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Acidification and eutrophication, 1989 – 2010

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Abstract

Changes in rainwater and groundwater quality as a result of atmospheric emission reductions. Acidification and eutrophication, 1989 – 2010.

During the eighties of the previous century acid rain was regarded as an important environmental issue and received ample attention. Forests died and organisms disappeared from rivers and lakes. Air pollution was identified as the cause of acid rain. Atmospheric emissions from industry, traffic and agriculture contain nitrogen and sulphur. These substances are transported through the atmosphere and reach the ground elsewhere, causing acidification and eutrophication of soil and water. This process adversely affects the quality of soil, water and biodiversity.

Measures taken at the international level to reduce the emission of nitrogen and sulphur appear to have yielded results. RIVM studies show that acidification is still ongoing at most monitoring locations in the Netherlands, but at a slower pace than before. Because of the reduced emissions, rainwater quality has improved between 1989 and 2010. Consequently, less nitrogen and sulphur now reaches the ground. This has a positive impact on shallow groundwater: the amount of nitrogen and sulphur has dropped by tens of per cents.

The current study is the first extensive analysis of the data collected within the framework of the National Acidification Trend Monitoring Network. This network, established in 1989, focuses on forested natural areas with sandy soils. The network monitors the impact of atmospheric deposition of acidifying and eutrophying substances on the groundwater quality at 150 locations in the Netherlands.

The literature shows that, despite the positive developments, ecosystems have not yet recovered from the acidifying and eutrophying impacts of air pollution. The eutrophication of nature areas in the Netherlands, induced by the atmospheric deposition of nitrogen, is still a major threat to plant species diversity. At two thirds of the locations investigated, deposition still exceeds the critical load. Acidification also poses a problem, but a less pressing one.

Keywords:
acidification, rainwater quality, leaching, groundwater quality, sandy soil

Publiekssamenvatting

Veranderingen in regen- en grondwaterkwaliteit als gevolg van atmosferische emissiereducties. Verzuring en vermesting, 1989 – 2010

In de jaren tachtig van de vorige eeuw stond ’zure regen’ als milieuprobleem sterk in de belangstelling. Bossen stierven erdoor af en organismen verdwenen uit rivieren en meren. Zure regen bleek te worden veroorzaakt door luchtvervuiling. De door industrie, verkeer en landbouw uitgestoten gassen bevatten stikstof en zwavel. Deze stoffen komen via de lucht elders op de bodem terecht, waardoor de bodem en het water verzuren en vermesten. Dit heeft een negatief effect op de kwaliteit van de bodem en het water, en op de biodiversiteit.

De maatregelen die internationaal zijn genomen om de uitstoot van stikstof en zwavel te verminderen, blijken hun vruchten af te werpen. Onderzoek van het RIVM laat zien dat op de meeste meetlocaties in Nederland nog wel sprake is van verzuring, maar minder sterk dan voorheen. Door de lagere uitstoot is de regenwaterkwaliteit tussen 1989 en 2010 verbeterd. Er komt daardoor nu minder stikstof en zwavel op de bodem terecht. Dit werkt in positieve zin door op het bovenste grondwater: de hoeveelheid stikstof en zwavel is met tientallen procenten gedaald.

Het voorliggend onderzoek is een eerste uitgebreide analyse van de meetgegevens van het TrendMeetnet Verzuring (TMV), dat in 1989 is opgezet in natuurgebieden op zandgrond. Het meetnet monitort op 150 locaties in Nederland de invloed van de neerslag van verzurende en vermestende stoffen uit de lucht op de kwaliteit van het grondwater.

Uit een literatuurstudie blijkt dat ondanks de positieve ontwikkelingen de ecosystemen nog niet zijn hersteld van de verzurende en vermestende effecten van luchtvervuiling. De vermesting door de neerslag van stikstof op de bodem in de Nederlandse natuur is nog altijd een van de grootste bedreigingen voor de variatie aan plantensoorten: bij tweederde van de onderzochte gebieden overschrijdt de depositie de norm. Verzuring is ook problematisch, maar in mindere mate.

Trefwoorden:
verzuring, regenwaterkwaliteit, uitspoeling, grondwaterkwaliteit, zandgrond

Content

Summary

Introduction
During the seventies and eighties of the previous century, the phenomenon of acid rain was at the centre of public and political interest. Acid rain was associated with forest dieback in parts of Central Europe and Scandinavia and the disappearance of aquatic life from rivers and lakes. Air pollution was identified as the cause of acid rain. Atmospheric emissions from industry, traffic and agriculture reach the ground elsewhere. Excessive deposition of nitrogen and sulphur induces acidification and eutrophication of the soil. This process adversely affects the quality of soil, water and biodiversity.

Policy framework
As air pollution is a transboundary phenomenon, international agreements have been reached on how to address the issue. The ’Convention on Long-Range Transboundary air Pollution’ (CLRTAP) has been in force since 1983. All European countries, the European Commission, the USA and Canada have signed this convention. More specific agreements have been formulated in a number of different protocols. In compliance with the Gothenburg Protocol, the Netherlands has taken various policy measures to limit air pollution (emissions).

National Acidification Trend Monitoring Network
The National Acidification Trend Monitoring Network (TMV) was established in 1989. This network monitors the impact of the atmospheric deposition of acidifying and eutrophying substances on groundwater quality. It also monitors the quality of the upper metre of the groundwater under nature areas (forest and heath) with sandy soils. Other than influx from the air, these areas have no other significant sources of acidifying or eutrophying substances, which are responsible for contaminating the groundwater. Sandy soils have a limited capacity to neutralise the effects of acidification. This is why the impacts of atmospheric deposition on groundwater quality and the effects of emission-reducing measures can be measured most effectively in nature areas with sandy soils.

This report comprises the first extensive trend analysis of this monitoring network since it was founded in 1989. We describe the changes in groundwater quality as measured at 150 TMV sampling sites in the Netherlands. To relate the monitoring results to emission-reduction measures, we have compared the groundwater monitoring data with data on emission trends (derived from earlier studies) and concentrations in rainwater (National Air Quality Monitoring Network). In addition, we investigated whether changes in shallow ground water quality could be retraced in deeper groundwater (10 m below the surface, National Groundwater Quality Monitoring Network).

Results
Our analysis of the network data shows that rainwater quality and groundwater quality in nature areas have improved significantly over the past 20 years. The impacts of lower emissions of nitrogen and sulphur are also found in rainwater, shallow groundwater (leachate from the root zone) and groundwater at 10 m below the surface:

- In 2010 the N concentration in rainwater decreased by 39% compared to 1988, while the S concentrationS concentration dropped by 73% during the same period;

- The concentrations of N and S in the upper groundwater decreased by 56% and 59% between 1988 and 2010;
- N and S concentrations also declined in deeper groundwater, but to a lesser degree.

In 2010 the pH and ANC were significantly higher than in 1989, and the aluminium concentration was significantly lower ($\alpha < 0.05$). Despite the increase, the ANC was still negative at 80% of the monitoring locations in 2010. This implies that acidification is still in progress but at a slower pace.

Previous research (Buijsman et al., 2010) shows that the emissions of sulphur and nitrogen by industry, traffic and agriculture have diminished due to policy measures and autonomous developments like the transition from coal to natural gas. According to the present research, lower emissions of nitrogen and sulphur are accompanied by less deposition of these acidifying and eutrophying substances on the surface. The current study also demonstrates that less deposition of these substances is reflected in a better groundwater quality.

The RIVM findings mentioned above are in line with research results in other countries.

Effects on ecosystems
Scientific literature shows that, despite the positive developments, ecosystems have not yet recovered from the acidifying and eutrophying effects of air pollution. Recent research has been conducted in the UK into the effects of diminishing acid deposition on the biodiversity in surface water. At each research site where biota were found to be recovering, the ANC of the water also proved to be on the rise. However, not all sites with a rising ANC showed signs of biological recovery. Research shows that biological recovery proceeds at a slower pace than the recovery of abiotic conditions. Furthermore, simulations up to 2050 indicate that, under the Gothenburg Protocol, surface water quality will continue to improve (i.e. the ANC will continue to rise). However, the buffering capacity of the soil will only recover slowly and only at a limited number of sites. It is also expected that the ecology will only recover slowly.

According to research done in the Netherlands, the eutrophying deposition of nitrogen in Dutch nature areas is still one of the biggest threats to plant diversity. At two thirds of the sites investigated, the nitrogen deposition exceeded the critical threshold. Nitrogen deposition remains a persistent problem for most locations, especially the Veluwe, the Utrechtse Heuvelrug and the coastal dune areas. Acidification is a limiting factor to ecological recovery as well, but to a lesser extent.

1 Introduction

1.1 Acidification

The environmental effects of atmospheric deposition of acidifying substances were first recognised in the nineteen eighties (Buijsman et al., 2010; Goffau et al., 2009). These effects were initially attributed to what is called ‘acid rain’. Acid rain is one of the causes of acidification. Various definitions are in use for the phrase ’acidification’. This report uses the term ’acidification’ in the following sense:

> *Acidification is interpreted as the damaging effect of acid-forming substances on the environment, whether or not in combination with ozone. Acidification results from air pollution that is directly or indirectly caused by acidifying substances such as nitrogen oxides (NO_x), sulphur dioxide (SO_2), which produces nitric acid and sulphuric acid, and ammonia (NH_3). Agriculture, industry and traffic are the principal sources of acidifying substances. These acidifying substances enter into the environment either by precipitation or as dry deposition.*

The supply of acidifying substances from the atmosphere to the soil has a wide range of effects (Buijsman et al., 2010). High concentrations of acidifying substances are poisonous to lichen and plants. In addition, the supply of acidifying substances may cause soil acidification.

‘Potential acid’ is defined as the maximum degree of acidification that can be caused in soil and water by sulphur dioxide, nitrogen oxides and their reaction products. The actual levels of acidification in soil and water can be lower as a result of the co-deposition of alkaline substances and anion uptake by plants. A substance’s acidifying capacity is usually expressed in ’acid equivalents’ per surface area. An acid equivalent is a measure of the amount of acid (H^+ in mol/ha) which can be generated in soil or water. The following applies in this definition:

- 1 mol of sulphur dioxide produces 2 moles of acid;
- 1 mol of nitrogen oxide produces 1 mol of acid;
- 1 mol of ammonia produces 1 mol of acid.

and:

Potential acid (eq) = 2 SOx + NOx + NHx.

Often, soil acidification is not immediately accompanied by an increase in acidity (i.e. a lower pH). Soils contain substances such as calcium carbonate, clay, humus and aluminium oxides. These substances form a buffer against acidification. As a result, cations and aluminium dissolve into the soil moisture. The addition of more acid causes a decrease in the buffering capacity. As long as there are buffering substances, the pH does not change significantly. However, the soil chemistry does change. This causes the leaching of calcium and magnesium into deeper groundwater and prevents plants from reaching these nutrimental elements. At low pH values, aluminium and heavy metals may also leach into the groundwater. These changes in soil chemistry may have all sorts of impacts on humankind and the ecosystem (Buijsman et al., 2010). Due to soil acidification, water leaching from the root zone contains relatively more alkaline cations and aluminium and relatively fewer anions than the deposition does.

Leachate in lime deficient soils in nature areas has a relatively high aluminium content, as is the case at the TMV sampling locations.

In order to assess the degree of acidification, TMV monitors the nitrogen and sulphur concentration in groundwater as well as its aluminium content and alkaline cation concentrations (sodium, potassium, calcium and magnesium). These elements affect the buffering process. The sum of cations minus the sum of anions is used as a measure for the alkalinity of groundwater. The literature often uses the term ‘acid neutralising capacity’ (ANC) instead of alkalinity (Evans et al., 2001).

$$\text{ANC (eq)} = K + Na + 2^* Mg + 2 * Ca - NO_3 - Cl - 2 * SO_4$$

Appendix 1 shows a more detailed explanation of the chemical processes.

1.2 Eutrophication

Eutrophication is the excessive supply of nutrients, notably nitrogen and phosphate. The transport sector and agricultural sector are the main sources of atmospheric nitrogen emissions. Nitrogen deposition can result in the eutrophication of soil and groundwater, which adversely affects biodiversity. Well-known examples are excessive grass growth on heathland and algal bloom in surface water.

1.3 Objective of the National Acidification Trend Monitoring Network

The foundation of the National Acidification Monitoring Network (TMV) was laid at the end of the nineteen eighties, in reaction to the wide public and political interest into the phenomenon of acid rain, and the many uncertainties concerning the effects of this phenomenon. The objectives of the network are (Goffau et al., 2009):

- to assess changes in groundwater quality in nature areas (forest and heath) with sandy soils;
- to describe and explain the water quality and the changes thereof, viewed in relation to environmental pressures (atmospheric emissions) and policy measures.

The programme has been sampling and analysing water from the upper metre of groundwater (i.e. leachate from the root zone) under nature areas with sandy soils at 150 different sites for these two purposes since 1989. This has allowed the TMV to assess water quality trends in terms of concentrations of nitrogen (N), sulphur (S), alkaline cations and aluminium.

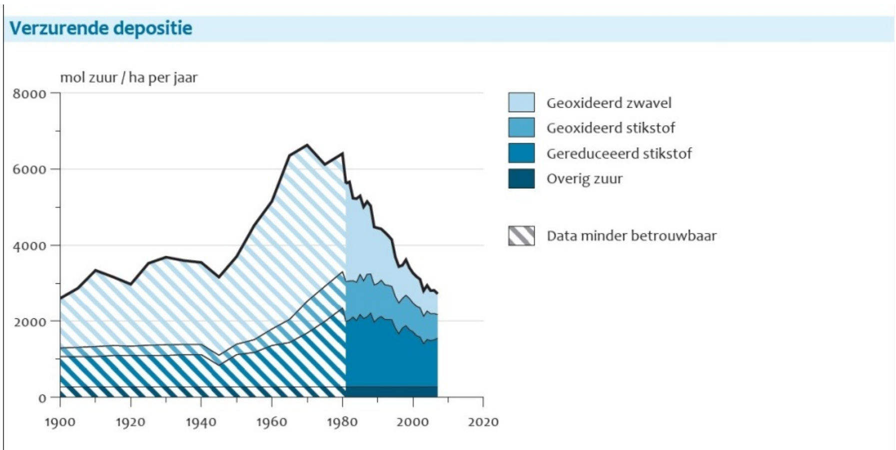
This report aims to meet the objectives of the TMV. We describe the changes in groundwater quality, as monitored in nature areas with sandy soils. We have investigated the effects of the emission policies on groundwater quality. For this purpose we tested whether the trends, found in the upper metre of groundwater and groundwater at a 10 m depth, can be related to known emission and deposition trends and to historical trends in rainwater concentrations. This study also examines whether changes in groundwater quality in the upper metre are reflected in changes in the deeper groundwater (10 m below the surface).

2 Changes in emissions and depositions, and the expected effect on rainwater and groundwater quality

2.1 Changes in atmospheric emissions and depositions over the years

During the past 100 years, atmospheric emissions of N and S initially increased, and then decreased. This led to changes in the deposition of N and S on the soil surface (Figure 2.1; Buijsman et al., 2010). S-emissions prior to 1960 can mainly be attributed to the combustion of coal. The deposition of S more than doubled in the period from 1900 to 1970, with a sharp increase after 1950. During the nineteen seventies, it was discovered that atmospheric emissions can travel long distances. This caused environmental problems such as the acidification of lakes in Scandinavia. In 1979 an international agreement on emission reductions was concluded (United Nations Economic Commission for Europe/Convention on Long-Range Transboundary Air Pollution; UNECE-CLRTAP). After 1975, government policies and autonomous developments, such as the transition from coal to natural gas and improved energy efficiency, led to lower S-deposition. Specific measures, largely conducive to lowering S-emissions, were the desulfurization of flue gas and the use of fossil fuels with lower sulphur content. Since 1980, these measures have been applied in power stations, refineries, industry and road traffic. A measure of major importance for the emission reduction of nitrogen oxides was the introduction of the three-way catalytic converter in cars (Buijsman et al., 2010).

In 2008 the S-deposition had dropped to one third of its 1900 level. Compared to 1980, there was a decrease by a factor of more than 5. In the period 1980-1990, the deposition of NH_x (reduced N) had doubled compared to the 1900-1950 period. After 1990, the deposition decreased again to about 150% of the 1900-1950 level. The deposition of nitrogen oxides more or less tripled between the periods 1900-1950 and 1980-1990. This deposition has now decreased again to a limited extent.



Bron: periode 1900-1980: Eerens & Van Dam (2001); periode 1981-2007: voorlopige gegevens van herberekeningen op basis van nieuwe inzichten

Figure 2.1 Evolution of acidifying deposition in the Netherlands (Buijsman et al., 2010).

Emission data are also available for more recent years; see Table 2.1 (PBL, 2012). These data show that the deposition of N and S decreased even further after 2008.

Table 2.1 Recent data on the emission of acidifying substances in the Netherlands.

	million kg					
year	1990	1995	2000	2005	2009	2010
Sulphur dioxide (SO_2)	192	130	73	65	38	33
Nitrogen oxide (NOx)	566	472	398	344	279	280
Ammonia (NH_3)	355	208	161	140	126	124

2.2 Effects of changing deposition on water quality

The expected effects of lower acid emissions of sulphur and nitrogen on water leaching from the root zone (leachate), surface water and groundwater are:

- lower concentrations of sulphate, nitrate, alkaline cations and aluminium;
- a rise in ANC and pH.

For some time now, reports have been emerging from Europe and North America confirming these expected effects of lower acid emissions. However, in some cases there have been unexpected effects as well.

Trends in sulphate concentration

Decreasing S concentrations have been reported for:

- Surface water (lakes, rivers and streams) in North America and Europe (Burns et al., 2006); Germany and France (Sucker et al., 2011); the Netherlands (Kleef et al., 2010); Ireland (Burton and Aherne, 2012); Norway (Dillon et al., 2003), Scotland (Harriman et al., 2001) and Europe in general (Prechtel et al., 2001);
- Catchment balance studies; Canada, United States and Europe (Watmough et al., 2005); Europe, North America (Stoddard et al., 2001) and Germany (Armbruster et al., 2003);
- Balance studies of monitoring locations (Forsius et al., 2001).

Balance studies frequently indicate that more S is being removed than supplied, resulting in delayed impacts of lower S emissions (e.g. Driscoll et al., 1998). Balance studies in the United Kingdom have provided no evidence of a delayed release of S (Cooper, 2005).

Trends in nitrate concentrations

Experiments performed under shelter have shown that the level of nitrate leaching swiftly reacts to lowered N-emissions (Bredemeier et al., 1998). Research during the nineteen eighties generally showed increasing nitrate concentrations. However, areas with the largest increase (Adirondack/Catskill Mountains and North/Central Europe) also showed the largest decline in concentrations during the nineteen nineties (Stoddard et al., 1999). During that same period, only a few regions experienced lower nitrogen deposition. Several studies found that nitrate concentration in water decreased, while deposition did not (Armbruster et al., 2003; Clow et al., 2003; Driscoll et al., 2003; Goodale et al., 2003; Cai et al., 2009). The leaching of nitrate appears to be governed by biochemical processes rather than by N-deposition (Cai et al., 2012). Occasionally, higher nitrogen concentrations are found in the water, though deposition has decreased. An explanation of this phenomenon is found in the saturation of the soil with nitrogen. A soil that is not yet saturated with nitrogen can become saturated even when N-deposition decreases. In those circumstances, nitrogen leaching may increase, while its deposition decreases. (Hill et al., 2002). A large portion of the soils in natural areas in the Netherlands are already saturated with nitrogen. We therefore expect that a decline in N-deposition will result in a reduction in nitrogen leaching.

Trends in the ANC

Hedin et al. (1994) found a decrease in the wet deposition of alkaline cations. They concluded that a lower deposition of nitrogen and sulphur does not necessarily bring about less acidification or an increase of the ANC. The decline in surface water sulphur concentrations was larger in the nineties than in the eighties. In Europe, that decline was associated with an increase of the ANC. In the United Kingdom, the ANC increased during the nineties because of an increase in alkaline cation concentrations, while the concentration of acid anions remained unchanged. In Scandinavian countries it was found that during the eighties the decrease in alkaline cations in surface water exceeded the decrease in sulphate concentrations. This changed in the nineties, when the ANC values rose (Stoddard et al., 1999).

Scientists have recently also found evidence of positive impacts of anti-acidification policies on soil quality and water quality in Sweden (soil moisture, groundwater and surface water), Belgium (soil moisture) and the United Kingdom (surface water) (Löfgren et al., 2011; Verstraeten et al., 2012; Murphy et al., 2012).

Löfgren et al. (2011) analysed records for the period 1996-2009 from a number of catchments in Sweden that were covered by integrated monitoring programmes. They demonstrate that the reduction in sulphur deposition weakly correlates with changes in sulphate, ANC and aluminium in soil moisture and ground water. In addition to sulphur deposition, other factors such as marine influences also showed a correlation with changes in water chemistry. There is no significant difference in the inclination of the trend lines of soil moisture or ground water. This shows that the variables are governed by common hydrological and soil chemical processes, irrespective of the medium. Verstraeten et al. (2012) analysed data on nitrogen and sulphur deposition and the chemical compositions of soil moisture from five ICP forest plots in Flanders during the period 1994-2010. During that period, sulphur and nitrogen deposition fell by 56-68% and 40-59% respectively. The soil moisture ANC increased significantly but remained negative. This shows that soil acidification is still ongoing. Murphy et al. (2012) demonstrate that from 1988 to 2008 the ANC in surface water rose in most monitoring locations in the United Kingdom.

Other reports suggest that increased ANC values in lakes may be attributed to higher temperatures in the northern hemisphere (Houle et al., 2010). During the nineties, no higher ANC values were generally found in North America, because the decline in alkaline cation deposition surpassed the decline in S-deposition.

Trends in DOC

Various studies have found an increase in concentrations of dissolved organic carbon (DOC) in natural waters. This rise is associated with diminishing S-deposition, resulting in an increased decomposition of organic material (Dangles et al., 2004; Evans et al., 2005; Burns et al., 2006; Vuorenmaa et al., 2006; Monteith et al., 2007; Hruška et al., 2009; Ekström et al., 2011; Sanclements et al., 2012). This is contrary to the expectation of a lower mobility of organic material under higher pH conditions. The rise in DOC concentrations is also attributed to higher temperatures (Clair et al., 2011).

2.3 Relation between rain water quality and groundwater quality

Total deposition consists of dry deposition and wet deposition. The dry/wet ratio for NO_x is about 1.6 and for SO_x about 1.3 (Aben, 2013). Therefore, the total deposition is more than double the deposition from rainwater only. Another relevant factor is the condensing effect caused by evapotranspiration (referred to as 'inspissation' from here on). According to Meinardi, the inspissation factors for current Dutch landscapes range between 3 and 5 (Meinardi et al., 2003), with an estimated average value of 4. This implies that about 200 of the 800 mm of gross precipitation enters the soil as precipitation surplus after evaporation. The exact magnitude of inspissation and dry deposition is unknown and can vary between years. In this report, we use the increase in the chloride concentration in the soil leachate and groundwater, as compared to rainwater, as a measure for the combined effects of dry deposition and inspissation. Chloride is absorbed by plants but does not react with the soil. We assume that the chloride concentration in the soil leachate is solely affected by deposition and the precipitation surplus.

Using the increase in chloride concentration to estimate the combined effects of dry deposition and inspissation requires a number of assumptions. The use of rainfall and evaporation data presents an alternative method for calculating the amount of leaching. Figure 2.2 illustrates this alternative method.

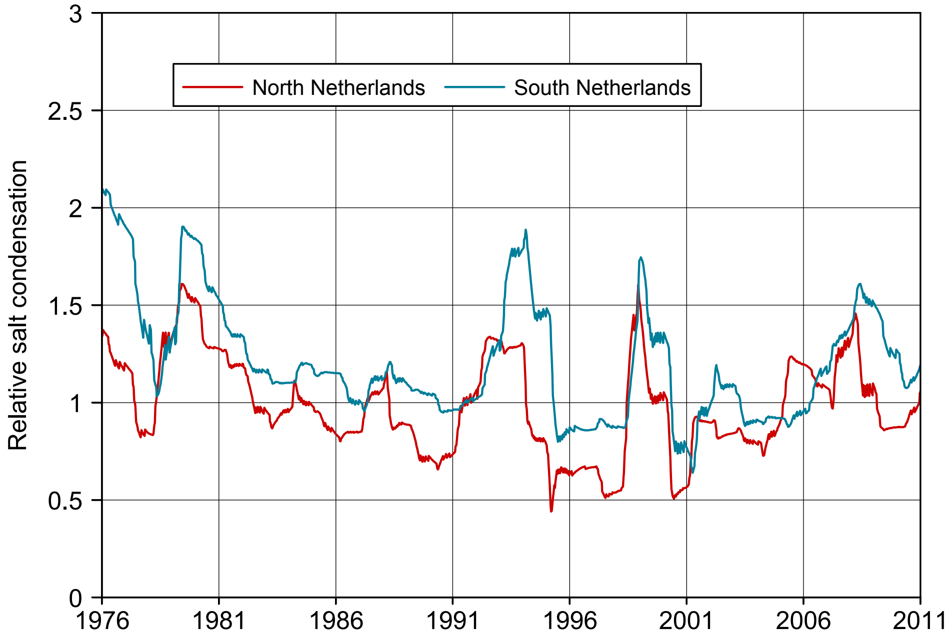


Figure 2.2 Calculated fluctuation of the concentration of deposited salt in the upper metre of the groundwater, due to the variation in precipitation and evaporation in the northern and southern parts of the Netherlands.

Figure 2.2 illustrates the variation in the concentration of deposited salt in the upper metre of the groundwater, resulting from the variation in precipitation and evaporation (or the precipitation surplus) occurring on grassland on windborne sand deposits. In the remainder of the text, we will refer to this phenomenon as 'condensation'. The figure is based on observed precipitation and evaporation data and a hypothetical salt deposition of one part per day. If the precipitation surplus is 365 mm, the calculated salt concentration (condensation) in the precipitation surplus will equal 1. The value used for soil porosity is 0.354. Therefore, a precipitation surplus of 365 mm will be sufficient to replenish at least the full upper metre of the groundwater, with an average condensation of 1.

If the average precipitation amounts to 800 mm, then the inspissation factor needed to reach a precipitation surplus of 365 mm is 2.2. For a precipitation surplus of 200 mm, corresponding to a rainfall depth of 800 mm and an inspissation factor of 4, the condensation will be 1.8 (365/200). This is clearly higher than the values calculated in Figure 2.2 for grassland on windblown sand deposits. Trees have a deeper rooting system than grass and can therefore evaporate water from greater depths. Long-term lysimeter studies (e.g. Hoeven, 2011) have found that the evaporation from barren sand receiving 800 mm of rain amounts to 200 mm. This represents an inspissation factor of 1.3 and a condensation of 0.6 (365/600). A lysimeter placed under a cover of shrubs evaporated 500 mm on average, resulting in a groundwater recharge of 300 mm. This corresponds to an inspissation factor of 2.7 and a condensation of 1.2 (365/300). A cover of oak trees also resulted in a groundwater recharge of 300 mm. A cover of fir trees, however, only gave a recharge of 150 mm, resulting in an inspissation factor of 5.3 and a condensation of 2.4 (365/150). The notion of 'inspissation factor' is more applicable to long-term averages of total rainfall (800 mm) and precipitation surplus (300 mm), while the notion of condensation is more applicable to the yearly process of precipitation and evaporation. To interpret the concentrations measured in the upper metre of the groundwater, variations in the precipitation surplus (the condensation) need to be taken into account.

Figure 3.2 presents the annual rainfall totals while Figure 2.2 shows the condensation in the upper metre of the groundwater. The annual rainfall has increased. At the same time, the condensation in the upper metre of the groundwater has not changed significantly. This implies that evaporation has increased. This can only be explained by increased precipitation during a period in which plants initially had insufficient water for evapotranspiration and/or if the length of the growing season was extended. Such climate changes can also have an impact on leaching concentrations, for example, because of increased denitrification or uptake by plants.

2.4 Expected results of water quality measurements

Based on the reduction of emissions and deposition and a literature review, we expect to find the following monitoring results in rainwater (Landelijk Meetnet Luchtkwaliteit; National Air Quality Monitoring Network), upper groundwater (TMV) and deeper groundwater (LMG):

For the concentration of S and N in rainwater, we expect to find nearly similar relative reductions as in the calculated deposition shown in Figure 2.1.

In groundwater (TMV and LMG) we expect to find, as a result of emission policies, a reduction in the concentrations of nitrogen (N), sulphur (S), alkaline cations (KAT), and aluminium (Al), and a rise in ANC and pH.

In the upper groundwater (water leaching from the root zone),

- we expect a more limited relative reduction for S than in rainwater, as a consequence of buffering processes in the soil;
- we expect decreasing concentrations for aluminium and alkaline cations;
- it is hard to make a prediction for nitrogen. The literature shows that both deposition and biochemical soil processes play key roles. The impacts from deposition on trends in N concentration may vary. Generally, we expect a drop in concentrations.

In the groundwater at a depth of 10 m, we expect smaller changes in N and S than in the upper groundwater layer. This expectation is based on the presence of buffering processes at larger depths, as well as the fact that this groundwater is a mixture of different ages.

We expect relatively higher N, S and Cl concentrations in the leaching water and groundwater compared to rain water. This is caused by the combined effects of dry deposition and inspissation.

2.5 Effects on ecosystems

In spite of the positive developments, ecosystems have not yet recovered from the acidifying and eutrophying impacts of acid rain.

Recent research has been conducted in the United Kingdom on the effects of diminishing acidification on biodiversity in surface water. All monitoring locations with evidence of recovering biota also showed increased ANC values. However, not every location with higher ANC values showed biological recovery. The research showed that biological recovery proceeds at a slower pace than the recovery of abiotic conditions (Murphy et al., 2012). Furthermore, simulations up to 2050 reveal that, under the Gothenburg protocol, surface water quality will continue to improve (i.e. the ANC will continue to increase). On the other hand, the soil buffering capacity will only recover slowly and only at a limited number of sites. Also, recuperation of the ecology is expected to be slow during the coming years (Helliwell et al., 2013). For the ICP Forests locations in Flanders, Verstraeten et al. (2012) demonstrated that despite its substantial drop the N-deposition will still surpass the ’critical load’ by 22 to 69%. The ’critical load’ is the highest level of loading acceptable without damaging vegetation diversity. Research by Van Wamelink et al. (2012) shows that eutrophication by nitrogen deposition is still the largest threat to plant species in natural Dutch landscapes: N-deposition surpassed the critical load at two thirds of the locations investigated. Nitrogen deposition remains a persistent problem for most areas. Especially the Veluwe, the Utrechtse Heuvelrug and the coastal dune belt are affected. Acidification also presents a limiting factor for ecological recovery, though to a lesser extent.

3 Data collection and processing

3.1 Total deposition

Total deposition is defined as the sum of dry and wet deposition. Unlike wet deposition, dry deposition is difficult to measure. Therefore, dry deposition is estimated by using models.

This report uses the calculated total deposition presented in Figure 2.1. For the purpose of this study, these data are subdivided into three periods:

- Period 1, from 1900 to 1978; only the calculated total deposition values presented in Figure 2.1 are available for this period;
- Period 2, from 1978 to 1988. The rainwater monitoring network was also operational during this period;
- Period 3, from 1988 to 2010. In addition to the rainwater monitoring network, the TMV was also operational during this period. The calculated data on deposition are only available up until 2008. However, the calculated total deposition values have been extrapolated until 2010 using the recent data on emissions (Table 2.1).

Unlike rainwater, water leaching from the root zone reacts to changes in emission and deposition with a delay of one to several years. This was taken into account when interpreting the data for this study.

Straight lines were visually fitted through the course of the top two lines for each of the three periods in Figure 2.1 (which was extrapolated until 2010). The end points of the fitted lines were used to estimate the S-deposition and N-deposition for 1978, 1988 and 2010. With these year-estimates, period-averaged deposition data were assessed for 1978-1988 and 1988-2010. We will come back to this in chapter 4 (see Table 4.1).

Concentrations in the air
In addition to occasional measurements of emission and deposition, concentrations of SO_2, NO_x, NH_3 in the air and their atmospheric conversion products are also monitored. Concentrations in the air are more directly linked to emissions than wet deposition. These measurements are used for the validation of calculated depositions of N- and S-compounds. A comparison of calculated concentrations with observed concentrations provides a method for checking the emissions and their atmospheric distribution. However, because no long-term records are available yet, these measurements were not used in this study.

Unknown sources
The input of substances from unknown sources or sources of unknown magnitude into natural areas is a difficult aspect when assessing the impacts of changing deposition on the degree of acidification. Examples of such sources are windblown dust from farm land, excrements of dogs and other animals, and vegetation removal by logging or burning. The evolution of concentrations of these substances in the leachate under the root zone will reflect the evolution of the total net deposition if:

- the net supply of the substances from sources of unknown magnitude is limited in comparison to atmospheric deposition;

- this supply (sources of unknown magnitude) does not follow a trend.

The evolution of the total net deposition is the resultant of emission policies and the rainfall surplus; after all, substances below the root zone are not emitted into the atmosphere. It is conceivable that at certain places, sources of unknown magnitude could have important effects on the concentrations in the water leaching from the root zone. We assume that concentrations in the leachate that result from atmospheric deposition are approximately normally distributed, and that departures from the normal distribution are caused by these sources of unknown magnitude. In other words: we assume that the impact of emission policies is more reliably represented by the relative change of the median concentrations in the leachate than by changes in the average concentrations.

3.2 Rain water quality

Since 1978, rainwater is systematically monitored in the Netherlands by the rainwater monitoring network. Initially, this was a joint project run by the RIVM and KNMI. Since 1989, the rain water monitoring network has been fully transferred to the RIVM. Observations are now carried out under the auspices of the ’Landelijk Meetnet Luchtkwaliteit’ (National Air Quality Monitoring Network).

In the period from 1978 to 1988, sampling was carried out with bulk collectors. In 1988 this equipment was replaced by wet-only collectors, because the bulk collectors overestimated concentrations due to the settlement of dry deposition on the funnel of the collectors. To adjust for this bias, correction factors were derived (Blom et al., 1988; Ridder et al., 1984). The factors listed below were used in this study:

Cl	0.9
NH_4	0.85
NO_3	0.75
SO_4	0.85

In 2006, the wet-only collectors were replaced in turn by more up-to-date wet-only-collectors (Swaluw et al., 2010a).

For this study, stations were selected that lay at an adequate distance from the coast (> 20 km) and are situated outside urban environments. These criteria were applied since TMV locations are also situated in rural settings beyond the influence of the sea. During the period 1978-2010, a number of stations were replaced and the total number of stations decreased. Figure 3.1 shows the location of stations selected for 2010.

We calculated the precipitation-weighted average concentrations for each year, based on measured concentrations in samples taken every four weeks.

The data-set until 1990 shows that concentrations for some substances (Cl, Ca, Mg) were reported being below the detection limit. The concentration in these data was estimated using the results of properly quantifiable parameters, such as the electric conductivity (EC). This was done using regression analysis.

The effect of the replacement of a number of stations between 1978 and 2010 on the overall annual concentrations was estimated with a statistical procedure (REML; GENSTAT). The year of observation was modelled as a fixed effect, and the monitoring station as a random effect. Subsequently, annual concentrations were estimated for a hypothetical situation in which all monitoring stations were present for the full period (see Figure 4.1).

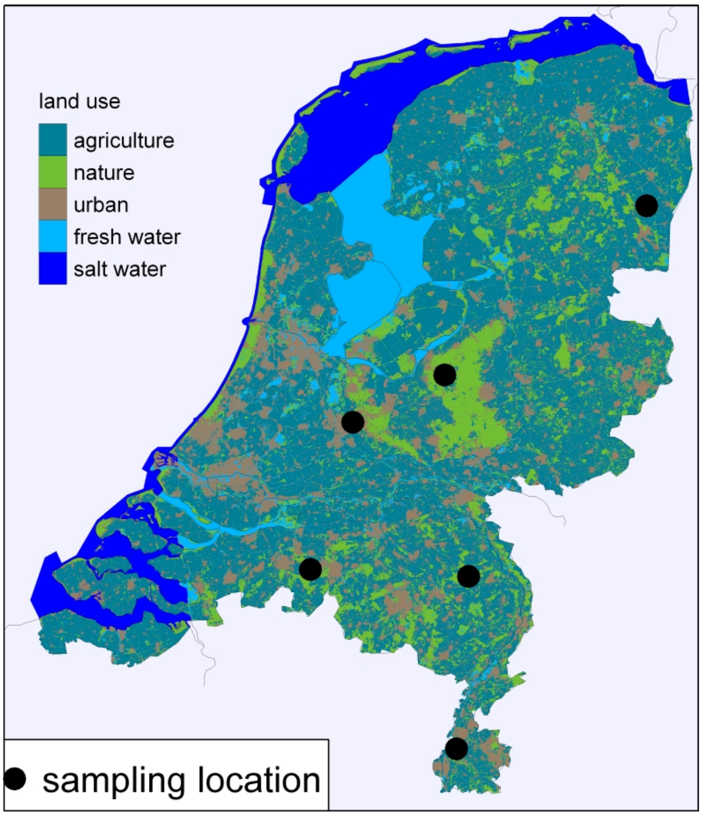


Figure 3.1 Rainfall stations selected for 2010.

3.3 Wet deposition

Wet deposition can be measured more easily than dry deposition, since wet deposition can be collected and chemically tested directly. The concentration of a substance multiplied by the amount of rainfall equals the amount of wet deposition. Variations in wet deposition throughout the years will therefore show a correlation with the annual amounts of rainfall. The average annual rainfall depth in the Netherlands is presented in Figure 3.2.

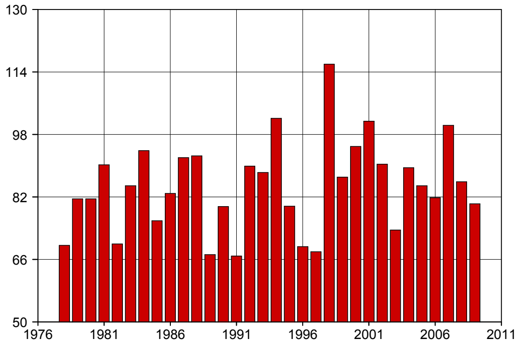


Figure 3.2 Average annual rainfall (cm) of all principal stations.

The precipitation-weighted average concentrations were calculated for each year. Data are missing at some stations for parts of the years. These missing data were filled in through correlation with other stations. To determine the wet deposition, the precipitation-weighted average annual concentrations were multiplied with the total annual rainfall, supplemented with the estimated values for periods with missing data. In addition, indexed wet deposition values were estimated. This means that deposition values were estimated for a hypothetical situation in which each measuring station was available for each year, with identical rainfall volumes during each year. These indexed average values are presented in Figure 4.1.

3.4 Groundwater quality – in the upper metre

Since 1989, the TMV has sampled the upper metre of the groundwater, or leachate from the root zone, in nature areas in the Netherlands (Boumans and Beltman, 1991; Goffau et al., 2009; Elzakker et al., 2009; Masselink et al., 2012). Leachate from the root zone is water 'that is about to move beyond the rooting zone of the soil' (Addiscot, 1996).

The National Acidification Trend Monitoring Network (TMV) was established by the RIVM in 1989/1990. It consists of about 150 measuring sites in nature areas on sandy soils (Figure 3.3). TMV periodically samples and analyses the upper groundwater at those measuring sites.

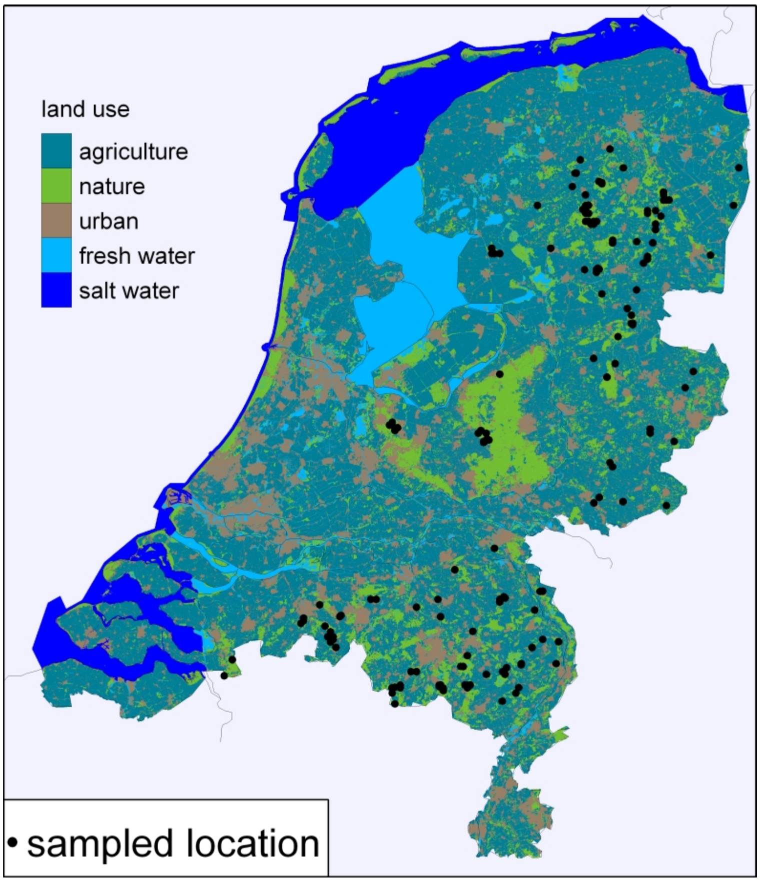


Figure 3.3 Nature areas sampled; sampling locations of the National Acidification Trend Monitoring Network.

When the monitoring network was first established, all locations were sampled in one single measuring round (round 1; previously named round 0) (Boumans and Beltman, 1991). About 10 locations were sampled annually from 1993 up to and including 1996. Since 2000, half of all the measuring locations (about 75) have been sampled each year. No sampling was done in the years 2004 and 2005. Table 3.1 Summary of TMV sampling rounds. summarises the different sampling rounds.

Table 3.1 Summary of TMV sampling rounds.

Round[a]		Period		Locations	
New	Old	From	Up to and including	Num-ber	Group[b]
1	0	October 1989	March 1990	158	X+Y
	1	February 1993		10	x+y
	2	1994		9	x+y
	3	February and July 1995		9	x+y
	4	January and December 1996		9	x+y
	5	November 1996		9	x+y
2	6	November 2000	February 2001	76	X
	7	October 2001	March 2002	77	Y
3	8	January 2003	May 2003	75	X
	9	November 2003	April 2004	76	Y
4	10	October 2006	January 2007	75	X
	11	December 2007	March 2008	75	Y
5	12	October 2009	April 2010	74	X
	13	September 2010	January 2011	76	Y
6	14	September 2012	February 2013	75	X
	15	September 2013	March 2014	75	Y

[a] Starting with the report by Masselink et al. (2012) a new numbering system for the sampling rounds was introduced; the new round numbers only refer to periods in which all TMV measuring locations are sampled.

[b] x is a sub-sample of X and y is a sub-sample of Y.

In the TMV, a measuring site covers the largest continuous extent of forest or heath in a 500 x 500 m grid cell. A number of parameters were taken into account when selecting for the grid cells during the initial setup of the network (Boumans and Beltman, 1991):

- areal extent of forest in the grid cell and in the eight adjoining grid cells;
- areal extent of heath in the grid cell and in the eight adjoining grid cells;
- areal extent of agricultural land in the grid cell and the eight adjoining grid cells;
- the calculated N-deposition in the grid cell.

For practical reasons, the TMV only selected sampling areas managed by the Dutch Forestry Commission (Staatsbosbeheer) and with an anticipated groundwater level of less than 6 m below the ground surface. The actual average groundwater level is 1.9 m below the surface. Ten sampling points were selected at each site. In principle, these sampling points are situated along the longest straight line (transect) with 50 m intervals. If the transect measures less than 450 m, the remaining sampling points are positioned along the perpendicular bisector of the transect. Sampling points are always situated at least 20 m from the edge of a forest or heath. During the start-up of the monitoring network (round 1), vegetation characteristics of sampling points were recorded in addition to the groundwater sampling. See Boumans and Beltman (1991) for more details.

Groundwater samples have been taken under the following vegetation types:

Mixed forest	15.2%
Deciduous forest	28.0%
Coniferous (pine) forest	44.1%
Open terrain (heath, barren, shrubbery)	12.7%

Ten samples were taken at each monitoring site. The sampling strategy was as follows (Van Elzakker et al., 2009):

> 'At each monitoring site, ten sampling points are marked out. At each of these ten sampling points a groundwater sample is taken by pumping from an open borehole. In the laboratory, these samples are combined into a composite sample, representative for the monitoring site. This composite sample is chemically tested for a large number of parameters. In the field, some specific tests are conducted for the individual groundwater samples at each sampling point. Samples are only taken when the groundwater level is at less than six metres below the surface. The peristaltic displacement pump in use does not function at a larger sampling depth.'

In addition to groundwater quality, other information recorded in the field includes soil texture and environmental parameters such as vegetation type, height of trees and thickness of the litter layer.

The following information is collected within the TMV:

- field analyses at each sampling point:
  - acidity (pH);
  - electric conductivity (EC);
  - dissolved oxygen;
  - nitrate (via colorimetric reaction).
- recording of location characteristics (not during every round):
  - type of landscape; and the type of vegetation, main tree species, tree top cover, height of trees, shrubbery coverage, herbal coverage and thickness of the litter layer within a 4 m radius around the sampling point.
- laboratory analyses of the composite sample for each monitoring location:
  - pH, EC and DOC;
  - heavy metals (cadmium, lead, chromium, copper, zinc and arsenic);
  - other metals (aluminium, barium, calcium, magnesium, manganese, sodium and strontium);
  - eutrophying substances (total phosphorous, phosphate, total nitrogen, ammonium, chloride, nitrate, sulphate and potassium).

Additional information on the TMV can be found in the TMV evaluation report (Goffau et al., 2009), in the most recent operational report (Masselink et al., 2012) and on the RIVM website (in Dutch).

Concentrations in the upper metre of the groundwater not only depend on deposition but also on the groundwater level and on condensation. These factors were taken into account by means of indexing: average annual concentrations were estimated for equal groundwater levels and identical condensation. The condensation was calculated assuming a grassland vegetation on wind-borne sand deposits. This was done for each meteorological district, time of sampling and groundwater level (Boumans et al., 2004). Thus, specific vegetation characteristics and soil types were not taken into consideration. Indexation is a statistical procedure, based on correlation, for estimating annual concentrations for identical values of condensation and groundwater levels. The absolute level of condensation is not important in indexation. The figures in chapter 4 show the measured values alongside the indexed average values.

3.5 Groundwater quality – 10 metre depth

The National Groundwater Quality Monitoring Network (LMG) comprises about 350 fixed wells throughout the Netherlands (Vliet et al, 2010). The LMG assesses the water quality of shallow and medium deep groundwater. For this purpose, the borehole at each monitoring location is equipped with three permanent filters at depths of about 10, 15 and 25 m below the surface from which water can be sampled by pumping. The LMG was set up between 1979 and 1984 by the National Institute for Drinking Water Supply (RID). In 1990, when the RID became part of the RIVM, the LMG’s operational management was also transferred to the RIVM. As of 2003, sampling and analyses are carried out by TNO, and data management by the DINO department of TNO Bouw en Ondergrond. The RIVM is responsible for the monitoring strategy, data checks and validation, data interpretation and reporting. The LMG is commissioned by the Ministry of Infrastructure and the Environment.

The location of all LMG observation points is shown in Figure 3.4.

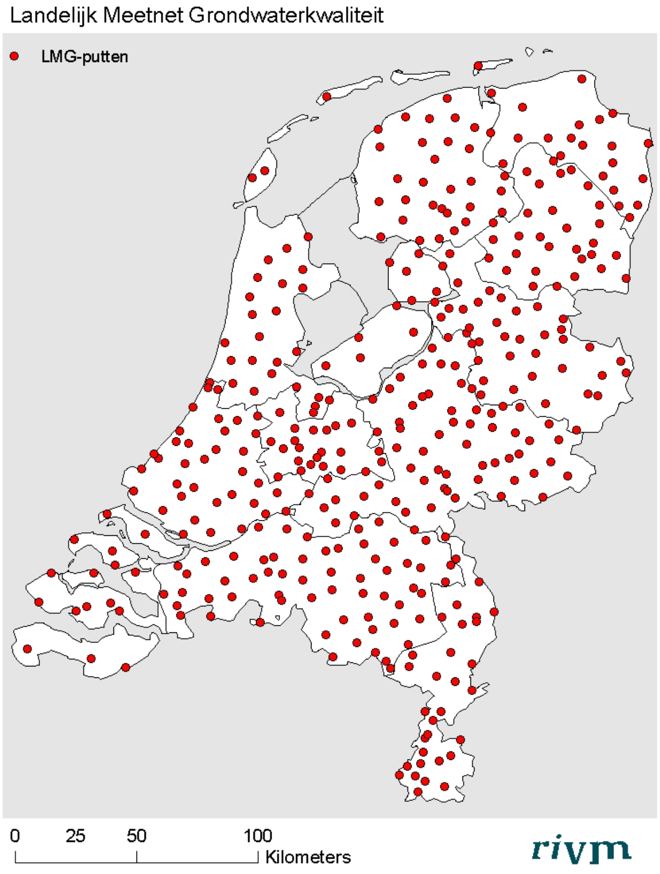


Figure 3.4 Location overview of all observation points in the National Ground Water Quality Monitoring Network.

Over time, a number observation points were taken out of operation and new monitoring points were installed. In 1997 and 1998, the LMG was optimised, which led in particular to an adjustment of the sampling frequency (Wever and Bronswijk, 1998). The sampling frequency depends on the vulnerability of the groundwater at the observation point. For the filters at 10 and 25 m below the surface, the frequency varies between once a year and once every four years:

- shallow filters in the sandy areas: once a year;
- shallow filters in the other soil type areas: once every two years;
- all deep filters: once every four years;
- shallow filters with a chloride content of more than 1000 mg/l: once every four years, irrespective of soil type.

The acidity (pH), temperature, electric conductivity (EC), oxygen and bicarbonate concentrations are measured in the field. Macro-ions and micro-constituents are analysed in the laboratory:

- macro-ions: NO_3, SO_4, NH_4, Cl, K, Na, Mg, Ca, Fe, Mn, total phosphorous and DOC;
- inorganic micro-constituents: Ba, Sr, Zn, Al, Cd, Ni, Cr, Cu, As and Pb.

Occasionally, additional monitoring programs were executed in which pesticides and other substances were analysed.

For the purpose of this study, boreholes were selected from the LMG observation points. We only selected boreholes situated on sandy soils (not coastal dunes), draining nature areas. The criteria for selection were an evident contribution of recent groundwater (i.e. in 1984, the relevant filter contained tritium) and a chloride content of less than 100 mg/l (Figure 3.5). Only the data from filter 1, at about 10 m below the surface, have been used.

In comparison to the TMV, a larger portion of LMG data originates from relatively large nature areas. The sampling for TMV is limited to nature areas with a groundwater table at less than 6 m below the surface. This is often found in relatively small nature areas. In LMG, samples are taken from 10 and 25 m below ground level. In practice, nature areas on sandy soils with a deep groundwater table often have a larger surface area (e.g. the Hoge Veluwe).

The filter length of the LMG filters is 2 m. The top level of the filters is in a range of 6.6 to 13.4 m below the surface, with an average of 8.9 m. The groundwater tables vary between 1.6 and 5.5 m below ground level, with an average of 3.2 m. This average depth is more than in the TMV (1.8 m below ground level).

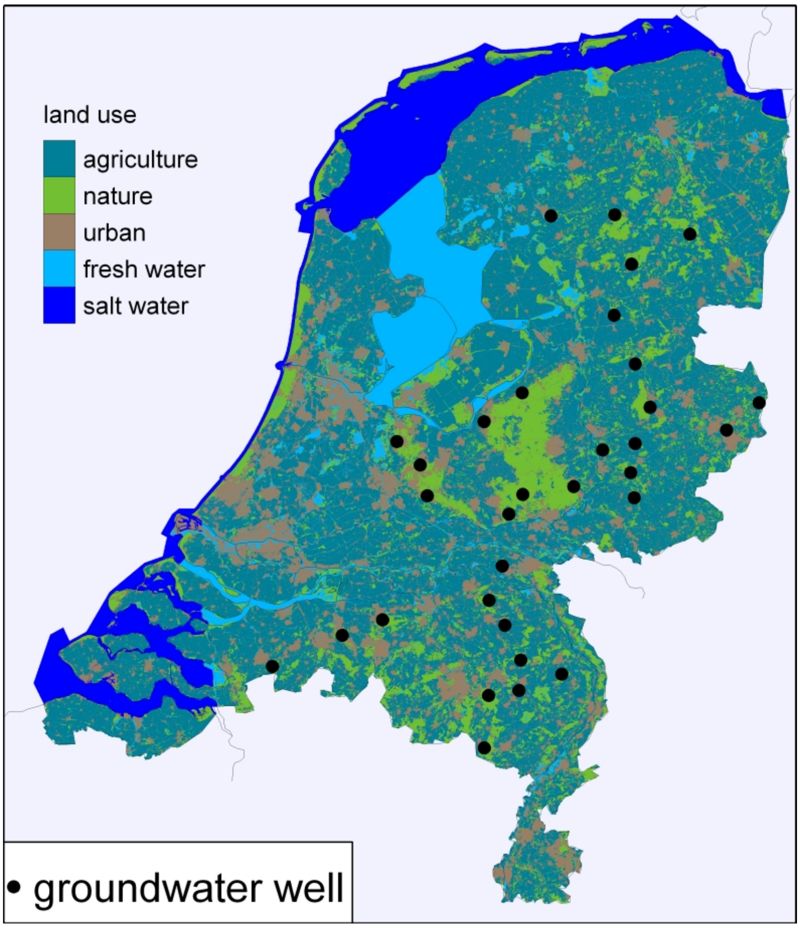


Figure 3.5 Location of selected LMG boreholes, with filter depth at 10 m below ground level.

4 Results

4.1 Rain water quality

Figure 4.1 shows the (precipitation-weighted) average annual concentrations for each rain gauge station and the amounts of wet deposition.

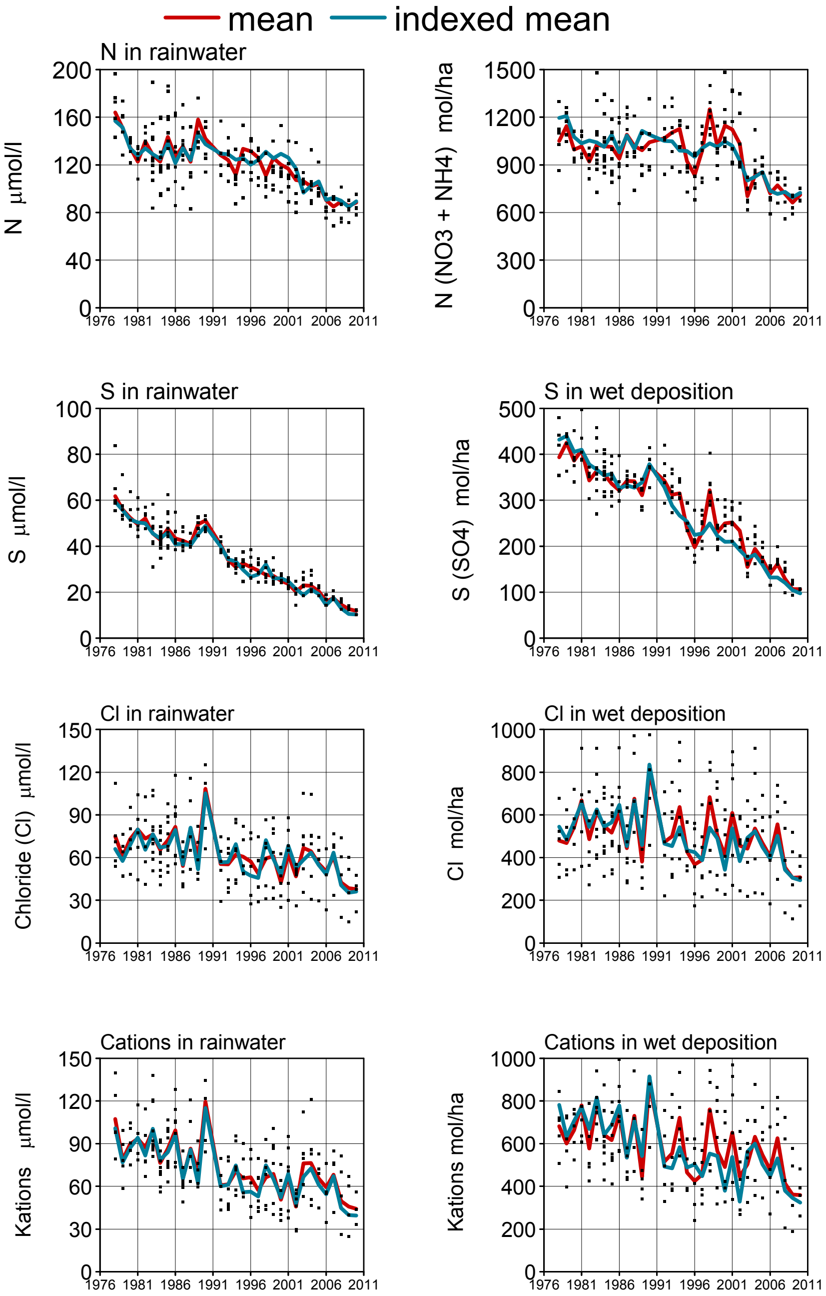


Figure 4.1 Mean annual (precipitation-weighted) concentrations and amounts of wet depositions per rainfall station.

Figure 4.1 shows both the annual average concentrations and the amounts of depositions per rainfall station, as well as their combined average value. Some of the higher concentration values may fall beyond the scale of the graphs; they do, however, affect the average values. Indexed averages are shown as well (blue lines). These indexed values take into account the change in observation stations, and the magnitude of the precipitation surplus for wet deposition (see paragraphs 3.2 and 3.3).

For the substances shown in Figure 4.1, there is no clear increase or decrease in rainwater concentrations or depositions in the period between 1978 and 1988. Between 1988 and 2010, however, there are some distinct decreases. The course of the average N concentration and S concentration is similar; this is also true for the chloride and cation concentrations.

The scatter around the annual average decreases over the years; this applies to S, but especially to N. It is to be expected that a declining average concentration will be accompanied by less scatter. This is probably the case for S; the scatter appears to diminish even more for N. We observed no diminishing scatter around the average annual values for chloride or cations.

Similar trends have been found in Swaluw et al. (2011). They describe the trend development of the wet deposition of ammonia, nitrate and sulphate in the Netherlands for the period 1992-2008.

4.2 Groundwater quality – upper metre

For each sampling round, Figure 4.2 shows the average, median and percentile values, as well as the individual site average concentrations of a number of parameters in the upper metre of the groundwater (leachate from the root zone), as measured at the 150 TMV sites. Indexed median concentrations have been calculated for N and S, assuming equal values of groundwater levels, condensation and identical observation points throughout the years. The difference between the median and indexed median values is small. The graphs do not present extreme location-averaged concentrations, the inclusion of which might have obscured the lines for average and percentile values. As for N in the leachate, only nitrate has been taken into account.

Similar to rainwater, a clear decline in concentrations of N and S was found in the groundwater. The decline in the indexed median values of N and S is larger than the decline of the directly observed median values. Contrary to the findings for rainwater, the chloride concentration does not show a clear decrease. The concentration of dissolved organic carbon (DOC) increases. This corresponds to earlier findings by Monteith et al. (2007). They found that a decline in sulphur deposition is accompanied by a rise in DOC in the surface waters in Northern Europe and North America.

A location-wise comparison of the observation data from 2010 and 1989, using a paired samples t-test, revealed that the pH and ANC in 2010 were significantly higher than in 1989, while the aluminium concentration was significantly lower ($\alpha < 0.05$). Despite the increase, the ANC was still negative at 80% of the monitoring locations in 2010. This implies that acidification is still ongoing but at a slower pace. This is corroborated by the decline in aluminium concentrations.

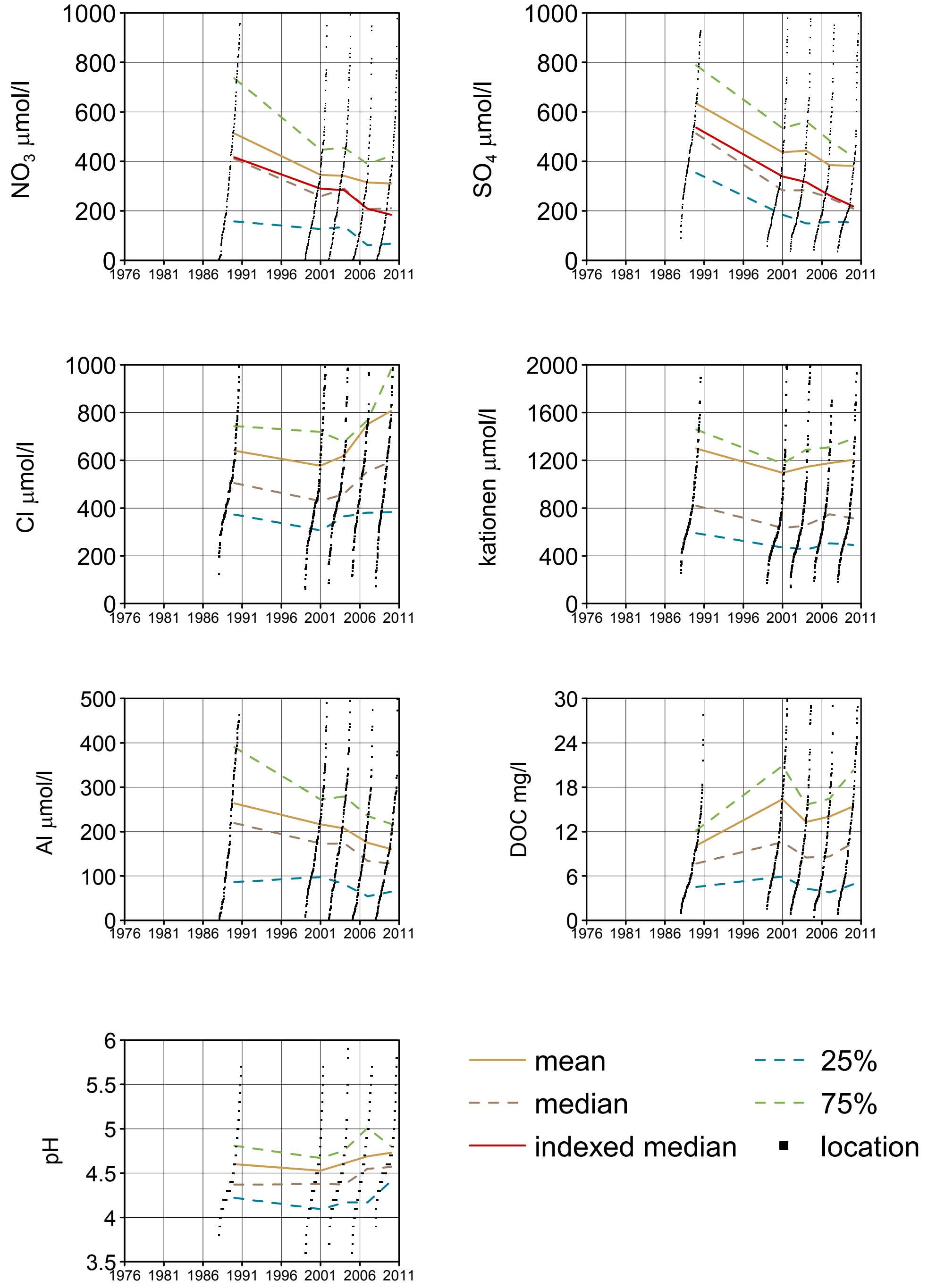


Figure 4.2 Annual averages, percentiles and individual observations of concentrations in the top metre of the groundwater (=leachate from the root zone).

The phenomenon of diminishing acid deposition accompanied by a decrease in aluminium concentrations is in accordance with the hypothesis by Ulrich et al. (1979).

The concentrations of S and Cl in the leachate from the root zone are higher than the N concentrations. The reverse is true for rainwater.

In addition to N, S and Al, the heavy metal concentrations in the water leaching from the root zone also show a marked decrease (Appendix 2).

4.3 Groundwater quality – 10 metre depth

The concentrations of S, Cl and cations in the groundwater at a depth of 10 m show a decrease (Figure 4.3). NO_3 concentrations increased between the mid-eighties and mid-nineties of the previous century, followed by a decline.

4.4 Relations between depositions and water quality

To further investigate the quantitative relations between depositions and water quality, we converted the information in figures Figure 2.1 (depositions)Figure 4.1, 4.2 andFigure 4.3 (water quality) into Table 4.1. This table distinguishes two periods (1978-1988 and 1988-2010). The second period of TMV monitoring started in the autumn of 1989. Table 4.1 quantifies depositions and concentrations at the end and at the start of the two periods. The starting point and end point were estimated with a straight line, in such a way that the sum of the deviations from this line equals zero. Therefore, the difference between the starting point and the end point represents an estimate of the period’s average value. The year 1988 is both the end of the first period and the start of the second period. Table 4.1 therefore contains two values for the year 1988.

4.4.1 Calculated total deposition and measured rainwater quality (wet deposition)

Figure 2.1 shows the total deposition for the Netherlands as a whole. For the calculation of the wet deposition, rainfall stations in the east were selected to exclude the influence of the sea.

The calculated total deposition of N during the two periods is 2.84 and 2.23 kmol/ha respectively. The average wet N-deposition amounts to 1.02 and 0.95 kmol/ha. During the first period, the calculated total N-deposition did not diminish, nor did the wet N-deposition. During the second period, from 1988 to 2010, a more or less similar decline is observed for both the total deposition and the wet deposition. The 2010 concentrations amount to 57 and 68% of the 1988 levels, respectively. The (calculated) total S-deposition and the (measured) wet S-deposition decreased in both periods.

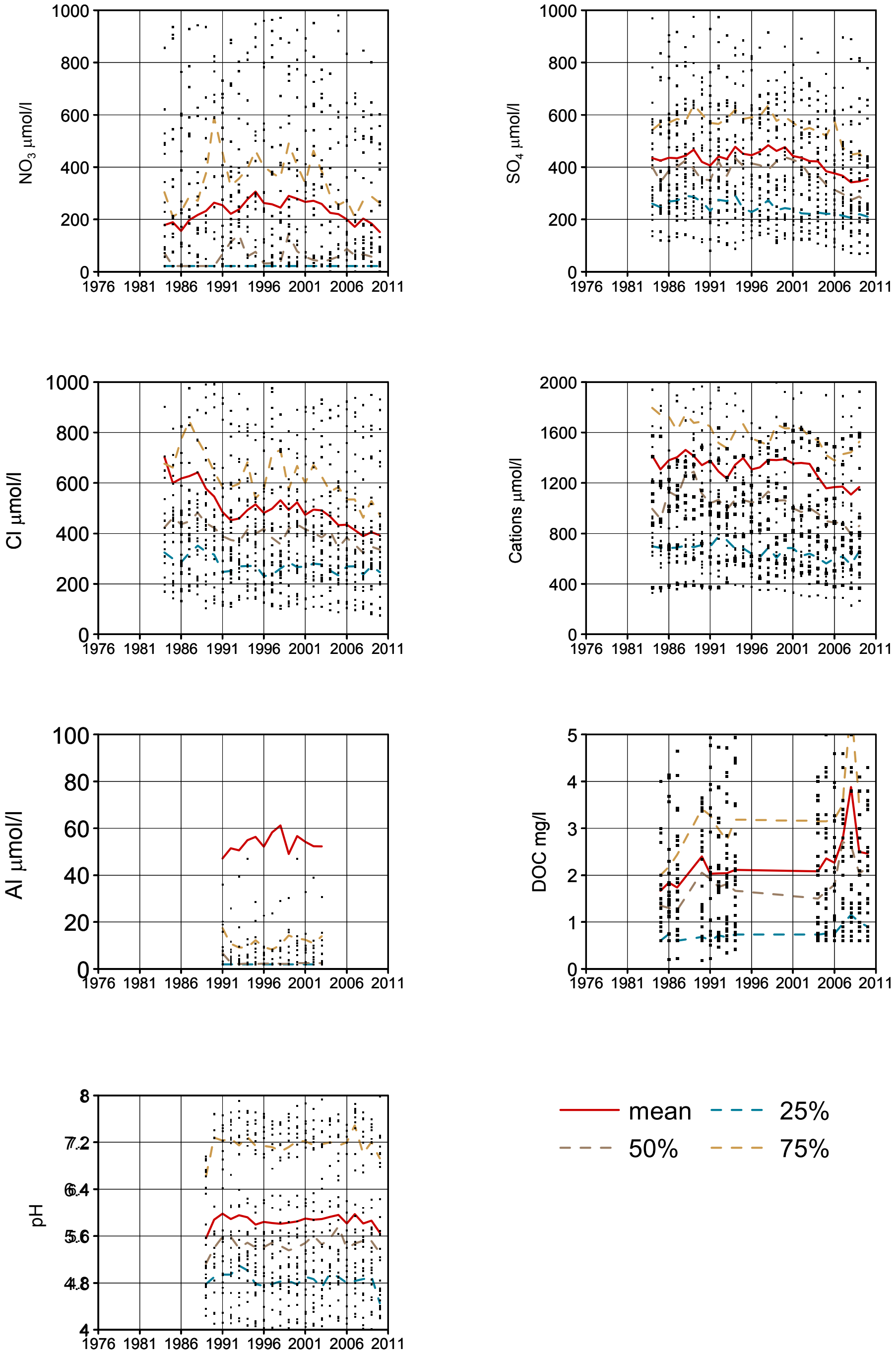


Figure 4.3 *Annual averages, percentiles and individual observations of concentrations in the deeper groundwater (10 m below surface level).*

Table 4.1 Calculated deposition and quality of rainwater, the upper [metre of the] groundwater and deeper groundwater.

			1978-1988			1988-2010			
			start	aver.	end	start	aver.	end	Comp. 1988 (%)
Calculated total deposition kmol/ha (Figure 2.1)	N		2.84	2.84	2.84	2.84	2.23	1.62	57
	S		1.56	1.16	0.77	0.77	0.47	0.16	22
wet deposition kmol/ha (Figure 4.1) indexed per station	N		1.04	1.02	1.00	1.13	0.95	0.77	68
	S		0.41	0.36	0.32	0.36	0.23	0.12	32
Rainwater concentration weighted µmol/l (Figure 4.1)	N		147	134	124	143	116	87	61
	S		57	48	40	45	29	12	27
	Cl		72	72	72	73	58	44	61
	ANC*		-207	-190	-176	-210	-150	-90	43
	KAT		96	88	81	81	67	54	67
	cation-eq.		126	111	99	96	80	65	68
Leachate µmol/l (Figure 4.2) indexed for groundwater level and condensation	N (NO_3)	average				536	387	239	45
		median				418	301	183	44
	S (SO_4)	average				659	483	306	46
		median				536	377	218	41
	Cl	average				680	719	758	111
		median				562	564	568	101
	KAT	average				1338	1222	1106	83
		median				995	898	801	81
	ANC	average				-492	-269	-46	9
		median				-515	-304	-92	18
	Al	average				272	212	152	55
		median				224	177	129	57
	pH	average				4.58	4.64	4.78	63
		median				4.56	4.61	4.76	63
Groundwater µmol/l (Figure 4.3)	N (NO_3)		230 (median = 55)						
	S (SO_4)		425 (median = 371)						
	Cl		504 (median = 404)						
	KAT		1316 (median = 1020)						
	Al		54 (median = 2.3)						

**ANC / alkalinity = cation equivalents – anion equivalents = cation equivalents – N – 2*S - Cl*

4.4.2 *Trend in rainwater acidification*

The cation concentration in the rainwater decreased gradually from 96 to 54 µmol/l, but the difference between cations and anions diminished as well. These changes occurred during the second period in particular. During this period, the anion surplus fell from 210 to 90. We also note that the contribution of Ca and Mg remained about the same (not visible in the table).

4.4.3 *Quality of the upper metre of the groundwater in comparison to rainwater*

The TMV was established in 1989, which is why data on the quality of the leachate from the root zone are only available for the second period (1988-2010).

As would be expected, concentrations of N and S declined both in rainwater and in the leachate from the root zone. However, we found that the N concentration in the leachate declined more than it did in rainwater (45 and 61% of the 1988 levels, respectively, meaning a 55% decrease in the leachate and a decrease of 39% in rainwater). There was less of a decrease in the S concentration (44 and 27%, implying a drop of 56% in the leachate and a decrease of 73% in rainwater). This difference is remarkable. It will be discussed further in the next section.

In 1988 the average pH of the upper metre of the groundwater was 4.58; in 2010 it was 4.78. In terms of H^+-ions, the concentration in 2010 was 37% lower than it was in 1988. In 1988, the ratio of aluminium/alkaline cations in the upper metre of the groundwater was 0.22; in 2010 this ratio was 0.16.

As expected, the concentrations of N, S and Cl in the leachate were higher than in the rainwater. However, the leachate contained less N (387 µmol/l) compared to the S (483 µmol/l), while the rainwater contained much more N (116 µmol/l) than S (29 µmol/l). This would imply that N, present in the rainwater, disappeared from the leachate and/or that S was released from the soil.

Over fifteen times more S (483 µmol/l) was found in the leachate than in the rainwater (29 µmol/l). The leachate also contained about twelve times more chloride (719 µmol/l) than the rainwater did (58 µmol/l).

Since the average values in the leachate are heavily affected by outliers (Figure 4.2), we based the subsequent findings on the median values. In doing so we implicitly assumed that, without disturbances (e.g. by unknown sources of deposition), concentrations would be distributed normally; under that assumption the average coincides with the median. Due to disturbances, we expected the average to change, but not the median. Therefore, the median represents the average effect of the deposition. During the period 1988-2010, the median for chloride in the leachate was about ten times higher than the average concentration in rainwater. Consider a hypothetical situation in which all the deposited chloride is leached. A tenfold increase as the combined effect of dry deposition and inspissation would be a high but acceptable value, because the leachate is primarily sampled from small nature areas with high groundwater tables, where dry deposition and evapotranspiration by trees are relatively high. Consider a hypothetical situation in which the median of N and S had also risen by a factor of ten, without the uptake by plants and other chemical processes. What we actually found in this research, was that the median sulphate concentration was thirteen times higher in the leachate than in rainwater, meaning that about 130% of the sulphate deposited was leached; thus about 25% of the sulphate in the leachate is to be attributed to an internal source.

The rise in S could be partly explained by the delay of one to several years in the leaching of rainwater, accounting for a few percentages of the difference. We therefore deduce that about 20% (25/130) of S in the leachate is derived from release by the soil.

The S/Cl-ratio in rainwater was 0.8 (=57/72 µmol/l) in 1978, 0.6 in 1988 and 0.2 in 2010. This ratio decreased from 0.9 (=536/562 µmol/l) in 1988 to 0.4 in 2010 in the leachate. This result also indicates that the share of S originating from release by the soil increased.

In 2010 the average nitrate concentration in the leachate was 2.7 times higher than N in rainwater (239/87 µmol/l). Given the increase by a factor of 10 for chloride, this result suggests that only about 27% of the nitrate deposited was leached. This order of magnitude has also been reported by others (Balestrini et al., 2006). Predictions are made that more N than S will be leached in the future (Curtis et al., 2005). A higher proportion of N than S deposition is expected in the Netherlands compared to other countries. In the Netherlands, the N/S ratio in the leachate increased only slightly between 1989 and 2010: from 0.78 (=418/536 µmol/l) to 0.84 (=183/218 µmol/l). This is due to a disproportional drop of N in the leachate, while S is affected by release from the soil.

The concentrations of all substances except chloride decreased. The fact that Cl did not decrease in the leachate, while other substances did, supports the hypothesis that N and S concentrations diminished because of lower levels of emissions and deposition, not because of a higher rainfall surplus. The drop in N concentration in the leachate was larger than in rainwater . Other studies have also found a larger decrease in N-leaching compared to wet N-deposition (see section 2.2).

The decrease of S-leaching and N-leaching is accompanied by lower concentrations of Al and heavy metals (see Annex 2). The phenomenon of lower heavy metal concentrations may not be an effect of less soil acidification, but rather the result of a decline in the atmospheric deposition of heavy metals. This is in line with previous research by the RIVM which demonstrated a significant lowering ($p < 0,05$) of the wet deposition of a number the heavy metals nickel, zinc, cadmium and lead for the period 1992-2004 (see Table 6 in: Swaluw et al., 2010).

4.4.4 *Possible explanations for the difference in the decline of N and S*

The bigger decline of N concentrations in the leachate as compared to rainwater could be explained by the position of the monitoring sites where the upper metre of the groundwater is sampled. In the presence of more atmospheric S, N will deposit closer to its source, that is, agricultural land. N and S interact, resulting in co-deposition. Since the atmospheric concentration of S has diminished, there is less co-deposition and N is deposited further away from the source. TMV samples the upper metre of the groundwater (the leachate from the root zone) in small nature areas, often situated near the source of N-emission. Thus, apart from lower emissions, the N-deposition at these locations may have experienced an additional reduction due to less local deposition.

A second explanation for the larger decline of N in the leachate as compared to rainwater may be the increased uptake by plants. This hypothesis is supported by the finding that more rainfall has been lost by evapotranspiration over the past ten years (Figure 4.4), meaning that plant growth has increased, either through more summer rain or due to a longer growing season.

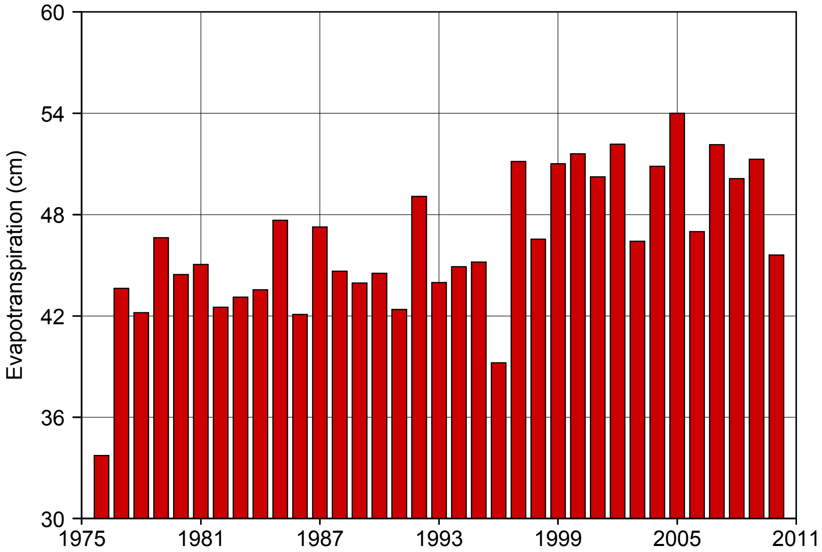


Figure 4.4 Annual average evapotranspiration in the Netherlands in the period 1975-2011 (KNMI).

Thirdly, it could be hypothesised that the current precipitation, containing considerably less S but still with higher levels of reduced N, is more alkaline. If denitrifying bacteria occur in the litter layer, the increasingly alkaline rainfall could induce increased denitrification, causing N to disappear as N_2. Higher pH values are measured in the leachate as well, which can lead to more denitrification below the root zone. As opposed to a situation where there is less co-deposition, we expect that especially the lower concentrations will decrease further under conditions with higher denitrification or larger uptake by plants.

Both hypotheses, that is, less local co-deposition and more denitrification/uptake by plants, have been investigated by comparing cumulative frequency diagrams (CFDs) of site-averaged nitrate concentrations per sampling round. The CFDs of Figure 4.2 have been aggregated into Figure 4.5. The differences between the CFDs of the first round and those of the second and third round underpin the hypothesis of less local co-deposition, because it is primarily the higher concentrations that have decreased. The difference between the second and third rounds compared with the fourth and fifth rounds supports the hypothesis of a growing impact from plant uptake/denitrification, since the higher concentrations are relatively less affected.

The larger decrease of N in the leachate as compared to rainwater could therefore be caused by less local co-deposition and by an increased uptake by plants or denitrification.

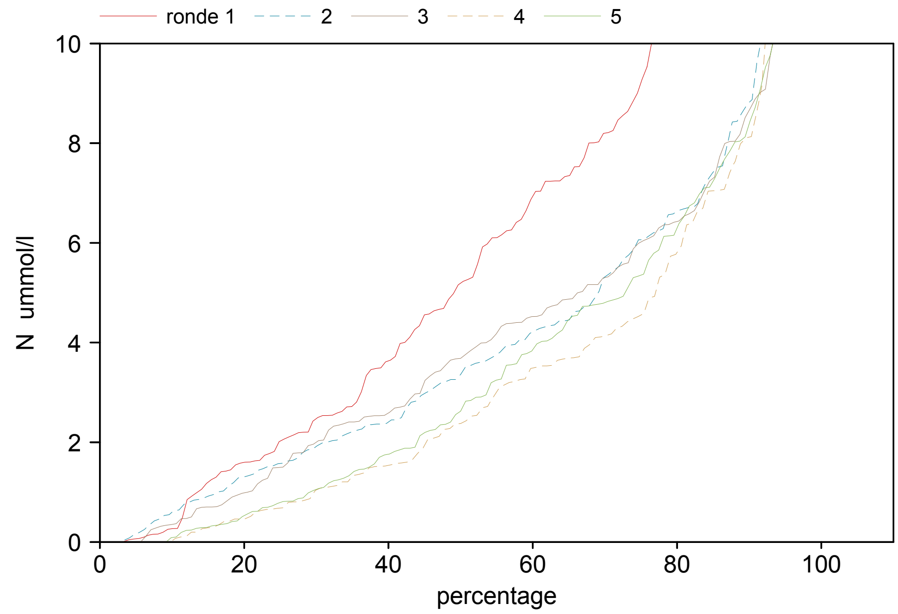


Figure 4.5 Cumulative frequency diagrams of location-averaged nitrate concentrations of the five TMV sampling rounds.

The lowering of nitrate concentrations in the leachate or upper metre of the groundwater can best be illustrated by a CFD showing the differences per location between the first and last sampling round; see Figure 4.6.

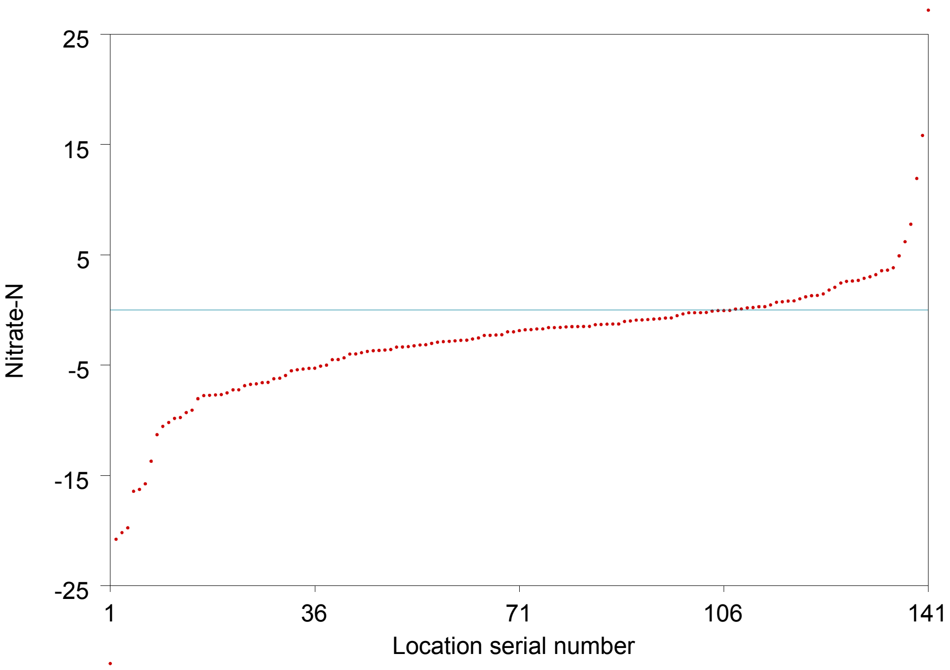


Figure 4.6 Cumulative frequency diagram of the differences between the location-averaged nitrate concentrations in 1989 and 2010.

4.4.5 Groundwater quality at a depth of 10 metres

All the aluminium in groundwater at a depth of about 10 m has been replaced by alkaline cations (see Table 4.1: the median Al concentration ranges from about 177 μmol/l in the leachate to 2.3 μmol/l in the deeper groundwater. Nitrate concentrations at a depth of 10 m are even lower than in the leachate. Between the mid-eighties and mid-nineties of the previous century, the NO_3-concentration showed an increase, followed by a decrease. S showed a decline as well, possibly setting in prior to the decrease of N. The groundwater consists of a mixture of leachate of different ages, causing changes in concentration to show up at a later stage and also more smoothened than in rainwater and the leachate. The evolution of the groundwater concentrations of N and S therefore confirm the general picture of the evolution of the total deposition shown in Figure 2.1.

When we assume that the chloride concentration in rainwater, prior to recharging the groundwater, was an average of 65 µmol/l ((72+58)/2) (see Table 4.1), then the ratio between the median chloride concentration in groundwater versus rainwater would have been an average of 6 (404/65). This is a realistic value for the deep groundwater. This factor is smaller than the one found for the leachate (10). Since the deeper groundwater is sampled in larger nature areas with deeper groundwater levels than the areas where the leachate is sampled (upper metre of the groundwater), the combined effect of dry deposition and inspissation in the groundwater is expected to be smaller.

The S/Cl-ratio in rainwater was about 0.8 (=57/72) in 1978, 0.6 (=45/73) in 1988 and 0.3 (=12/44) in 2010. The ratio of (median) concentrations dropped in the leachate from 0.9 (=536/562) in 1989 to 0.4 in 2010, indicating that the contribution of S released by the soil had increased. In the period 1990-2010, the S/Cl-ratio in the groundwater was about 0.9 (=371/303), corresponding with the ratio in the leachate of 1989 and in the rainwater of 1978.Chloride and sulphate concentrations in the groundwater decreased to the same extent, causing their ratio to remain fairly constant. In the period prior to 1978 it is likely that there was proportionally more sulphate than chloride in the rainwater (Figure 4.1). The S/Cl-ratio in 1978 exceeded 0.8. This factor may explain the high S/Cl-ratio in the groundwater.

5 Conclusions

Earlier research (Buijsman et al., 2010) shows that the emission of sulphur and nitrogen by industry, traffic and agriculture has diminished thanks to policy measures and autonomous developments such as the transition from coal to natural gas. This study shows that the emission reduction of nitrogen and sulphur is accompanied by lower levels of deposition of acidifying and eutrophying substances on the soil surface. The reduced deposition of these substances is reflected in a better groundwater quality.

Results
The effects of emission reductions of N and S can be seen in rainwater, the upper metre of groundwater and the groundwater at a depth of 10 m:

- In 2010, the concentrations of N and S in rainwater amounted to 61% and 27% of the 1988 levels, respectively. This means that by 2010 the N concentration in rainwater had decreased by 39% compared to the 1988 level, and the S concentration by 73%.
- In 2010, the concentrations of N and S in the upper layers of the groundwater amounted to 44% and 41% of the 1988 levels, meaning that the concentrations of N and S were 56% and 59% lower in 2010 than in 1989.
- A decrease was also found in concentrations of N and S in the deeper groundwater, but at a smaller magnitude.

In addition, the following results were found:

- In 2010, the aluminium concentration in the upper groundwater had decreased to about 56% of the 1988 level.
- The average pH in the upper groundwater rose from 4.58 in 1988 to 4.78 in 2010.
- The acid neutralising capacity (ANC) of the upper groundwater has increased significantly. However, the ANC in the upper groundwater was still negative at 80% of the sites investigated in 2010.
- This implies that acidification is still ongoing, though at a slower pace.

The analysis of the combined observations shows that the measures taken to reduce emissions have resulted in less acidification in nature areas with sandy soil. The RIVM findings presented above are comparable to research results from other countries.

However, there are some remarkable aspects:

- During the period 1988-2010, the N-decrease in the upper groundwater was larger than would be expected on the basis of the decline in the calculated total deposition and the decline of N measured in rainwater.
- It is estimated that only 27% of the N deposited actually leached in 2010, and that this percentage was higher at the start of the 1988-2010 period.
- The calculated S-deposition and the observed wet S-deposition decreased more than the observed S concentration in the upper groundwater. The more limited decrease of S in the leachate during the period 1988-2010 as compared to the decrease in rainwater concentration, and the higher S/Cl-ratio in the leachate in comparison to

rainwater, make it likely that there was a delayed release of S from the soil of about 20%.

- The nature areas where the upper groundwater is sampled have a shallower groundwater table and are smaller in size than the nature areas where the groundwater was sampled at a depth of 10 m. Due to this, the combined effect of dry deposition and inspissation is probably larger at sampling locations of the upper groundwater than at locations where the deeper groundwater was sampled. At the former locations, the chloride concentration in the leachate was ten times higher than the rainwater concentration; at the groundwater sampling locations at a depth of 10 m, the groundwater concentration was six times higher.
- A decrease has been observed in the heavy metal concentrations in the leachate. This may not be caused by less soil acidification. It could be caused by a decline in the atmospheric deposition of heavy metals. Earlier research by the RIVM has established that the wet depositions of a number of heavy metals decreased over the 1992-2004 period.

Effect on ecosystems
Scientific literature shows that, despite the positive developments, ecosystems have not yet recovered from the acidifying and eutrophying effects of air pollution. Recent research was conducted in the UK on the effects of the diminishing acid deposition on the biodiversity in surface water. At all research locations where biota were found to be recovering, the ANC of the water also proved to be on the rise. However, not all sites with an increasing ANC showed signs of biological recovery. Research shows that biological recovery proceeds at a slower pace than the recovery of abiotic conditions. Furthermore, simulations up to 2050 indicate that, under the Gothenburg Protocol, surface water quality will continue to improve (i.e. the ANC will continue to rise). However, the buffering capacity of the soil will only recover slowly and only at a limited number of sites. It is also expected that the ecological conditions will only recover slowly in the coming years.

According to research conducted in the Netherlands by Wamelink et al. (2012), the eutrophying deposition of nitrogen in nature areas in the Netherlands is still one of the biggest threats to plant diversity. At two thirds of the sites investigated, the nitrogen deposition exceeded the critical threshold. Nitrogen deposition remains a persistent problem for most locations. Especially the Veluwe, the Utrechtse Heuvelrug and the coastal dune belt are affected. Acidification is a limiting factor to ecological recovery as well, but to a lesser extent.

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Appendix 1 Chemical reactions in the atmosphere and soil

The formation of acids in the atmosphere
Sulphuric acid originates where sulphur dioxide is oxidised by oxygen in the atmosphere into sulphur trioxide:

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3$$

Subsequently, sulphur trioxide hydrolyses in the presence of water vapour:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Nitric acid is formed in a similar way. Ammonia is oxidised to form nitrogen oxide, which in turn hydrolyses into nitrous and nitric acid.

$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Nitric acid may also be formed by the dimerization of nitrogen dioxide into dinitrogen tetraoxide:

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

Soil acidification
When rainwater containing sulphuric acid or nitric acid enters a lime deficient soil, various chemical processes are set in motion. Soil acidification is usually not immediately accompanied by increased acidity or lower pH values. Soils contain substances like calcium carbonate, clay, humus and aluminium oxides. Acids are buffered by this soil material, whereby cations and aluminium dissolve in the soil moisture. When more acids are added, the buffering capacity slowly diminishes. As long as buffering substances remain available, the pH hardly changes. The soil chemistry, however, does change, resulting in nutrients such as calcium and magnesium to leach to deeper groundwater where plants are no longer able to reach them. When the buffering substances are exhausted, the pH starts to fall. At low pH values, aluminium and heavy metals may also leach into the groundwater. Since organisms can only survive within a specific range of pH values, this leaching can lead to ecological damage.

One mol of N-deposition (NO_y or NH_x) produces, after leaching from the root zone, one mol of acid. For this purpose, the reduced N (NH_x) needs to be oxidised first; hence the term ‘potential acid’. Reduced N in the soil (NH_4^+) is less mobile than nitrate. The concentration of NH_4^+ in the leachate primarily depends on the presence of clay and organic material within the solid phase of the soil, and to a lesser extent on the deposition of reduced N. NH_4^+ is released when organic soil material decomposes.

Oxidised N (nitrate) can be converted into N_2 (gas), as a result of which N disappears from the leachate and from the groundwater. This process is called denitrification. There are indications that denitrification takes place in the litter layer of Dutch acid forest soils, under the influence of higher temperature, humidity and pH; but the amount of denitrification is not clear (Laverman et al., 2001). Denitrification in acid forest soil also takes place deeper in the profile, as a consequence of high groundwater levels in the vicinity of the root zone

(Breemen et al., 1987); 2,5 kmol/ha; (Tietema and Verstraten, 1991). If nitrate is being denitrified above the root zone, this nitrate does not contribute to soil acidification. If this occurs in the upper groundwater layer below the root zone, the process does contribute to acidification. If denitrification takes place in the upper groundwater under the root zone, the symptoms of acidification in the upper groundwater layer will subside; see the equation below:

$$2NO_3^- + 10\ e^- + 12\ H^+ \rightarrow N_2 + 6\ H_2O$$

If, after a number of wet years, the groundwater table is higher, more denitrification will take place under the root zone. This factor is to be taken into account.

After leaching from the root zone, oxidised sulphur produces two mols of acid. Sulphate may also be adsorbed into the soil, resulting in less acidification. Under conditions of lower S-deposition, this sulphate is released again (Civerolo et al., 2003; Forsius et al., 2005; Watmough et al., 2005).

Appendix 2 Heavy metal concentrations in the National Acidification Trend Monitoring Network

Zinc

year	n	aver	min	5.0%	15.0%	30.0%	median	70.0%	85.0%	95.0%	max
1990	152	8.97	0.20	0.67	2.20	3.65	5.36	8.72	13.98	34.66	71.12
2001	149	4.99	0.20	0.60	1.29	2.02	3.50	5.00	9.03	16.78	29.91
2004	145	3.60	0.20	0.39	0.84	1.34	1.97	3.47	5.47	13.66	28.65
2007	137	3.80	0.20	0.25	0.74	1.29	2.18	3.23	5.09	12.66	66.47
2010	145	3.86	0.20	0.44	0.91	1.56	2.68	3.95	6.81	12.46	22.53

Cadmium

year	n	aver	min	5.0%	15.0%	30.0%	median	70.0%	85.0%	95.0%	max
1990	152	0.021	0.000	0.001	0.002	0.004	0.007	0.018	0.035	0.101	0.281
2001	149	0.017	0.000	0.001	0.001	0.002	0.005	0.016	0.037	0.083	0.163
2004	145	0.015	0.000	0.001	0.002	0.003	0.004	0.012	0.030	0.063	0.164
2007	137	0.014	0.000	0.000	0.001	0.002	0.004	0.010	0.022	0.061	0.209
2010	145	0.013	0.000	0.001	0.001	0.002	0.005	0.012	0.026	0.054	0.142

Nickel

year	n	aver	min	5.0%	15.0%	30.0%	median	70.0%	85.0%	95.0%	max
1990	0	*	*	*	*	*	*	*	*	*	*
2001	149	0.34	0.02	0.04	0.06	0.09	0.13	0.25	0.56	1.26	4.89
2004	145	0.30	0.02	0.03	0.05	0.08	0.12	0.21	0.40	1.00	4.80
2007	137	0.23	0.02	0.02	0.04	0.07	0.11	0.19	0.30	0.76	3.29
2010	145	0.21	0.02	0.03	0.04	0.07	0.10	0.17	0.40	0.85	2.44

Copper

year	n	aver	min	5.0%	15.0%	30.0%	median	70.0%	85.0%	95.0%	max
1990	0	*	*	*	*	*	*	*	*	*	*
2001	149	0.08	0.02	0.02	0.03	0.03	0.05	0.09	0.14	0.24	0.81
2004	145	0.08	0.02	0.02	0.02	0.03	0.05	0.09	0.12	0.24	0.57
2007	137	0.07	0.02	0.02	0.02	0.02	0.04	0.08	0.12	0.21	0.44
2010	145	0.07	0.02	0.02	0.02	0.02	0.04	0.06	0.11	0.22	0.48

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