Chapter 8
Nitrogen Deposition within the Littoral-Highlands County of Croatia Between 1996 and 2008

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Abstract Temporal trends in bulk nitrogen ($NH_4^+ + NO_3^-$) deposition at four sites within the Littoral-highlands County of Croatia are discussed. The selected sites included: the remote island Site 1, an urban and industrial coastal Site 2 (Rijeka), Site 3 which is a settlement and Site 4 a hunting resort located in the highlands area, claimed to suffer from acidic deposition. The lowest deposition of nitrogen (N) was measured at the remote Site 1 (5.6–11.2 kg N ha^{-1} $year^{-1}$), while higher values were obtained at the urban Site 2 (7.6–17.9 kg N ha^{-1} $year^{-1}$) due to the local washout of the atmosphere, and at the highlands Sites, 3 (10.3–32.1 kg N ha^{-1} $year^{-1}$) and 4 (5.6–24.9 kg N ha^{-1} $year^{-1}$) because of higher precipitation. The bulk nitrogen (N) deposition at the highlands Sites 3 and 4 is below the critical load for the corresponding soil-vegetation type (CL = 64.4 kg N ha^{-1} $year^{-1}$). In the period 1996–2003 NH_4-N made up 66 % of the N deposition at all sites, but since 2004 this ratio has diminished to 50 %, due to the increase in NO_3-N deposition. Overall there has been almost no change in N deposition at all except Site 4, where N deposition has increased, reflecting an increase in NO_3-N deposition but no significant decline in NH_4-N.

Keywords Bulk deposition • Inorganic nitrogen • NH_4^+/N-tot ratio

8.1 Introduction

As a result of human activities the input of reactive nitrogen (N_r) to terrestrial ecosystems worldwide has more than doubled (Smil 1990). Most of this input was confined to the developed regions of the world, due to fertilizer use, fossil fuel combustion and biomass burning, but is now rapidly increasing in the developing regions (Galloway and Cowling 2002). The observed responses of terrestrial systems to nitrogen (N) deposition can be understood within the context of the so called "nitrogen saturation" model developed from temperate–forest ecosystems

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(Aber et al. 1989). This model predicts that N limited systems will initially retain anthropogenic N, using it for plant and microbial growth, as well as accumulation in biomass and soil organic matter; then at the point when inputs of N begin to exceed the biotic (and possibly abiotic) demands for N within the ecosystem, the system is predicted to lose its N retention capacity. As a consequence, the excess of N can be lost in solution or via gaseous emissions. Furthermore, the model predicts a decrease in production in response to: cation losses, nutrient imbalances or increased susceptibility to stress such as frost, ozone or insect attack.

Increased N availability due to atmospheric N deposition leads to enhanced growth and dominance of fast growing, nutrient demanding species, over slow-growing nutrient economical ones, with a decline in species richness. Also alteration of plant tissue chemistry and timing of growth is likely to change the interaction between plants and herbivores (Matson et al. 2002).

Reduced biodiversity due to long-term N deposition has been observed in grasslands across Great Britain (5–35 kg N ha^{-1} $year^{-1}$), even at quite low annual nitrogen deposition. Species adapted to infertile conditions were systematically reduced at high nitrogen deposition. At the mean chronic N deposition rate of Central Europe (17 kg N ha^{-1} $year^{-1}$) there was a 23 % reduction in species compared to grasslands receiving the lowest levels (5 kg N ha^{-1} $year^{-1}$) of N deposition (Stevens et al. 2004). According to Hautier et al. (2009), competition for light is a major mechanism of plant diversity loss in response to eutrophication.

Though analysis of precipitation chemistry within the Littoral-highlands County started in 1984 (Alebic-Juretic 1994) with the determination of sulphates and nitrates, the analyses were only extended to include ammonium in 1996. As NO_3^- and NH_4^+ form approximately 85 % of the nitrogen species in precipitation (Kieber et al. 2005), their sum may be used as an indicator of reactive N deposition. Wet deposition (1,200–2,000 mm of rain annually) dominates in this area. Here we present temporal trends in bulk total nitrogen ($NH_4^+ + NO_3^-$) deposition at four sites within the Littoral-highlands County of Croatia. The contribution of dry deposition was not measured. The major source of oxidized nitrogen is industrial combustion (power plant, petroleum refinery) and traffic at the urban Site 2, the latter being the only source at highlands town Site 3. Refrigerating units in the harbour and petroleum refinery were industrial sources (with unknown emission) of ammonia at urban Site 2, while humans as ammonia sources can be considered in Sites 2 (Alebic-Juretic 2008) and 3. Due to the infertile nature of the soil and orography, agriculture is not an important economic activity and ammonia source in this area. Sites 1 and 4 are uninhabited remote locations.

8.2 Materials and Methods

8.2.1 Location of Sampling Sites

The locations of the sampling sites are given in Fig. 8.1.

Site 1 (Vrana) is a remote island site, approximately 100 km south from Rijeka, 250 m above sea level (a.s.l.) Site 2 (Rijeka) is an urban site (approximately 145,000

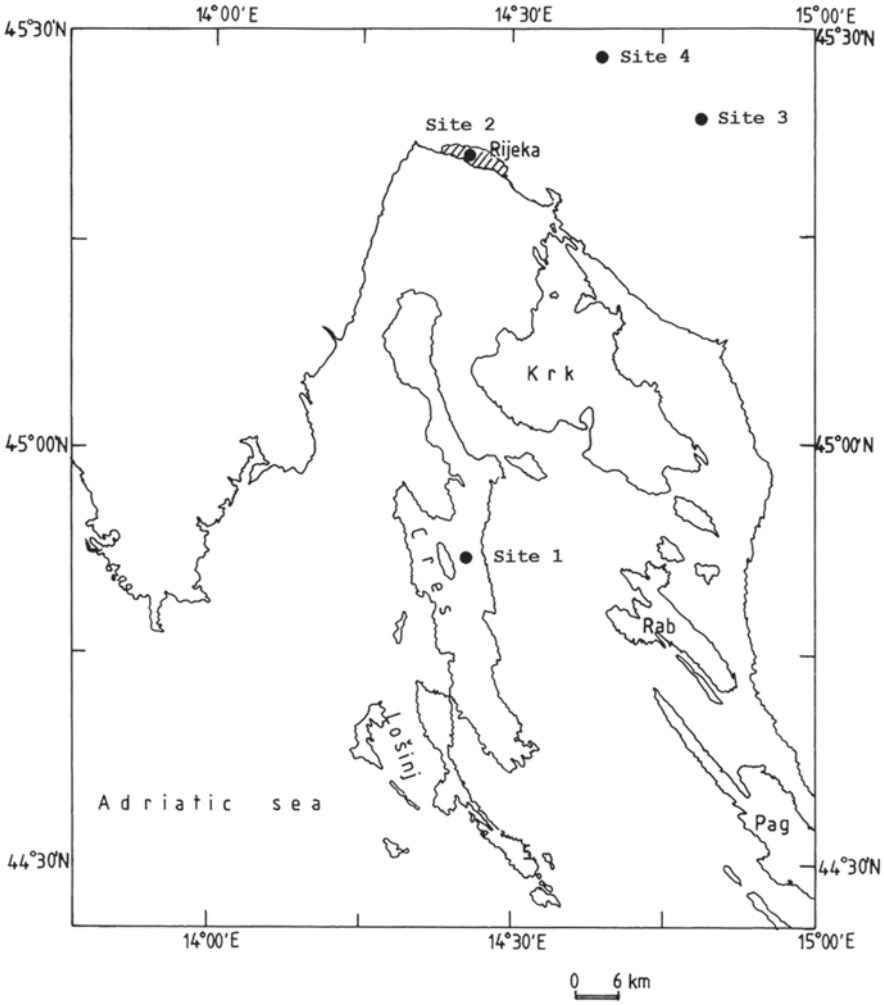

Fig. 8.1 Location of sampling sites

inhabitants), based at the Institute building in the wider city centre, 20 m above street level, at the divide between the harbour and residential area. Site 3 (Delnice) is a small settlement (approximately 6,200 inhabitants) in a mountainous area, 700 m a.s.l., approximately 40 km east of the city. Site 4 (Lividraga) is an uninhabited hunting resort in a mountainous area 930 m a.s.l., approximately 25 km north-east from Rijeka.

8.2.2 Methods of Analyses

Daily bulk rainwater samples were collected in open polyethylene buckets having 12 cm diameter and 15 cm height. The buckets were supported in aluminium

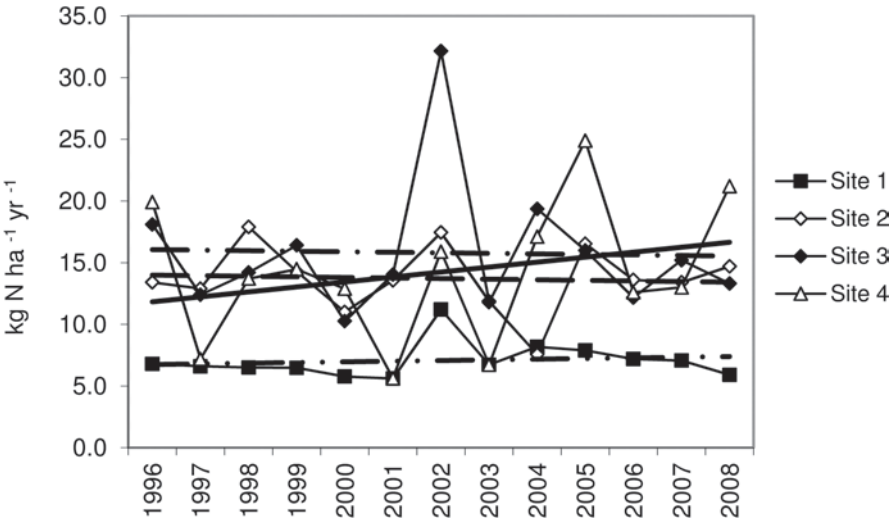

Fig. 8.2 Bulk total-N ($NO_3^- + NH_4^+$) deposition at four selected sites (kg N ha^{-1} $year^{-1}$) showing a particularly large Saharan dust episode in 2002

brackets 2 m above the ground. The buckets were replaced with clean ones once a day to avoid uncontrolled contamination by dry deposition.

The rainwater acidity was determined by measuring pH with pH-meter. Concentrations of ammonium and nitrate were determined by UV-VIS spectrometry (WHO 1976; APHA 1985). The respective lower detection limits (LDL) were: 0.1 mg/l for ammonium and 0.2 mg/l for nitrates. Annual deposition rates were obtained from the concentration of N species and the rainwater volumes collected over the year. The annual depositions of N were compared with critical loads for corresponding soil-vegetation type, where available. Irregular precipitation patterns during the seasons led to different deposition rates of N (and other species).

8.3 Results and Discussion

In an earlier examination of the precipitation data it was clear that orography was playing an important role in the deposition of acidic species: local wash out of the atmosphere in the wider urban area of Rijeka, an industrialized city within the Rijeka bay (Alebic-Juretic 1994), and greater precipitation in the background Highlands District (Alebic-Juretic 2008). The Highlands District was claimed to suffer from acidic deposition (Coz-Rakovac et al. 1995), though the first precipitation analyses started only in 1996, by which time SO_2 emissions had decreased by ~70% and NO_x emissions had fallen by ~40% relative to the mid-eighties in the Rijeka Bay area (Matkovic and Alebic-Juretic 1998). Such trends were similar to those observed in Europe (Toerseth et al. 2001). These lower emissions resulted in a decline

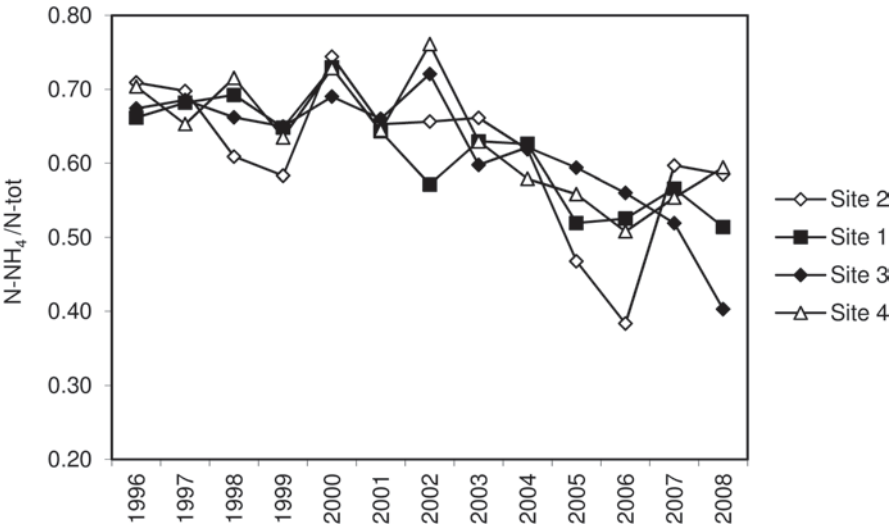

Fig. 8.3 Proportion of reduced NH_4-N at four selected sites

in the background air pollution for both SO_4-S and to a lesser degree NO_3-N deposition within the Rijeka Bay area (Alebic-Juretic 2008).

Deposition of total-N at the selected sites is given in Fig. 8.2. The lowest N deposition was obtained at the remote Site 1 (5.6–11.2 kg N ha^{-1} $year^{-1}$), while higher values were obtained at urban Site 2 (7.6–17.9 kg N ha^{-1} $year^{-1}$) due to the local washout of the atmosphere and at the highlands Sites, 3 (10.3–32.1 kg N ha^{-1} $year^{-1}$) and 4 (5.6–24.9 kg N ha^{-1} $year^{-1}$) reflecting the enhanced precipitation. Bulk N depositions at the highlands Sites 3 and 4 are below the critical loads (CLs) for the corresponding soil-vegetation type (*Abietatum dolomiticum/Calcic cambisol with redzina*) with $CL_{tot\text{-}N}$ = 64.4 kg N ha^{-1} $year^{-1}$ (Jelavic et al. 1998). Such a high CL reflects the buffering capacity of the alkaline composition of the underlying geology. However, exceedance might have been possible at the most sensitive area within the Highlands District (*Querco-Carpinetum orientalis/Chromic cambisols*) with $CL_{tot\text{-}N}$ = 24.4 kg N ha^{-1} $year^{-1}$ (Jelavic et al. 1998) in 2002, when a severe Saharan sand episode led to unusually high N and sulphur (S) deposition. Saharan sand episodes, the so called 'yellow rain' are characterized by high pH and high deposition of sulphates, nitrates, ammonium, and also calcium and iron. The quantity of Saharan sand deposited during an exceptionally severe episode of 'yellow rain' on April 12th 2002 was estimated to 11,000 t for the whole County area (1,320 km^2) bearing 1,239 kg of sulphates, 206 kg of nitrates and 159 kg of ammonium (Alebic-Juretic 2005).

In the period 1996–2003 NH_4-N made up 67% of total-N deposition at all sites, but since 2004 this ratio has fallen down to 50% reflecting the increase in nitrate-N (Fig. 8.3) from increased traffic in the wider region. The increase in nitrate-N offset the decline in ammonium-N so that overall there was no change in reactive N deposition at all Sites, except Site 4 (Fig. 8.4). This remote forest site showed no significant

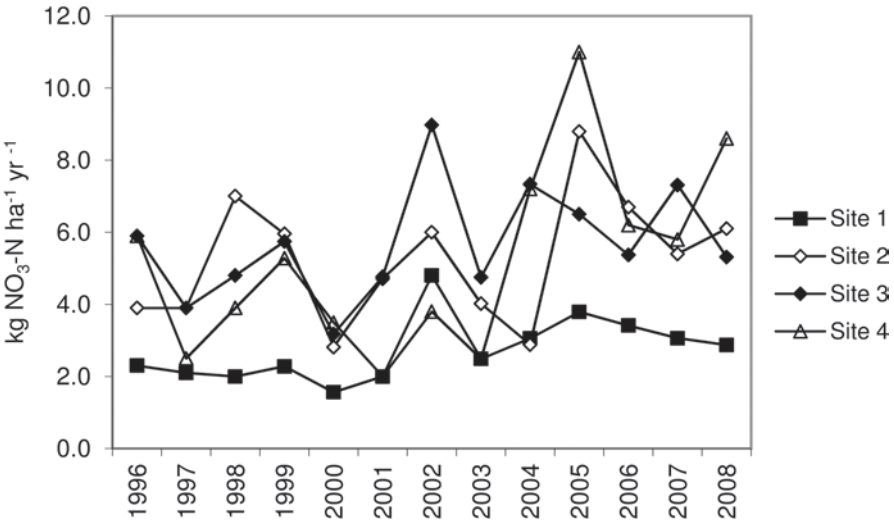

Fig. 8.4 Deposition of NO_3-N^- at four selected sites (kg NO_3-N ha^{-1} $year^{-1}$)

decline in ammonium-N, since the natural vegetation and the underlying soil are both ammonia sources (Langford and Fehsenfeld 1992; Bouwman et al. 1997).

8.4 Conclusion

The 12-year survey of bulk N deposition (wet + dry excluding occult) shows no exceedances of CLs for reactive N deposition in the area studied. These findings therefore contrast with the decline in forests observed in the mountainous Highlands District (Gorski kotar). This suggests that the observed forest decline was caused by factors other than N, or that the CL is too high to protect the ecosystem. Recent studies in boreal forests, where background N deposition is extremely low, suggest this might be the case (Nordin et al. 2005). An increase in vehicular use in the wider region appears to account for the increase in nitrate deposition since 2004.

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