



Soil Acidification on Dry Heaths in Jutland, Denmark—Trends in pH Over a Century

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Abstract Anthropogenic airborne pollution has lowered soil pH for decades, while partial chemical recovery has been documented in recent years in northwest Europe; however, it remains uncertain how naturally acidic ecosystems, such as dry heaths, have responded. Here, we attempt to elucidate scale changes over decades in surface soil pH in dry heath ecosystems by encompassing 1336 historic measurements from 120 sites covering a time span from 1920 to 2015, an unmatched timespan. The data set had soil pH (1:1 soil–water) ranging from 3.06 to 6.38 with a mean of 3.86 ± 0.01 . When analyzing the data in a change point model, initially a minor non-significant drop in pH (0.99) was seen before the change point followed by a weak non-significant positive trend. This may indicate that either there was a drop

from the 1920s to 1942, after which soil pH probably increased, or that there has been no change in the entire period. We propose that the change is related to either (1) that the sulphur deposition peaked in the early 1980s and, as result, sulphur deposition decreased, which caused a small recovery of soil pH, or (2) that anthropogenic acidification did not significantly change soil pH in this naturally very acidic ecosystem.

Keywords Soil pH · Dry heaths · Soil acidification · Heathlands · Change point model

1 Introduction

Dry heaths, with their characteristic cover of dwarf shrubs and nutrient-poor acidic soils, have especially been widespread in the westernmost regions of Denmark (De Graaf et al., 2009; Degn, 2019). However, their extent has been in rapid decline over the past two centuries (Schmidt, 2015). The functioning and biodiversity of dry heaths [EU habitat code 4030] are threatened by climate change, invasive species, eutrophication, fragmentation and acidification (Dise et al. 2011; Fagúndez, 2013). Heaths maintain or create acidic soil (Miles, 1985), and in some parts of northwest Europe are maintained by a millennium trajectory of human-nature interactions (Odgaard, 1992, 1994). Monitoring results and manipulation experiments reveal that their unique flora and ecosystem

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are changing, mainly due to deposition of sulphur and nitrogen (Bähring et al., 2017; Southon et al., 2013; Van Breemen & Wright, 2004), which, among other adverse effects, also alters soil pH (Reynolds et al., 2013). Consequently, contemporary conservation management attempts to mitigate the negative effects of especially nitrogen deposition and restore the ecosystem by removing topsoil, using extensive grazing, mowing, cutting turf, controlled burning and adding lime (Kleijn et al., 2008; Olmeda et al., 2019). Dry heaths are naturally very low pH environments due to organic acid production and Ericoid mycorrhizae forming Podzols (Blume et al., 2016; Degn, 2016; Hansen et al., 1999). However, soil pH has been affected by the anthropogenic atmospheric deposition in the past decades, which has contributed with much acidic deposition (the sum of H^+ , SO_x , NO_y and NH_x), and precipitation and weather also seem important for annual fluctuations in soil pH (Hansen & Nielsen, 1998; Helliwell et al., 2010; Nielsen et al., 2017).

Soil acidification is the process in which there is a decrease in Acid Neutralizing Capacity (ANC) or, alternatively, an increase in Base Neutralizing Capacity (BNC) (Blake, 2004) with potential Al toxicity at $pH < 4.5$. These changes act over decades in natural ecosystems (Blake et al., 1999). During acidification, saturation of the cation exchanger surface changes, and in soils with pH around or below 4.5, they become saturated with Al^{3+} , as aluminium becomes soluble in oxic water after which Al silicates start to act as buffers (Blume et al., 2016). There are different processes that cause acidification in the pedosphere. Recently, atmospheric pollution has caused increased acid precipitation, which is the most significant process in respect to natural dry ecosystems; the main chemical component that causes acid precipitation is sulphuric acid, but also dissimilar nitrogen species act as acidifying agents (Hansen et al., 1999; Steudel, 1995). During the past two centuries, increased amounts of S deposition have led to soil acidification (Engardt et al., 2017; Smith et al., 2011). In Europe and North America, sulphur emissions had their peak around the late 1970s to the early 1980s, and major S-emissions started in the nineteenth century as a consequence of the industrial revolution (Engardt et al., 2017; Smith et al., 2011).

Even though there has been a reduction of S deposition by 70% compared to the deposition at the

beginning of the twentieth century due to science-political policy-making (Grennfelt et al., 2020), S deposition is still above the natural background level of $0.061 \text{ eq/m}^2/\text{year}$ (Engardt et al., 2017; Bak pers. comm. October 2020). Also, N deposition has been shown to influence plant communities in acidic ecosystems, such as heaths, favoring non-ericaceous species, e.g. *Carex arenaria* L., which due to high growth plasticity and tolerance of high metal concentrations may start to dominate the dune ecosystem (Remke et al., 2009). Moreover, N deposition reduces plant species richness on dry heaths and similar habitats (Southon et al., 2013).

Soil acidity is an edaphic factor playing a pivotal role in root growth, plant nutrition and, hence, plant community structure (Hansen, 1976; Riesch et al., 2018). Riesch et al. (2018) found that 10% of the variation of plant community composition depends on soil pH. Especially broadleaved herbs tend to occur on soils with higher pH (Hansen, 1976; Schmidt, 2015), and reports from the twentieth-century document a decline of broadleaved herbs on heathlands (Hansen, 1976; Schmidt, 2015). In addition, Van Den Berg et al. (2005) highlighted that many acid-sensitive plants could be in decline due to lower ANC, since pH facilitates availability of (micro)nutrients, mineralization, metal availability, respiration, tolerance ranges and other key processes (Aciego Pietri & Brookes, 2008; Blume et al., 2016; Sauvé et al., 2000). Aluminium toxicity is a key process in very acidic soils and, as heathland have surfaces horizons naturally around or below the threshold around pH 4.5 (Blume et al., 2016), further lowering of soil pH would increase the, for some plant species, toxic effect. Moreover, this toxic effect could be amplified on the Ericoid mycorrhizae community on dry heaths with decreased soil pH.

Acidification studies from Northwest Europe include measurements of pH from heathlands and similar acidic habitats (Nielsen et al., 1999; Reynolds et al., 2013). For example, the British “Country-side Survey” on heathland soils showed a significant increase from 1978 to 1998 and a non-significant increase from 1998 to 2007 (Reynolds et al., 2013). Sites in the study by Reynolds et al. (2013) were chosen randomly from a square of $1 \times 1 \text{ km}^2$, and data were analyzed in a mixed model. In the entire period, they reported a rise in soil pH from 1978 to 2007. Reynolds et al. (2013) conclude from the study that

the significant increase in acidic soil pH was due to a decrease in S deposition. A study from the Netherlands by Kleijn et al. (2008) treats different abiotic factors that affect plant species on heathlands and acid grasslands. They conclude that the biogeochemistry of soils is closely related to pH, which they report to vary from 3 to 6. From Denmark, several older studies include measurements of soil pH from heathlands (Hansen, 1976; Weis, 1929, 1932). A noteworthy study is from Hansen (1976), who reports the mean pH on inland heathlands in Jutland to be 3.94 in the mor layer (O horizons) and 4.27 in the bleached sand layer (E horizon). In comparison, Nielsen et al. (1999) found that soil pH on heaths was 3.85 in the OA layer in Denmark.

Data on soil pH from Danish heathlands date back to 1920 (Müller, 1924). Data from 1920 to 2015 are primarily sampled based on soil horizons, O, A and OA, while soils were sampled by different techniques and measured by different equipment (Hansen, 1976; Müller, 1924; Weis, 1929, 1932). By converting early twentieth century pH measurements to values comparable to contemporary measurement, it is, however, with some caution possible to compare soil information from such a long period.

The aim of this study is to investigate possible trends in soil acidity in dry heaths from Jutland on a century-long time scale. Based on knowledge about the changes in atmospheric deposition of sulphuric acid and concomitant soil acidification in particular, our hypothesis is an anticipated initial drop in soil pH after which we expect an increase in soil pH. Furthermore, an alternative hypothesis may be that since dry heath is a semi-natural ecosystem at least 6000 years old (Odgaard, 1992, 1994) and adapted to a cool, humid climate on highly leached soil with $\text{pH} < 5$, inorganic strong acids from the air pollution only contribute a smaller or negligible part of the explanation for changes in the heathland flora, as Al in the mineral soil already acts as a proton buffer.

2 Method

2.1 The Data Set and the Study Region

A systematic review of both older and recently published and unpublished reports (Petersen, 2014) made it possible to compile a data set with soil pH

measurements from the early twentieth century to 2015 (Table 1). Data came from 20 sources including pH measurements from heathland soils. Some of the first reported Danish soil pH measurements were taken from a soil depth of 0–10 cm ($n=7$) and are in the present study classified as an OA horizon, as no further descriptions are available, Weis (1932). All other classifications of soil horizon from the older studies can be found in Table 1.

The measurements by Hansen (1976) are from O horizon only ($n=106$). From recent times, there are NOVANA data ($n=1183$) in which samples were taken from a depth of 0–5 cm, which is here interpreted as the OA horizon. All measurements were from A, A/E, OA or O, horizons, with a majority from the OA horizon (Table 2a in Supplementary Material). The report from Hansen (1976) is the most notable of the older studies, with 106 measurements of pH. Data not published in peer-reviewed papers were included when the pH measurements were considered reliable. These data were from the main gas transmission work at Frøslev-Egtved (1981), Vesterhavet-Egtved (1983) and the so-called Kvadratnettet mapping 1987–1988 (Breuning-Madsen & Jensen, 2001; Danish Agricultural Advisory Service 1990). In total, our data set includes 1336 measurements from 120 different sites, which encompass a period from 1920 to 2015.

Our study area comprises the western part of Denmark, the peninsula Jutland (Fig. 1). Soil parent materials are generally quartzitic sand to loamy sand and are fluvio-glacial and periglacial of origin formed during the last glaciation. The present-day climate is temperate with a mean temperature of 8.3 °C (1981–2010) and characterized by wet winters with a mean precipitation of 746 mm (1981–2010) and wet summers (212 mm) with an annual precipitation surplus of ca. 300 mm in some parts of Jutland (Vejr fra DMI, 2020). A digital soil map (Jordartskort) was retrieved from the Geological Survey of Denmark and Greenland (Geus webshop, 2020).

2.2 Assumptions and Selection Criteria

When compiling this data set, some assumptions and criteria were applied. One assumption was that all data before 1969 came from dry heaths. This assumption is difficult to verify because of missing knowledge of the condition of the vegetation of, namely,

Table 1 Summary of literature sources for dry heaths, year the study was conducted, the number of samples for pH measurements from each study, the soil horizon they were taken from and pH conversion to pH in a soil–water ratio (1:1)

References	Year	Horizon(s)	pH conversions	Sources for pH conversion	<i>N</i>	Mean	SD
Müller (1924)	1920–1921	A	$\text{pH}(1:1) = 1.1602 * \text{pH}(1:2) - 0.79$	Petersen (2014)	8	4.33	0.31
Weis (1929)	1924	A/E	$\text{pH}(1:1) = 1.1602 * \text{pH}(1:2) - 0.79$	Petersen (2014)	2	4.00	0.00
Weis (1932)	1929	OA	$\text{pH}(1:1) = 1.1602 * \text{pH}(1:2) - 0.79$	Petersen (2014)	7	3.82	0.31
Böcher (1941)	1931	O	Measured in 1:1	-	7	4.71	0.41
Petersen (1976)	1968	A, A/E, O	$\text{pH}(1:1) = 1.1602 * \text{pH}(1:2) - 0.79$	Petersen (2014)	4	3.73	0.21
Hansen, (1976)	1970	O	$\text{pH}(1:1) = 1.27 * \text{pH}(1:5) - 1.41$	Petersen (2014)	106	3.61	0.31
Petersen, (1972)	1971	A	Measured in 1:1	-	1	3.40	
Projekt: Frøslev-Egtved (Petersen, pers. comm.)	1981	A	Measured in 1:1	-	1	4.10	
Projekt: Vesterhavet-Egtved (Petersen, pers. comm.)	1983	A	Measured in 1:1	-	3	4.53	0.42
Sloth, (1990)	1986	A	Measured in 1:1	-	1	3.71	
Sørensen, (1988)	1986	A	Measured in 1:1	-	4	3.92	0.17
Danish Agricultural Advisory Service, (1990)	1987	A	Measured in 1:1	-	1	4.00	
Danish Agricultural Advisory Service, (1990)	1987	A	Measured in 1:1	-	1	4.00	
Danish Agricultural Advisory Service, (1990)	1988	A	Measured in 1:1	-	2	3.70	
Danish Agricultural Advisory Service, (1990)	1988	A	Measured in 1:1	-	1	3.90	
Madsen, H. Birch (1991)	1990	A	Measured in 1:1	-	1	3.76	
Nørnberg, (1995)	1993	A	Measured in 1:1	-	1	3.74	
Mossin et al. (2002)	1998	A	Measured in 1:1	-	1	4.00	
Sundberg et al. (1999)	1999	OA, E	Measured in 1:1	-	1	4.40	
NOVANA (2004–2015)	2004–2015	OA	$\text{pH}(1:1) = 1.02 * \text{pH}(\text{CaCl}_2) + 0.44$	Reuter et al. (2008)	1183	3.87	0.40
Total					1336	3.86	0.41

heathlands, which have since disappeared. Additionally, one of the limitations with the older data (here before 1980) is related to the lack of precise geographic coordinates, which makes it difficult to assess whether or not a particular site is still a heathland (Fig. 1a). Here, we took the conservative approach and classified all sites without dry heath vegetation to a different habitat code they are therefore not included in the dry heath data set, except some sites at Randbøl Hede, which is acid grassland at present (See Supplementary Material). Historic data from Hansen (1976)

combined with post 2004 data from NOVANA (a Danish habitat surveillance program) and the present NATURA 2000 habitat information (Natura 2000: Birds and habitats directives — European Environment Agency, 2020) indicate that at least one-quarter of all sites (ca. 26.5%) from which Hansen (1976) gathered samples were dry heaths. The one-quarter result from Hansen (1976) points to the likelihood that a significant proportion of the eradicated heaths were dry heaths, thus, making the assumptions listed above more plausible.

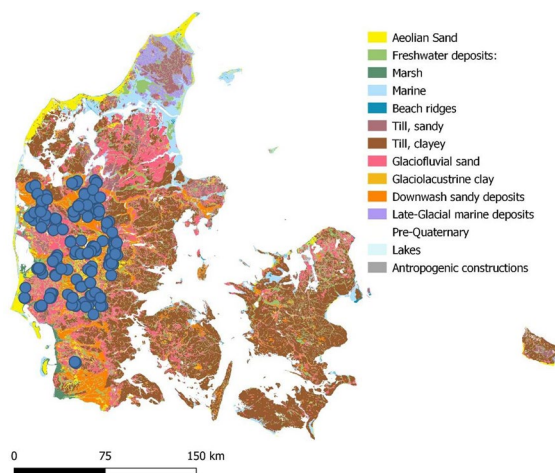


Fig. 1 Map showing soil types in Jutland and sampling sites for dry heaths, scale 1:200,000 reproduced from Pedersen et al. (2011). Here, sampling sites are shown as blue dots ($n = 1336$). Permission granted from the author

Enhanced leaching of base cation has a long-term effect on soil acidity and, hence, pH (Blake et al., 1999; Blume et al., 2016). However, our assumption here is that leaching of base cations has a minor effect on the pH in heath soil because these Podzols were already heavily acidic prior to 1920, and most have been so for millenniums (Odgaard, 1992). Therefore, changes in base cation leaching and NBC are not taken into account in the following modelling. Here, pH measured in 1:1 soil:H₂O was chosen as the most sensitive proxy for soil acidification changes. Aligning data from different periods was necessary in order to compare pH values. For transforming the NOVANA data to pH in 1:1 H₂O, Reuter et al.'s (2008) algorithm was used because it is the pedotransfer function based on the largest data transformation in acidic soils (Supplementary Material). Initial data exploration indicated that the increased distance to Jutland's west coast leads to a small negative trend in pH, as measured pH decreased by 2.63×10^{-6} M, likely due to effects from near-coastal atmospheric deposition of sea salt and pollutants (Hansen & Nielsen, 1998). This trend was not investigated further in this study and was, by necessity, omitted as a variable that might affect soil pH on inland heaths.

Selection criteria were used to align measurement values so that they could be compared on a temporal and geographic scale. Regarding the latter, only sites from Jutland with the longest heathland continuation

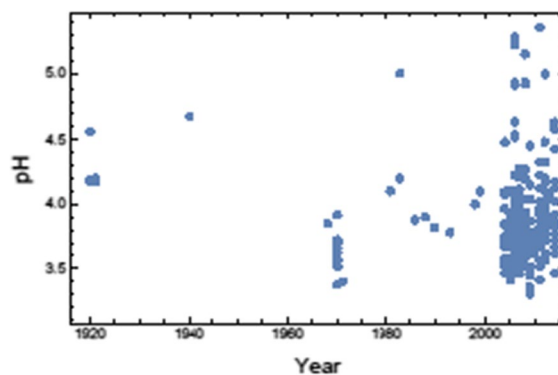


Fig. 2 Plot of means of the pH data on sites with at least two pH measurements ($n = 106$)

in Denmark (Odgaard, 1992) and sites > 5 km from the coastline, to avoid strong coast effects, were included (Fig. 1). No sites north of Limfjorden were included, as no data prior to the 1970s existed from this area (Fig. 1). Another geographic criterion was that all measurements were from the generally sandiest parts of Jutland (georegion 1, 3, or 6) due to differences in pH level between these and the other georegions (Fig. 2a. Supplementary Material). The soil types were primarily downwash sandy deposits 37%, glaciofluvial sand and/or gravel 35% and aeolian sand 17% (Pedersen et al., 2011). Sites in georegion 3 are located outside of the Scandinavian Ice Shield Main Stationary line, respectively on fluvio-glacial outwash plains and hill islands formed prior to the Last Glacial Maximum. Moreover, in georegion 6 (Eastern Jutland), no NOVANA data more than 10 km east of data from the period 1920–1989 were included (Figs. 1 and 2a). Climate plays an important role in pedogenesis and acidification. For this reason, only locations with annual precipitation exceeding 900 mm were selected, as S and N depositions are dependent on precipitation in Jutland (Damgaard et al., 2014; Hansen & Nielsen, 1998) (see also Fig. 2a. in Supplementary Material). Finally, no measurements from only mineral E horizon were included, as the pH values from this mineral soil horizon were significantly different from other horizons (data not shown). This is also in line with findings by Nielsen et al. (1999) and Hansen (1976). Moreover, no significant difference in soil pH between the generally sandy soils on the oldest hill island landscape or Weischelian glaciofluvial deposits could be found. When preparing the

data set for modelling, we selected sites with a least two records ($n = 106$ sites).

Data from 1920 to 1970 (Böcher, 1941; K. Hansen, 1976; Müller, 1924; L. Petersen, 1976; Weis, 1929, 1932) did not have exact coordinates, only site names, and habitat codes were assigned based on data from NOVANA. If a habitat designation was not possible, codes from NATURA 2000 were used to assign contemporary habitat codes (Danmarks Arealinformation, 2020). Due to imprecise coordinates, especially at the site Randbøl Hede (see Fig. 1a), all sampling sites here were listed as dry heaths based on the original site descriptions. Next, Hansen's data (1976) did not contain habitat codes, so habitat codes were assigned using NOVANA data or NATURA 2000 habitat information. Not all data from Hansen (1976) could be used, as not all sites were within NATURA 2000 habitat polygons or near to NOVANA stations. NOVANA stations are identified by a site number and not by the name of the specific heathland it lies within. Thus, when assigning site names to NOVANA data, only sites that were part of the same heathland, from where name information was available, were assigned the same habitat name. To determine whether there was an unbroken stretch of heathland between site(s) without a site name and with a site name, orthophotos from Google maps were inspected (Google Maps, 2020). NOVANA stations that were not assigned a site name kept their original site number as an identifier. For large heathlands (e.g. Boris and Randbøl Hede), all sites were assigned to one site name.

2.3 Soil Horizons and Measured pH Considerations

The measuring equipment and methods differ from 1920 to 2015. Soil pH from 1920 to 1940 was measured using Kinhydron and Electrometric instruments (Böcher, 1941; Weis, 1929, 1932). Some older sources measured pH in other soil–water ratios than 1:1, among these was Hansen (1976), who measured pH in a soil–water ratio of 1:5. Therefore, standardization was needed to compare pH values. Soil pH for different soil–water ratios was measured on 135 soil samples by Petersen, 2014, in order to make a pedotransfer function that could convert data from Hansen (1976) to a comparable 1:1 soil–water ratio. Soil pH was measured in CaCl_2 in the NOVANA data

set and, consequently, a transformation equation by Reuter et al. (2008) was used to make these data comparable with 1:1 soil–water measurements (Table 1a in Supplementary Material), although Wamelink et al. (2012) use another pedotransfer function. Soil pH (1:1 soil–water) for all measurements ranged from 3.06 to 6.38, with a mean of 3.86 ± 0.01 (standard error of the mean). Figure 2 shows the plot of means of soil pH in the time series.

The relevant pKa of sulphuric acid and nitric acid is similar, 2.0 and 2.2 respectively, giving them a similar acid strength in soil. However, SO_x potentially contributes with twice as many protons (Hansen & Nielsen, 1998). The increasingly higher concentration of carbon dioxide in the atmosphere during our study period has likely not affected dry heath soil acidity significantly, as water pH in equilibrium with 400 ppm CO_2 lowers to 5.6 only. Soil acidity changes caused by variations in the production of strong organic acids during decomposition of the humus layers and soil organic matter are likely insignificant on the studied multi-decade to century timescale.

2.4 Hierarchical Model

The trend in pH was examined by fitting the data with two hierarchical models: a linear model and a change point model, as for instance treated by Page (1954). The residual variation was assumed to be normally distributed and this assumption was checked by visual inspection of residual plots. The predictive ability of the models was examined using WAIC (Watanabe, 2010).

The measured soil pH at a site i and year t was denoted, $y_{i,t,j}$, where j are the individual measurements. The hierarchical soil pH data were fitted using a hierarchical model, where the true, but unknown, mean pH at site i and year t was modelled by latent variables $x_{i,t}$ and assumed to have normally distributed measurement and sampling errors,

$$y_{i,t,j} \sim N(x_{i,t}, \sigma_m) \quad (1)$$

where σ_m is the standard deviation of the measurement, pedotransfer and sampling error.

The yearly change in pH was assumed to be the same for all sites and was modelled by the slope, α , and a normally distributed process or structural error,

$$x_{i,t+\Delta t} \sim N(x_{i,t} + \alpha\Delta t, \sigma_p) \tag{2}$$

where Δt is the number of years between successive pH measurements at a given site, and σ_p is the standard deviation of the process error.

The slope was modelled by either (i) a constant slope model or (ii) a change point model, where the slope differed before α_1 and after α_2 , an estimated change point, τ . The realized slope of the change point model was modelled as,

$$\alpha = \begin{cases} \alpha_1 & t + \Delta t < \tau \\ \alpha_2 & t > \tau \end{cases} \tag{3}$$

$$\alpha = \frac{(\tau-t)\alpha_1 + (t+\Delta t-\tau)\alpha_2}{\Delta t} \quad t < \tau, t + \Delta t > \tau$$

2.5 Estimation of Soil pH

The joint Bayesian posterior distribution of the parameters was calculated using Bayesian Markov chain Monte Carlo MCMC (Metropolis–Hastings) simulations of 50,000 iterations with a burn-in period of 10,000 iterations and normal candidate distributions (Carlin & Louis, 1996). The prior of all parameters and latent variables was assumed to be uniformly distributed in their specified domains, except standard deviations that were assumed to be inverse gamma distributed with parameters (0.1, 0.1). Plots of the deviance and trace plots of all parameters were inspected to check the fitting and mixing properties of the used sampling procedure. The statistical inferences were assessed using the calculated credible intervals, i.e. the 95% percentiles of the marginal posterior distribution of the parameters. All calculations

were done using Mathematica (Wolfram Research 2019).

3 Results

For both models, the mixing properties of the sampling iterations were acceptable. The linear model showed a non-significant negative trend in soil pH (Table 2), whereas the change point model indicated a negative trend in soil pH before the change point τ and a small positive trend after the change point (Table 2). The change point was estimated to a median of 1942 with a wide credibility interval from 1931 to 1982. The WAIC for the change point model was 705.8, and 762.0 for the linear model, indicating that the change point model was the model that was best supported by the data. Consequently, we conclude that the trend

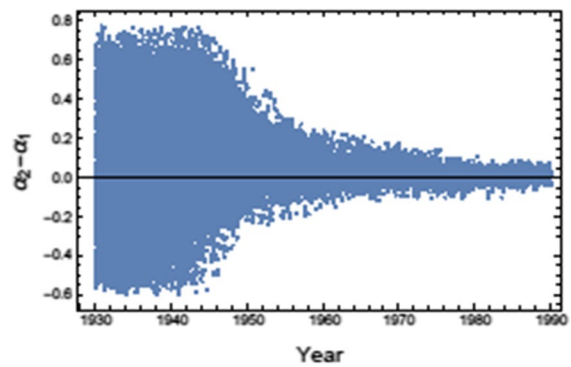


Fig. 3 Scatter plot of the posterior distribution of the difference between the two slopes in the change point model ($\alpha_2 - \alpha_1$) at the estimated change point (63% of the sampled differences are larger than zero)

Table 2 Credibility intervals for the parameters shown by 2.5%, 50% and 97.5% percentiles

Parameter		0.025	0.500	0.975	$P(X > 0)$
<i>Linear model</i>					
ν	SD of the measurement and sampling error	0.284	0.296	0.309	-
α	Slope	-0.019	-0.002	0.016	0.415
σ	SD of the process error	0.208	0.241	0.278	
<i>Change point model</i>					
ν	SD of the measurement and sampling error	0.283	0.296	0.311	-
α_1	Slope before change point τ	-0.583	-0.045	0.433	0.370
α_2	Slope after change point τ	-0.016	0.001	0.018	0.540
τ	Change point	1930.6	1942.3	1981.5	-
σ	SD of the process error	0.206	0.238	0.276	-

in soil pH was not constant over the studied period. Furthermore, there was a non-significant result that the slope before the change point was lower after the change point (Table 2, Fig. 3). This suggests that there was a minimum in soil pH at an intermediary time within the studied period.

These results do not contradict the prior specified hypothesis, where we anticipated an initial drop in pH followed by a subsequent increase. A competitive, but less likely, interpretation of our results could be that soil pH has been relatively constant during the studied past ~100 years than due to relatively few data points in the beginning of the studied period.

4 Discussion

Our results suggest that S deposition might be the cause of initially lowered soil pH, which from 1920 to 1942 decreased by 0.99 units followed by an increase of 0.073 units since S deposition peaked from the mid-1970s to early 1980s in West Europe (Aas et al. 2019; Engardt et al., 2017). While the N deposition peaked two decades later (Hansen et al. 2011) and the increases in air temperature and net precipitation continue to rise throughout the study period (Cappelen 2018), our observed minimum in pH (i.e. change point) came either before, at, or after the S deposition peaked. If it (the minimum) came before the aggregated effect of many years of S deposition, this (a) may be hypothesized to have affected soil pH on a longer time scale and there was a lag phase or, alternatively, (b) something not measured affected soil pH. If the effect(s) was instantaneous, the changing point and S deposition followed each other. The last option (c) is that the changing point came after the S deposition peaked; in this case, there would also be a lag phase, as the soil pH took time to change due to, for the authors, unknown reasons. Our data and results support the prior hypothesis (a), with a drop in pH from the 1920s to around early 1940s followed by an increase in soil pH although the slopes are non-significant. However, we do not know if soil pH is 0.92 units lower in 2015 compared to former levels in the 1920s. If there has not been a pH drop before 1920, factors other than S deposition, such as N eutrophication, climate change with warmer and wetter seasons and management or new species, are more likely to be governing the observed floral changes on dry heaths.

A possible explanation for the non-significant drop in soil pH between 1920 and 1942 is that tipping points for strong Al toxicity and Al mediating as pH buffer in soil were naturally surpassed for this type of vegetation even before air pollution began. Additional H⁺ from atmospheric deposition has thus affected the acidity of dry heaths very little or, perhaps, not at all. The minor increase in soil pH after the change point may indicate that the acidic podzol will not turn into a brown soil with higher pH and depodzolization, as shown after old heath vegetation has been invaded by grasses and oak shrubs (Nielsen et al. 2000; Nielsen et al., 1999).

A limitation to the study was the lack of data from the period 1932 to 1967, as any change in soil pH during this period cannot be quantified. Consequently, despite the long study period 1920–2015, it is challenging to assess the overall development and whether it had a minimum during this data paucity. In addition, only a few of the heathlands sampled before 1968 still remain, making it difficult to assess whether a measurement was from dry heath or another habitat. Given the uncertainty in coordinates from 1920 to 1970, it is problematic to assess the habitat type and eventual changes during this period.

Nevertheless, based on the data (Figs. 2 and 3, Table 2) we suggest that soil pH fluctuations have been minor in the studied period, but were at a minimum (3.39) in the mid-twentieth century. If soil pH did not change, then it could imply that acidification from especially S deposition throughout the period did not affect pH levels significantly on dry heathland soils, or that soil pH was already lowered prior to the 1920s on these highly leached soils. In the latter case, we suggest that the ANC could have been significantly lowered as early as 1920, affecting the soil buffer system and, thus, pH. In the former case, the natural very low pH in this ecosystem with Al–silicate buffering would have prevented any further measurable pH decrease.

Data from Reynolds et al. (2013) did not show a significant increase in soil pH from British heathlands between 1998 and 2007; this is in line with our exploratory analysis of NOVANA data and results from the change point model (Table 2). Contrary to our results, Reynolds et al. (2013) report a significant increase in pH from 1978 to 2007, also when uncertainty was taken into account. Our results are not

significant; however, our model supports the conclusions from Reynolds et al. (2013) with no pH change in recent years and a non-significant increase since the change point. For evaluating long-term trends on soil pH, the presented 100 years of data are, to our best knowledge, unique, but there are major uncertainties regarding trends, as discussed above. This is not the case with the data set presented by Reynolds et al. (2013).

Evaluating the century-long anthropogenic pH changes on dry heaths more thoroughly is difficult, since we do not have additional measurements of soil pH from dry heaths in Denmark or archived soil samples, as we do for other ecosystems in Denmark and the UK (Blake et al., 1999; Christensen & Johnston, 1997). Similar studies from other countries with dry heath and different depositions of S and N and with different parent materials could shed light on how soil pH responds to air pollutants during the Anthropocene. Studies on similar dwarf shrub habitats would be exciting, for instance whether wet heath has the same changes in soil pH, as time series here are shorter (Damgaard et al., 2014). Moreover, most of the remnants of heathlands in Northwestern Europe have been heavily affected by agricultural intensification and air pollution, rendering comparison with other inland heathlands possible. Therefore, the observed change of 0.92 units from 1920 to 2015 could, in theory, be comparable to other dry heaths in Western Europe, but the consequences for dry heaths ecosystem, with this status quo in soil pH, are probably minor, as other factors (e.g. N deposition) are probably one of the primary drivers of the flora changes on dry heaths (Fagúndez, 2013). However, a lower soil pH could reduce the realized niche for plants with requirements of a higher Ellenberg R (Bak, 2013).

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was done by Mathias Emil Kaae. The draft of the manuscript was, with exception of two sections in the “Method”, i.e. the “Hierarchical Model” section and “Estimation of pH” section, written by Mathias Emil Kaae. Data analysis was done by Christian Frølund Damgaard, Mathias Emil Kaae and Jesper Leth Bak. All authors commented on the final manuscript. The final manuscript was approved by all authors and all authors made substantial contributions to the manuscript.

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Data Availability Data can be obtained from the first author.

Declarations

Conflict of Interest The authors declare no competing interests.

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