:

170 kg N ha^{-1} yr^{-1} (or 250 kg N ha^{-1} yr^{-1} with derogation)

N/S ratio for stabilisation: 1.24

170 kg N ha^{-1} yr^{-1} requires **137 kg S** ha^{-1} yr^{-1} → $[SO_4]$:137 mg/l
250 kg N ha^{-1} yr^{-1} requires **202 kg S** ha^{-1} yr^{-1} → $[SO_4]$:202 mg/l

Residual liquid from chemical Air scrubbers

Production by 2010 estimated at 3.9 Kt NH_3-N yr^{-1}

Requiring: 4.5 Kt S yr^{-1} (N/S ratio: 0.87)

Spread over:

- All agricultural land: deposition **2.2 kg S** ha^{-1} yr^{-1}
- On factory livestock farms only: deposition **44 kg S** ha^{-1} yr^{-1}

6. Scenarios and impacts: result

Acidification of manure:

- S-application beyond plant S-requirement
- [SO_4] in groundwater / surface water above guideline/target value
- impact on national scale.
- Formation of sulphides in surface water
- Increased risk of eutrophication
- Not in accordance with objectives of WFD

Residual aqueous waste of Air scrubbers:

- potentially local problem.
- No problem if its use spread over large area

6. Conclusions

Acidification of manure with sulphuric acid (mitigating the problem of ammonia-emissions) can cause high sulphate concentrations in groundwater and surface water, with consequent ecological problems in surface water

If application of S-enriched manure accepted, amounts of sulphur should be regulated / maximised.

THANK YOU

ANY QUESTIONS / REMARKS

Context

Problem: **Acidification of the Environment**

Measures: Reduction of Atmospheric emissions

- sulphur
- nitrogen

Impacts:

- sulphur deficiency soils → demand sulphur
- Ammonia sulphate as waste product/fertiliser → Availability of sulphur containing fertiliser

demand sulphur ⟺ Availability of sulphur containing fertiliser

Question: impacts of using sulphur enriched fertiliser

3 Sulphate in natural waters. **Material & Methods**

Assessment of present situation and past evolution of sulphur in surface water and ground water. Collection and analyse data on sulphate in

- leachate from the root zone (top 1 m of groundwater) + ditch water (since 1992, at 100 to 650 farms)
- Ground water at 10 and 25 m below ground level

  (since 1980, at 398 locations scattered across the country)
- Surface water

  (since 1991, at 800 – 3,000 locations in local and regional waters in summer and winter)

Distinction between soil regions.
Clay and peat soils different from sand and loess soils

Reduction of emissions of NH_x

Important culprit for emissions: production of manure & emissions from factory livestock farming

Lowering of pH in manure to stabilise NH_x, by adding H_2SO_4

Air scrubbers: removing ammonia from stables

Common process:

$$2NH_3 + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4$$

When applied as fertiliser:

$$(NH_4)_2SO_4 + 3O_2 \rightleftharpoons 2NO_2^- + SO_4^{2-} + 4H^+ + 2H_2O$$

$$NO^{2-} + \tfrac{1}{2}O_2 \rightleftharpoons NO_3^-$$

Reduction of emission and deposition of SO_x

Success-story

- Conversion from coal/oil to gas
- Desulphurisation of flue gas
- Increased fuel efficiency

Year	Emission Tons SO_2/year	Deposition kg S/ha
1965	1,000,000	
1980	490,000	82
2010	40,000	10

On the down-side:

S-deficiency in certain soils for certain crops
Normal crop requirement 20 – 40 kg S/ha

4 Scenarios and impacts

Application of gypsum from flue gas desulphurisation for soil improvement

Rate: 2.5 – 10 T gypsum ha^{-1}
corresponding to: 460 – 1,840 kg S ha^{-1}

Principal use on clay soils in young polders

General risks

- Risk of sulphide in surface water
- Dissolution of phosphates from bottom sediment
- Increased risk of eutrophication

- Low pH – impact on plant growth, soil biota, leaching and availability of elements in the soils
- Neutralisation with e.g. $CaCO_3$ (resulting in increased CO_2 emissions).

Assuming:

Agricultural area: 2 x 10^6 ha

N-content: 8 kg/ton

application: 40 T manure/ha

i.e. 320 kg N/ha