Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Assessing the Environmental Impact of Geothermal Power Utilization Using Isotope Ratios (C, N, S, Pb) in Moss (*Rhacomitrium Lanuginosum*)

Bjarni Gautason[1)] and David Widory[2)]

1) Iceland Geosurvey, Rangarvellir Akureyri, Iceland. 2) GEOTOP/University of Quebec in Montreal, (UQAM) Canada

e-mail: bjarni.gautason@isor.is

Keywords: Isotopes, S, C, N, Pb, moss, Rhacomitrium lanuginosum, hydrogen-sulfide, pollution

ABSTRACT

Conventional geothermal power plants are sources of industrial waste including spent fluids and non-condensable gases. Increasingly spent fluids are being re-injected in to the geothermal systems reducing significantly the environmental impact of power production and sustaining pressure within the system. While efforts are afoot to sequester some of the non-condensable gases (e.g. CO2 and H_2S) a significant portion of the gases are currently vented to the atmosphere. Little is known of the effects of long term exposures to low levels of hydrogen sulfide. However, it has been suggested that H_2S plays a role in the decline of vegetation around the geothermal power plant in Hellisheiði. In this study we examine the stable isotopic composition of woolly fringe moss (*Rhacomitrium lanuginosum*) from lava-fields around geothermal power plants in south-west Iceland. A sample suite originally collected for trace element analysis was analyzed for the isotopic composition of sulfur (S), nitrogen (N), carbon (C) and lead (Pb).

The isotope ratio of sulfur varies by about 16 per mil and is controlled by binary mixing, with the most probable end members being i) hydrothermal/magmatic (“mantle-derived”) sulfur and ii) marine-derived sulfur. The isotopic composition of N ($\delta^{15}N$) varies from -10.3 to -6.0 (‰ PDB). The more enriched (less negative δ-values) samples are more variable in terms of N content and are have comparatively high Pb content. The isotopic composition of C ($\delta^{13}C$) varies from -26.1 to -23.0 (‰ PDB). The more enriched samples have typically lower C content possibly reflecting addition of dust (carbon free) to the samples. The dust may contribute Pb to the moss samples. The change in discrimination for the heavy isotopes (^{15}N and ^{13}C) may be a result of environmental factors such as reduced precipitation or due to an increased anthropogenic influence.

The results do not support the contention that geothermal H_2S is responsible for the decline in vegetation around geothermal power plants. Other inputs are suggested by the data, including locally derived bedrock dust (e.g. construction activities), possibly heavy traffic (car exhaust, road dust) or other environmental factors such as reduced precipitation.

1. INTRODUCTION

The environmental impact of geothermal energy utilization compares favorably with other sources of energy. However, concomitant with geothermal utilization, for electrical production in conventional power plants, is an acceleration of the release of various environmentally harmful gases from natural sources (e.g. H_2S and CO_2). Increasingly methods are being developed and tested to mitigate the environmental impact of power plants by e.g. capturing and neutralizing or re-injecting the effluent. However large quantities of potentially harmful gases are still being vented to the atmosphere, a situation that is unlikely to change in the near future.

Mosses have been used extensively as monitoring organisms of atmospheric pollutants (Gerdol *et al.*, 2002, Migaszewski *et al.*, 2010). Mosses are regarded as useful bio-indicators of air quality because they can accumulate sulfur and other elements to a greater level than is necessary for their physiological needs. Moss also has a tendency to capture and “archive” fine particulate matter from the atmosphere which among other things has led to the use of moss bags as sample collectors in pollution studies.

Since the pioneer works of Keeling (1958) and Patterson (1987), the use of stable isotope compositions to elucidate and constrain the budget of atmospheric pollutants has vastly proven its added value compared to more classical approaches (Kelly & Ondov, 1990). Recent studies demonstrated that a multi-isotope approach could unambiguously backtrack sources of air pollutants and help characterise secondary processes occurring post-emission (e.g. Widory *et al.*, 2004, 2007, 2010). Still, the isotope tracing of atmospheric pollutants is usually achieved by either directly collecting gases (e.g. McManus *et al.*, 2010), and/or filtering aerosols (e.g. Chiarada & Cupelin, 2000) or indirectly by sampling meteoric water or snow (e.g. Nakano & Tanaka, 1997; Chabaux *et al.*, 2005). However, the use of bioindicators to monitor/assess the quality of different environments offers numerous advantages, such as the possibility of highly bio-concentrating both organic and inorganic contaminants or access to time-integrated information (Conti and Cecchetti, 2001). Mosses and epiphytic lichens are widely recognised as the best bioindicators of the air quality due to their ability to accumulate chemical elements (including sulphur and metals) in amounts exceeding their physiological needs. This attribute is resulting from their physiological properties: lack of cuticle, absence of protecting organs (which could limit the adsorption of toxic substances), large exchange surface. This is also why they are capable of absorbing both soluble and insoluble mineral nutrients they need to survive from air aerosols and precipitations with a negligible loss (Gerdol *et al.*, 2002; Liu *et al.*, 2007).

It is well documented that S, derived from human activities, has exceeded the average natural amount released into the atmospheric system. It has been considered as the central trigger in the acid deposition process since the early 20th century (Brimblecombe *et al.*, 1989). The current S biogeochemical cycle is largely controlled by anthropogenic atmospheric inputs. It is thus of both environmental and ecological importance to understand the level and sources of atmospheric S deposited onto vegetation and soil

(Puig *et al.*, 2008). The stable isotope composition (δ^{34}S) of S is probably the most commonly used systematic in the biomonitoring study of environmental quality, and particularly when tracing S sources of pollution. The δ^{34}S has been known as an important tool providing source-specific information that can serve as a fingerprint to identify S sources at scales ranging from highly localised to regional or even global (e.g. Krouse, 1977; Nriagu *et al.*, 1991; Alewell and Novak, 2001). Both mosses and lichens buffer the mean isotope signal of the atmospheric S (SO_2 and dissolved sulphurous compounds; Krouse, 1977; Winner *et al.*, 1978; Case & Krouse, 1980). The S assimilation by these organisms induces an isotope fractionation (Δ^{34}S) that can be considered negligible (Mektiyeva *et al.*, 1976, Trust & Fry, 1992). Nevertheless most of the studies so far have focused on pine trees needles and barks. Studies of the δ^{34}S from mosses and lichens are mostly recent (Winner *et al.*, 1978; Galuszka *et al.*, 2005) but already promising.

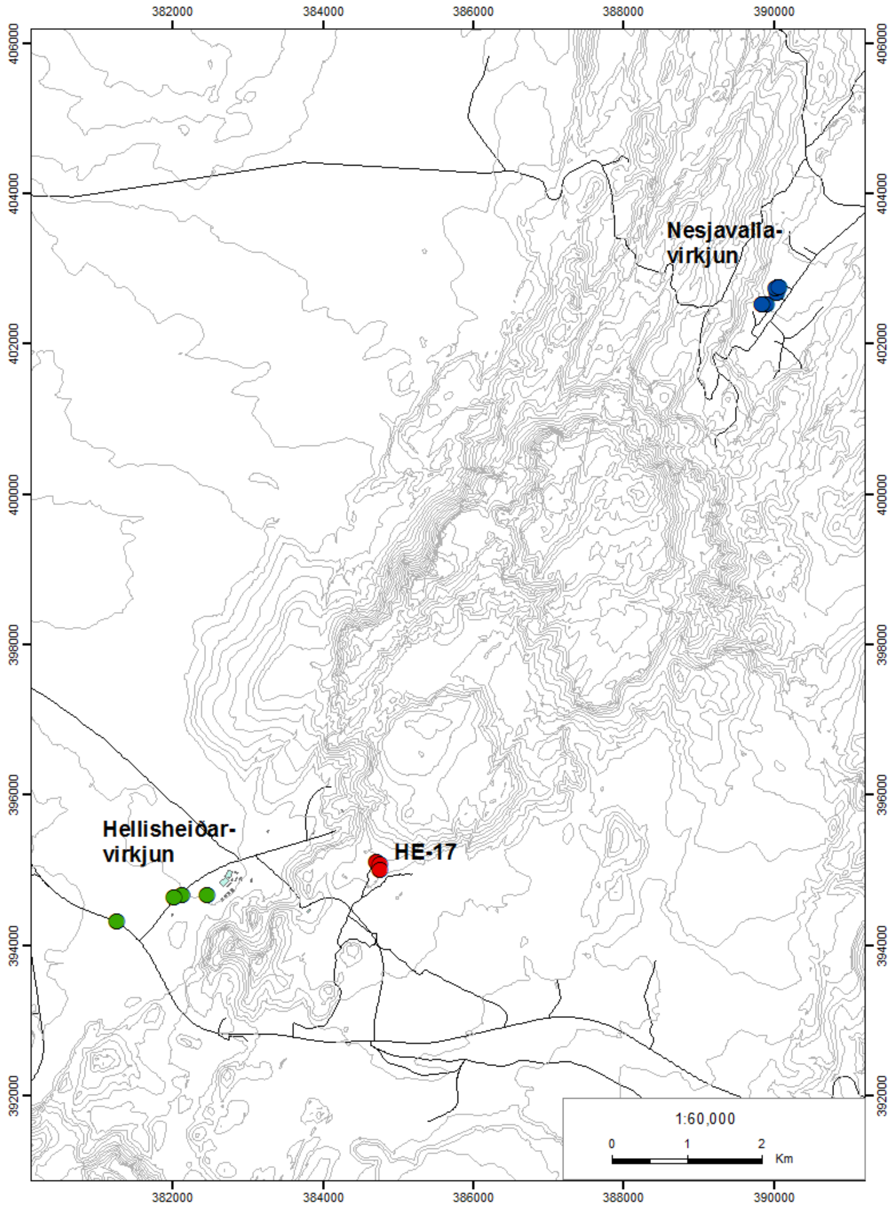

Figure 1: Map showing the location of the sampling sites around the power plants at Hellisheiði (green circles) and Nesjavellir (blue circles) and at well HE-17 (red circles).

The possibility to trace the sources of atmospheric Pb by the use of its isotope ratios (^{207}Pb/^{206}Pb, ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and $^{207\text{Pb}/204}$Pb) in lichen was oftentimes demonstrated (Carignan & Gariépy, 1995; Monna *et al.*, 1999; Purvis *et al.*, 2004; Spiro *et al.*, 2004). Carignan and Gariépy (1995) successfully backtracked the origin of atmospheric Pb in Québec using ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb isotope ratios in epiphytic lichens and vegetation samples.

The present paper is aimed at testing the potential of using stable isotopes to study the environmental impact of geothermal power plants. We adopted a multi isotope approach, using C and N isotopes to study the elements essential to the organism biological functions, S isotopes as a key hydrothermal indicator and Pb isotopes as an indicator of other anthropogenic inputs in the region of study. Analyses were made on the woolly fringe moss (*Rhacomitrium lanuginosum*) that is common in the lava fields of SW-Iceland. A series of samples originally collected for trace element analysis (Bragason and Yngvadóttir, 2009) were prepared for stable isotope analysis. Previously, *Hylocomium splendens* has been used in Iceland to monitor heavy metal deposition and study specifically the effects of large smelter operations on the environment (e.g. Magnússon and Thomas, 2007). In addition stable C and N isotopes in moss and other plants have been used for ecological and archeological studies (Skrzypek *et al.*, 2008; Wang and Wooller, 2006; Ascough *et al.*, 2014). Isotopically labelled nitrogen compounds have been used to study the effects of N deposition on woolly fringe moss in SW-Iceland (Jónsdóttir *et al.*, 1995).

2. GEOLOGICAL AND ENVIRONMENTAL SETTING

Moss samples were collected from the areas around the Hellisheiði and Nesjavellir power plants in SW-Iceland (Fig. 1). These power plants are located within the Hengill volcanic systems in SW-Iceland. The Nesjavellir power plant is located north-east of the Hengill mountain and the Hellisheiði power plant south-west of that same mountain. For comparison to the samples proximal to the power plants we also analyzed moss samples from the Blafjöll area, several kilometers away and far removed from the effects of hydrothermal power plants. The Bláfjöll moss samples were taken at an altitude similar to that of the samples in the Hengill region. Finally we analyzed a few moss samples moss from the Reykjanes peninsula sampled in the vicinity of the Svartsengi power plant.

The samples were collected in the fall of 2008. In Hellisheiði samples were collected from an area southwest of the power plant and south of well HE-17. The previous summer (growing season) wind from the north had been dominant. At Nesjavellir samples were collected from the immediate vicinity of the power plant, both to the south and north of the power station. At Svartsengi samples were collected at three sites in the lavafield north of the power plant. Several samples were taken from each site.

At the time of sampling a 90 MW power plant had been operating for two years at Hellisheiði. Intense drilling in the area had been ongoing for ~5 years. Typically high-temperature wells are vented for several weeks or a few months after completion and thermal recovery. In contrast, the power plant at Nesjavellir had been in operation for 12 years. The plant was expanded in 2006 and power production was increased. During the 5 year period from 2003 to 2008 the Nesjavellir power plant released a little over 50 10^6 kg H_2S compared to a total release of a little over 20 10^6 kg at the Hellisheiði power plant for the same period (Orkuveita Reykjavíkur, 2012).

Geological mapping (Saemundsson *et al.*, 2010) and drilling in the area has revealed that the Hengill area is characterized by prominent Pleistocene sub-glacial eruptive units that are intercalated with lava flows from ice free periods and cross cut by dikes. The succession is cut by numerous faults, many extending to the surface where graben like structures associated with rifting are also common. From approximately 1 km to 2 km depth the successions are characterized by surface lavas and dikes. Hengill, the most prominent feature in the area in terms of relief, is draped by recent lava flows to the north and south. The youngest eruptive unit is ~1900 y old. The bedrock is predominantly composed of basaltic rocks (olivine-tholeiites and tholeiites) with rare and volumetrically insignificant occurrences of either more mafic rocks (picrites) or more silicic rocks (andesites) (Saemundsson *et al.*, 2010).

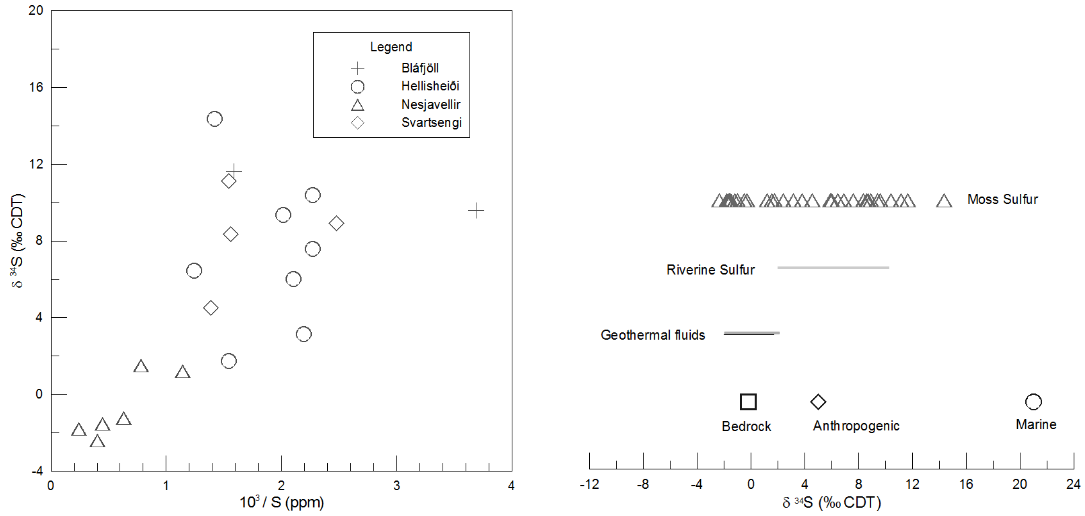

Figure 2. Variation in δ^{34}S versus S concentrations (left panel) for moss samples and a comparison of the δ^{34}S range in mosses with various "reservoirs" (right panel). Riverine sulfur and averages for bedrock and anthropogenic reservoirs are taken from Gislason and Torssander (2006), geothermal fluids from Marty *et al.* 1991, and marine sulfur from Rees *et al.* (1978).

3. ANALYTICAL METHODS

The samples analyzed for stable isotopes are predominantly from the active top 5 cm of the growing moss strands but a few samples of the "inactive" central part (approximately the center 5 cm) and bottom part of mosses are included as well. The growth rate (stem elongation) of *Rhacomitrium lanuginosum* is dependent on a number of environmental factors but typical rates are from a few millimeters up to 10 to 12 mm per year (Tallis, 1964). Experimental work indicates that the moss is active at temperatures down to -5°C (Kallio and Heinonen, 1975). Samples of moss were rinsed in distilled water and dried overnight at 48 °C. Samples were then ground to a fine powder in an agate mortar. For δ^{34}S, the powders were combusted using a Parr oxygen bomb and then converted to $BaSO_4$ (Novak *et al.* 2001). C and N isotope compositions (δ^{13}C and δ^{15}N, respectively) were determined using an

Elemental analyzer connected to an Isoptope Ratio Mass-Spectrometer (CF-IRMS). The results for S, C and N are reported in the standard δ-notation in ‰ (‰) relative to international standards (CDT, PDB, Air). For δ^{13}C and δ^{15}N the precision is better than ± 0.1 ‰. For δ^{34}S precision is better than 0.2‰. Isotopic ratios of Pb were determined following the procedure used for atmospheric particulate material described in Widory *et al.*, (2004). For routine analyses the uncertainty level is 0.01% for ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb, and 0.1% for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb.

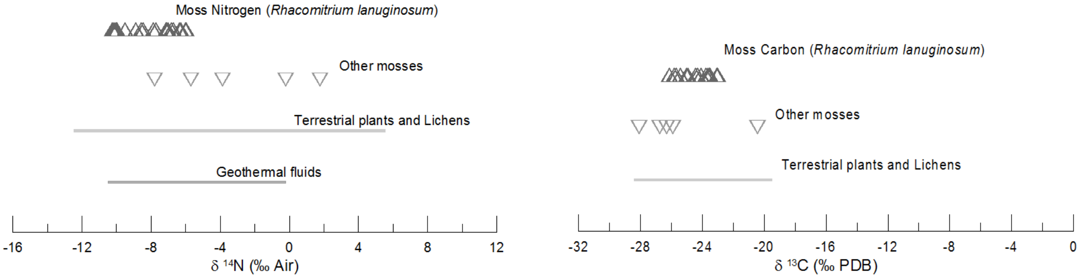

Figure 3. Range of δ^{15}N and δ^{13}C observed in mosses *(Rhacomitrium lanuginosum)* from SW-Iceland compared to other terrestrial plants in Iceland ((Skrzypek *et al.*, 2008), (Wang and Wooller, 2006), Ascough *et al.*, 2014).

4. RESULTS

4.1 Sulfur

Sulfur isotope ratios in moss are highly variable (Fig. 2). The most depleted δ^{34}S-depleted samples are commonly below -1.0 ‰ and extending to -2.4 ‰. The most enriched samples are commonly between ~+6.0 and +12.0 ‰ with a single sample at +14.4 ‰. The most depleted samples are the most sulfur rich (Fig. 2).

The large δ^{34}S range in our *Rhacomitirium lanuginosum* samples is compared to potential sulfur sources in Fig. 2. Marine sulfur is homogenous with a δ^{34}S value of +22.4 ‰ (Rees *et al.*, 1978). Volcanic bedrock (fresh and altered) in Iceland display a fairly narrow range of δ^{34}S values with most of the analyzed samples falling between -2.0 and +1.0 ‰. Following Gislason and Torsander (2006) we assume an average bedrock δ^{34}S value of -0.2‰. Reflecting their relatively homogenous "magma" reservoir geothermal fluids are similarly depleted and fairly homogeneous source of sulfur with a δ^{34}S centered around 0‰. The S-isotopic values of riverine sulfur (predominantly dissolved as sulfate) are shown for comparison in in Fig. 2.

Riverine sulfur is considered to be derived from bedrock and particulate load from the respective catchments with a considerable contribution of marine sulfur delivered as sea-spray to the catchment (Gislason and Torssander, 2006). Importantly, for the present study, riverine sulfur is responding to a reduction in anthropogenic S-output in N-America in spite of increased local output of anthropogenic sulfur. While riverine sulfur is not strictly considered a potential source for moss the chemistry of riverine sulfur has important implications for the present work.

Sulfur in moss has a cumulative aspect to it in particular since the samples represent averages of ~5 years of growth (assuming a 10 mm/yr average growth rate). Riverine sulfur on the other hand is much closer to a snapshot of the S budget at the time of sampling. Detecting anthropogenic S in the mosses is problematic since it is intermediate between marine and hydrothermal sources unless the anthropogenic component completely dominates the total sulfur budget. This is not the case and given the apparent decline of anthropogenic S in the riverine S budget we conclude that the anthropogenic contribution to the moss sulfur is negligible

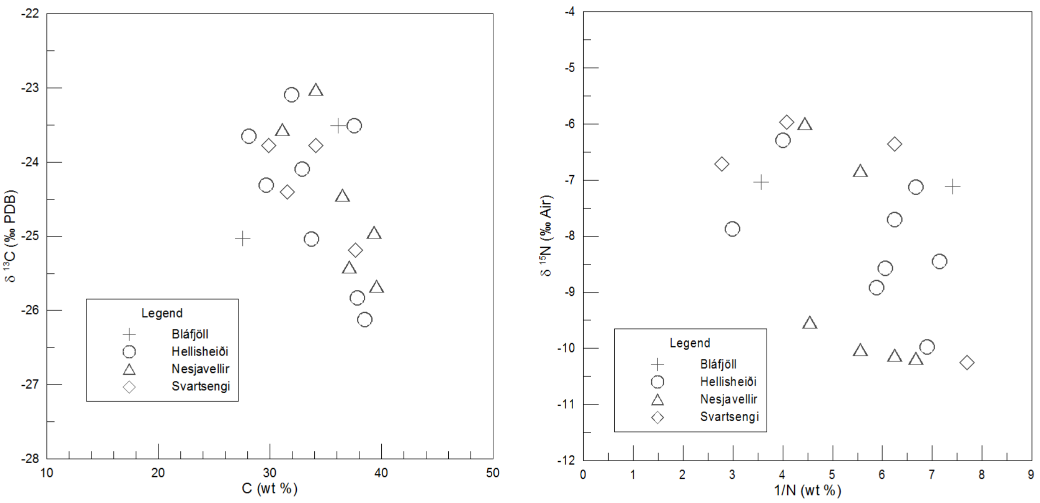

Figure 4. Variation in δ^{15}N vs. reciprocal N concentration (left panel) and variation of δ^{13}C vs. C concentration (right panel) in moss samples. Note that the most isotopically depleted (most negative δ-values) samples have uniform and low N content but high C content. Samples with high N and low C content are isotopically more enriched and/or isotopically variable.

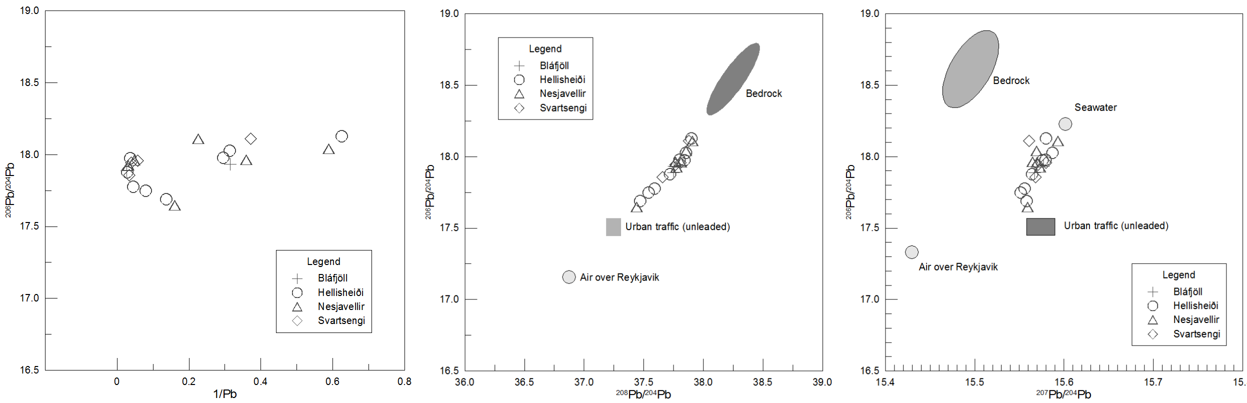

Figure 5: Pb isotope plots showing: reciprocal of Pb concentration vs. $^{206}Pb/^{204}Pb$ (left); $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (center); and $^{206}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (right). Literature values are as follows: Air (Bollhöfer and Rosman, 2001); Bedrock (Peate *et al.*, 2009); Seawater (Zubrick *et al.*, 2013); Urban traffic (Widory *et al.*, 2004).

4.2. Nitrogen

The $\delta^{15}N$ nitrogen values of the moss samples also cover a relatively narrow range of values from -6.0 to -10.3‰. This is within the range of values previously recorded for terrestrial plants (Fig.4) but these moss samples are more depleted than the previously reported values for moss from other localities in Iceland. This may be related to moss species but that cannot be confirmed because very few samples have been published in the literature and in some cases information on specific species is lacking.

4.3 Carbon

The moss $\delta^{13}C$ values spread over a relatively limited range of values from -23.0 to -26.1 ‰. These values are similar to those reported for mosses from other areas (Skrzypek *et al.*, 2008; Wang and Wooller, 2006) in Iceland (Fig. 3). When other terrestrial plants are included (lichens, ferns, grasses, herbs etc.) the $\delta^{13}C$ values cover an even larger range of values. The $\delta^{13}C$ values are typical of what is observed in bryophytes in northern hemisphere that follow the C_3 photosynthetic pathway (Rundel *et al.* 1979; Proctor *et al.* 1992; Loader *et al.* 2007).

4.4. Lead

While Pb concentrations in moss samples display large variations, the corresponding Pb isotope ratios (e.g. $^{206}Pb/^{204}Pb$) are fairly uniform (Fig. 5). Results show that the isotope variations may be explained by at least a ternary mixing involving: i) locally derived bedrock dust with relatively radiogenic $^{206}Pb/^{204}Pb$ and a narrow range of $^{207}Pb/^{204}Pb$, ii) road traffic emissions, that may contribute to samples having relatively high $^{207}Pb/^{204}Pb$ coupled to relatively low $^{206}Pb/^{204}Pb$, and finally iii) seawater-derived Pb.

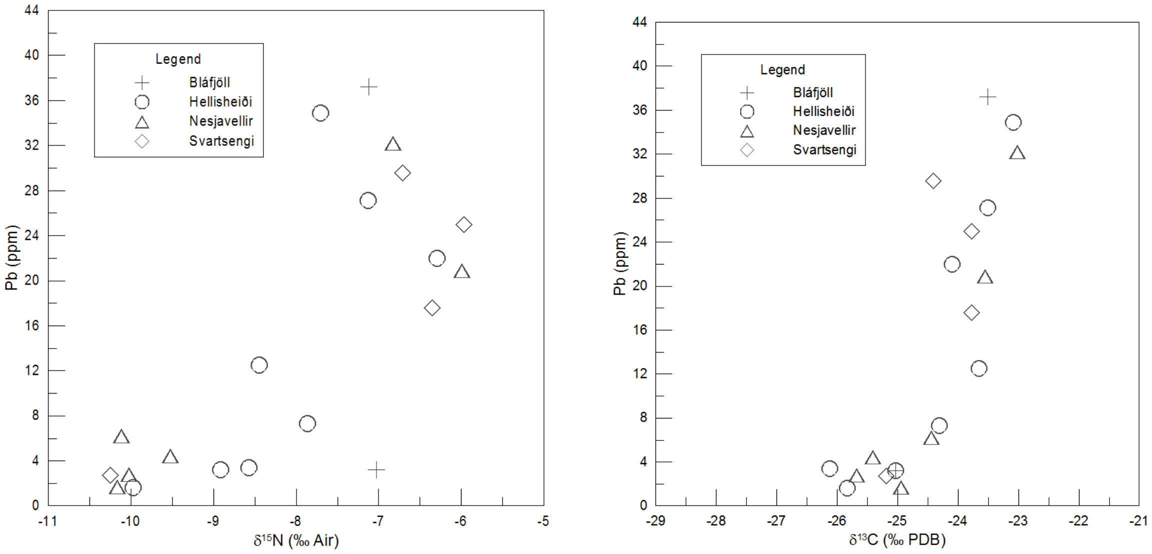

Figure 6. Lead concentration in moss as a function of isotope ratios of N (left), C (right).

5. DISCUSSION

The $\delta^{34}S$ shows a rough negative linear trend with S concentrations, especially for samples from both Hellisheidi and Nesjavellir. The most ^{34}S-depleted and sulfur rich samples are observed at Nesjavellir. This may be related to the fact that the Nesjavellir power plant has been in operation for considerably longer than the Hellisheiði power plant. At the time of sampling, Nesjavellir was also releasing more H_2S than did Hellisheiði. Furthermore Nesjavellir is sheltered, to some extent, by the Hengill mountains from southerly winds carrying precipitation into the region. Hence a reduced flux of marine sulfur into the Nesjavellir area compared to the Hellisheiði area may be expected. This may lead to the moss around Nesjavellir power plant being subject to a greater flux of depleted (hydrothermal/magmatic) sulfur than at Hellisheiði, and a relative diminished flux of marine-derived enriched sulfur.

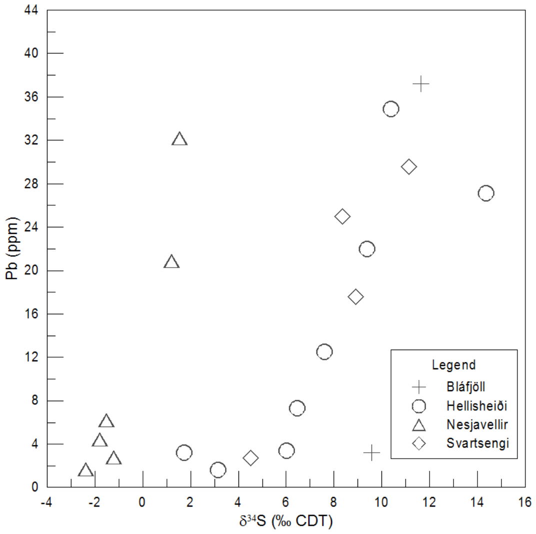

Figure 7. Variation in δ^{34}S vs. lead content in the moss samples.

We note in all sample sites, that samples from the lowermost 5 cm of the moss vegetative stems are significantly enriched in ^{34}S compared to the top 5 cm, suggesting that sulfur is not redistributed through the whole vegetative stem. This isotope difference between bottom and top sections is more pronounced in the Hellisheiði samples compared to the Nesjavellir ones. This pattern may reflect moss growth. Only the uppermost part of the moss is photosynthetically active. The lower part of the moss is photosynthetically inactive but participates in the life cycle of the plant by other means (Tallis, 1963; Kallio and Heinonen 1975). The bottom section (inactive) of the moss retains a δ^{34}S signature from the time it was actively growing. In the case of the Hellisheiði samples that would be prior to the startup of the power plant. Another possibly contributing factor could be that the top of the moss mostly incorporate S from the atmospheric SO_2 gaseous form, while its lower section receives marine sulfur through precipitation to a much larger extent.

Lead isotopes have widely been used to constrain sources of atmospheric aerosols and to distinguish between natural and anthropogenic inputs to particulate matter in the air (e.g. Bollhöfer and Rosman, 2001; Kylander *et al.*, 2010; Widory *et al.*, 2004). Isotope ratios of Pb in the moss samples suggest at least three different sources for lead (Fig. 5). Anthropogenic Pb may be derived from automotive exhaust and other particulate matter derived from vehicles in addition to road dust from roads covered with asphalt. In this regard it is noted that samples from Hellisheiði that are more distal to the power plant are progressively more proximal to a busy road connecting the capital to the southern lowlands in Iceland. The load of dust (from bedrock) locally generated is probably increased significantly during any type of construction.

Pb concentration in the moss samples vary systematically with δ^{13}C and δ^{15}N (Fig. 6). With increasing Pb concentration the moss discriminates less against the heavy ^{15}N isotope and the corresponding δ^{15}N-value increases. Similar patterns have been observed in urban areas or areas close to heavy traffic (Pearson *et al.* 2000; Gerdol *et al.* 2002). The data suggests that concomitant to the Pb addition there is deposition of N in the moss (compare Fig. 4 and Fig. 6). A similar pattern is observed for C where a reduction of C concentration is due to particulate addition (including Pb) to the moss matrix. With increasing Pb the moss becomes less discriminatory towards the heavy isotopes of ^{15}N and ^{13}C. The change in discrimination may be related to a change in the isotopic composition of the pool of C and N being brought to the plant, which could be due to anthropogenic factors. Alternatively, by comparison with *Sphagnum* mosses, environmental factors such as reduced precipitation may diminish discrimination against ^{13}C (Rice, 2000).

Pb also shows a strong, but more complex, correlation when plotted against δ^{34}S (Fig. 6). The samples from Nesjavellir follow a distinct trend compared to the other moss samples. This may reflect a lower flux of marine S into the Nesjavellir area compared to the other sampled areas. Is Pb derived from sea-spray in the same manner as is S? The correlation with Pb concentration at relatively enriched δ^{34}S values would certainly suggest that. However the Pb isotope discrimination plot suggests a more complex picture with at least three distinct sources of Pb and there may be additional sources that are not isotopically distinct from the mixing trends established by the end-members.

6. CONCLUSIONS

δ^{34}S in mosses varies systematically with S abundance. The most depleted samples (δ^{34}S < 0.0) are the most sulfur rich and occur close to point sources (geothermal power plant or high-temperature wells) of geothermal sulfur. Samples of moss more distal to the point sources are relatively enriched (δ^{34}S from +8.0 to +12.0) similar to control-samples from an area distal to any geothermal power plant. The S isotope chemistry is consistent with S being a mixture derived from two main sources hydrothermal and marine with possibly a minor contribution from anthropogenic sources.

The isotopic composition of C and N in the moss is similar to what has been observed before in mosses and other non-vascular plants in Iceland and also comparable to that of bryophytes in the northern hemisphere in general. However, mosses with relatively high Pb contents discriminate less against the heavy isotopes ^{15}N and ^{13}C. Similar variation in discrimination has been observed in bryophytes elsewhere as a response to anthropogenic input or other environmental factors such as variation in humidity.

Isotopic varitation of Pb in the samples suggest at least three different source for Pb in this sample suite of *Rhacomitrium lanuginosum*. They are: marine derived Pb, anthropogenic Pb, and bedrock derived Pb. The most δ^{34}S depleted samples (and therefore most S –rich) rich samples contain relatively little Pb. Moss samples with relatively high concentrations of Pb are more variable and more enriched in the heavy isotopes of C and N than moss samples with low Pb content. This change in discrimination for the heavy isotope is a result of environmental stress that appears not to be related to geothermal activity. The data therefore does not support the contention that H_2S is a primary cause of moss decline in the area.

Stable isotope studies of plant materials have contributed greatly to our understanding of the ecology of the environment and the flow of matter and energy through the web of life. This preliminary study suggests that stable isotopes provide a great tool for deciphering the environmental effects of geothermal energy production. Stable isotope studies of plant material should also be able to provide valuable data on the recovery of areas that have been subjected to the effects if geothermal effluent when operations cease or effluent is greatly reduced due to re-injection or other mitigating measures are put into effect.

REFERENCES

Alewell, C. and Novak, M.: (2001) Spotting zones of dissimilatory sulfate reduction in a forested catchment: the 34S-35S approach, Environmental Pollution, 112, (2001), 369-377.

Ascough, P.L., Church, M.J., Cook, G.T., Einarsson, Á., McGovern, T.H., Dugmore, A.J., Edwards, K.J.: Stable isotopic (□13C and □15N) characterization of key faunal resources on Norse period settlements in North Iceland. J. North Atlantic. (2014, in press).

Bollhöfer, A., and Rosman, K.: Isotopic source signatures for atmospheric lead: the Northern Hemisphere, Geochimica et Cosmochimica Acta, 65, (2001), 1727–1740.

Bragason, Á., and Yngvadóttir, E.: Rannsóknir á mosa við jarðvarmavirkjun Orkuveitu Reykjavíkur á Hellisheiði. EFLA Engineering, (2009), 27 pp.

Brimblecombe, P. and Clegg, S.L.: The solubility and behavior of acid gases in the marine aerosol, Journal of Atmospheric Chemistry, 7, (1988), 1-18.

Carignan J. and Gariépy C.: Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Quebec, Canada, Geochimica Cosmochimica Acta, 59, (1995), 4427-4433.

Case J.W. and Krouse H.R. Variations in sulfur-content and stable sulfur isotope composition of vegetation near a SO2 source at Fox Creek, Alberta, Canada, Oecologia, 44, (1980), 248-257.

Chabaux, F., Riotte, J., Schmidt, A.D., Carignan J., Herckes, P. Pierret, M.C. and Wortham, H.: Variations of U and Sr isotope ratios in Alsace and Luxembourg rain waters: origin and hydrochemical implications, Comptes Rendus Geoscience, 337, (2005), 1447-1456.

Chiarada, M., and Cupelin, F.: Behaviour of airborne lead and temporal variations of its source effects in Geneva (Switzerland): comparison of anthropogenic versus natural processes, Atmospheric Environment, 34, (2000), 959-971.

Conti M.E. and Cecchetti G.: Biological monitoring: lichens as bioindicators of air pollution assessment - a review, Environmental Pollution, 114, (2001), 471-492.

Galuszka, A.: The chemistry of soils, rocks and plant bioindicators in three ecosystems of the Holy Cross Mountains, Poland, Environmental Monitoring and Assessment, 110, (2005), 55-70.

Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S., Bovolenta, A., and Coppi, S.: Use of moss Tortula muralis for monitoring organic and inorganic air pollution in urban and rural sites in Northern Italy: Atmospheric Environment, 36, (2002). 4069–4075.

Gislason, S.R., and Torssander, P.: Response of sulfate concentration and isotope composition in Icelandic rivers to the decline in global atmospheric SO2 emissions into the North Atlantic region: Environmental Science & Technology, 40, (2006), 680–686.

Jónsdóttir, I.S. Callaghan, T.V., Lee, J.A.: Fate of added nitrogen in a moss-sedge Arctic community and effects of increased nitrogen deposition, Science of the Total Environment, 160 (1995), 677-685.

Kallio, P., and Heinonen, S.: CO2 exchange and growth of Rhacomitrium lanuginosum and Dicranum elongatum. In, Wielgolaski, F.E., (ed.): Fennoscandian tundra ecosystem, Ecological Studies 16, (1975) 138-148.

Keeling, C.D.: The Concentration and Isotopic Abundances of Atmospheric Carbon Dioxide in Rural Areas, Geochimica et Cosmochimica Acta, 13, (1958), 322-334.

Kelly, W.R. and Ondov, J.M.: A theoretical comparison between intentional elemental and isotopic atmospheric tracers, Atmospheric Environment (Part A), 24, (1990), 467-474.

Krouse, H.R.: Sulfur isotope abundance elucidate uptake of atmospheric sulfur emissions by vegetation, Nature, 265, (1977), 45-46.

Kylander, M.E., Klaminder, J., Bindler, R., and Weiss, D.J.: Natural lead isotope variations in the atmosphere: Earth and Planetary Science Letters, 290, (2010), 44–53.

Liu et al. (2007) Liu, X.-Y., Xiao, H.-Y., Liu, C.-Q., Li, Y.-Y.: d13C and d15N of moss (Haplocladium microphyllum (Hedw.) Broth) for indicating environment variations and canopy retention on atmospheric nitrogen deposition. Atmospheric Environment, 41, (2007), 4897–4907.

Liu, X.-Y., Xiao, H.-Y., Liu, C.-Q., Xiao, H.-W. and Wang, Y.-L.: Assessment of atmospheric sulfur with the epilithic moss Haplocladium microphyllum: Evidences from tissue sulfur and d34S analysis, Environmental Pollution, 157, (2009), 2066-2071.

Liu, X.-Y., Xiao, H.-Y., Liu, C.-Q., Li, Y.-Y., Xiao, H.-W., and Wang, Y.-L.: Response of stable carbon isotope in epilithic mosses to atmospheric nitrogen deposition: Environmental Pollution, 158, (2010), 2273–2281.

Loader, N.J., McCarroll, D., Van der Knaap, W.O., Robertson, I. and Gagen, M.: Characterizing carbon isotopic variability in Sphagnum, The Holocene, 17, (2007), 403-410.

Magnússon S.H. and Thomas B.: Heavy metals and sulphur in mosses around the aluminium smelter in Straumsvík in 2005, Náttúrufræðistofnun, NÍ-07003, (2007), 52 pp.

Marshall, W.A., Clough, R., and Gehrels W. R.: The isotopic record of atmospheric lead fall-out on an Icelandic salt marsh since AD 50, Science of the Total Environment, 407, (2009), 2734-2748.

Marty B., Gunnlaugsson, E., Jambon, A., Óskarsson, N., Ozima, M., Pineau, F. and Torsander, T.: Gas geochemistry of geothermal fluids, the Hengill area, Southwest rift zone of Iceland. Chemical Geology, 91 (1991) 207-225.

McManus, J.B., Nelson, D.D. and Zahniser, M.S.: Long-term continuous sampling of 12CO2, 13CO2 and 12C18O16O in ambient air with a quantum cascade laser spectrometer, Isotopes in Environmental and Health Studies, 46, (2010), 49 — 63.

Mektiyeva, V.L., Gavrilov, E.Y. and Pankina, R.G.; Sulfur isotopic composition in land plants. Geochemistry International 13, (1976), 85–88.

Migaszewski, Z.M., Dolęgowska, S., Halas, S., and Trembaczowski, A.: Stable sulphur isotope ratios in the moss species Hylocomium splendens (Hedw.) BSG and Pleurozium schreberi (Brid.) Mitt. from the Kielce area (south-central Poland): Isotopes in Environmental and Health Studies, 46, (2010), 219–224.

Monna, F. Aiuppa, A. Varria, D. and Dongarra, G.: Pb isotope composition in lichens and aerosols from eastern Sicily: Insights into the regional impact of volcanoes on the environment, Environmental Science and Technology, 33, (1999), 2517-2523.

Nakano, T. and Tanaka, T.: Strontium isotope constraints on the seasonal variation of the provenance of base cations in rain water at Kawakami, central Japan, Atmospheric Environment, 31, (1997), 4237-4245.

Nriagu, J.O., Coker R.D. and Barrie, L.A.: Origin of sulfur in Canadian Arctic haze from isotope measurements, Nature, 349, (1991), 142-145.

Orkuveita Reykjavíkur: Umhverfisskýrsla (Environmental report), (2012), 53 pp.

Patterson, C.C. and Settle, D.M.: Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, Marine Chemistry, 22, (1987), 137-162.

Pearson, J., Wells, D.M., Seller, K.J., Bennett, A., Soares, A., Woodall, J. and Ingrouille, M.J.: Traffic exposure increases natural 15N and heavy metal concentrations in mosses, New Phytologist, 147 (2000), 317-326.

Peate, D.W., Baker, J.A., Jakobsson, S.P., Waight, T.E., Kent, A.J., Grassineau, N.V., and Skovgaard, A.C.: Historic magmatism on the Reykjanes Peninsula, Iceland: a snap-shot of melt generation at a ridge segment: Contributions to Mineralogy and Petrology, 157, (2009), 359–382.

Proctor, M.C.F., Raven, J.A. and Rice, S.K.: Stable carbon isotope discrimination measurements in Sphagnum and other bryophytes: physiological and ecological implications, Journal of Bryology, 17 (1992), 193-202.

Puig, R.; Avila, A.; Soler, A.: Sulphur isotopes as tracers of the influence of a coal-fired power plant on a Scots pine forest in Catalonia (NE Spain), Atmospheric Environment 42 (2008), 733-745.

Purvis, O.W., Chimonides, P.J., Joness, G.C., Mikhailova, I.N., Spiro, B., Weiss, D.J., Williamson, B.J.: Lichen biomonitoring near Karabash Smelter Town, Ural Mountains, Russia, one of the most polluted areas in the world, Proceedings of the Royal Society B-Biological Sciences 271, (2004), 221-226.

Rice, S.K.: Variation in carbon isotope discrimination within and among Sphagnum species in a temperate wetland, Oecologia, 123, (2000), 1-8.

Rundel, P.W., Stichler, W., Zander, Richard H and Ziegler, H.: Carbon and hydrogen isotope ratios of bryophytes from arid and humid regions, Oecologia, 44, (1979), 91-94.

Skrzypek, G., Paul, D., and Wojtu'n, B.: Stable isotope composition of plants and peat from Arctic mire and geothermal area in Iceland: Polish Polar Research, 29, (2008), 365–376.

Spiro, B; Weiss, DJ; Purvis, OW, Mikhailova, I., Williamson, B.J., Coles, B.J., Udachin, V. Lead isotopes in lichen transplants around a Cu smelter in Russia determined by MC-ICP-MS reveal transient records of multiple sources, Environmental Science & Technology, 38, (2004), 6522-6528.

Tallis, J.H.: Growth studies on Rhacomitrium Lanuginosum, The Bryologist, 67, (1964) 417-419.

Thirlwall M.F., Gee M.A.M., Taylor N., Murton B.J. Mantle components in Iceland and adjacent ridges investigated using double-spike Pb isotope ratios. Geochim. Cosmochim. Acta 68 (2004), 361–386.

Trust, B.A. and Fry, B.: Stable sulfur isotopes in plants- a review, Plant Cell and Environment 15, (1992), 1105-1110.

Wang, Y., and Wooller, M.J.: The stable isotopic (C and N) composition of modern plants and lichens from northern Iceland: with ecological and paleoenvironmental implications: Jökull, 56, (2006), 27–38.

Widory, D.: Lead isotopes decipher multiple origins within single PM10 samples in the atmosphere of Paris: Isotopes in environmental and health studies, 42, (2006), 97–105.

Widory, D., Petelet-Giraud, E., Le Bihan, O., Le Moullec, Y., Quetel, C., Snell, J., Van Bocxstaele, M., Hure, A., Canard, E., Joos, E., Forti, L., Bullen, T. and Johnson, T.: Les métaux dans les particules atmosphériques: les isotopes peuvent-ils aider à discriminer les pôles d'émission potentiels ?, Pollution Atmosphérique, Septembre 2010, (2010), 75-81.

Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A., and Guerrot, C.: The origin of atmospheric particles in Paris: a view through carbon and lead isotopes: Atmospheric Environment, 38, (2004), 953–961.

Widory, D., Xiande, L., Dong, S.: Isotopes as tracers of sources of lead and strontium in aerosols (TSP & PM2.5) in Beijing, Atmospheric Environment, 44, (2010), 3679-3687.

Winner, W.E., Bewley, J.D., Krouse, H.R. and Brown, H.M.: Stable sulfur isotope analysis of SO2 pollution impact on vegetation, Oecologia, 36, (1978), 351-361.

Zurbrick, C.M., Gallon, C. and Flegal, A.R.: A new method for stable lead isotope extraction from seawater, Analytica Chimica Acta, 800, (2013) 29-35.