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Smelter emissions deposited in the environment around the Horne smelter, Quebec: comparison of regional snow, peat, soil, and lake-sediment and lake-water surveys

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Abstract: Regional patterns in the concentration of smelter-emitted metals in snow, the surfaces of ombotrophic peat hummocks, the humus horizon of soil, lake water, and lake sediment around the copper smelter at Rouyn-Noranda, Quebec, are generally similar. They are all approximately circular, centred on the smelter, and elongated somewhat toward the east due to the prevailing wind directions. Typically, the footprint extends on average about 65 km from the smelter, perhaps 5 km more than this toward the east and 5 km less toward the west. The pattern is anisotropic, but weakly so. The ratio of (Cu+As)/(Al+Fe) is a useful indicator for source apportionment. The value of the ratio, which changes as a function of distance from the smelter, reflects the mixing and dilution of emissions with non-smelter dust and aerosols. Snow and peat measurements allow the deposition rates of metal (mass/unit area/time) to be modelled as a function of distance from the smelter, and the integration of this model over a radial area permits the determination of metal tonnages in the smelter-centred anomaly. The proportions of emissions accounted for within 150 km of the smelter are as follows: Cu, 25 to 50%; Pb, 10 to 20%; Zn, 25%; As, 5%; and Cd, 20 to 25%. Metals in excess of these proportions are likely transported outside the immediate smelter footprint and beyond 150 km, but deposition of smelter-emitted metals becomes so small and so mixed with metals from other sources that it impossible, from these data, to discriminate between smelter and non-smelter sources.

Résumé : Aux alentours de la fonderie de cuivre de Rouyn-Noranda (Québec), la répartition régionale des concentrations de métaux émis par la fonderie est généralement similaire dans la neige, à la surface de buttes de tourbe ombrotrophe, dans l'horizon d'humus du sol, dans l'eau lacustre et dans les sédiments lacustres. Elle est plus ou moins circulaire, centrée sur la fonderie et quelque peu allongée vers l'est en raison des vents prédominants. En moyenne, les concentrations de métaux sont réparties dans un rayon d'environ 65 km de la fonderie, valeur qui peut s'avérer supérieure de 5 km à l'est et inférieure de 5 km à l'ouest. Leur répartition est légèrement anisotrope. Le rapport de (Cu+As)/(Al+Fe) est un indicateur de source utile, et sa valeur, qui change selon la distance par rapport à la fonderie, reflète le mélange des émissions avec des poussières et des aérosols non issus de la fonderie, ainsi que leur dissolution dans ces substances. L'analyse de la neige et de la tourbe permet de modéliser les taux de dépôt de métaux (masse surfacique pour un intervalle de temps) en fonction de la distance par rapport à la fonderie, tandis que l'application de ce modèle à une surface radiale permet de déterminer le tonnage de concentrations de métaux dans l'anomalie centrée sur la fonderie. Les proportions d'émissions relevées à moins de 150 km de l'usine sont les suivantes : cuivre, de 25 à 50 %; plomb, de 10 à 20 %; zinc, 25 %; arsenic, 5 %; et cadmium, de 20 à 25 %. Les métaux présents dans des proportions supérieures à celles-ci sont probablement transportés à l'extérieur de la zone immédiate de concentrations significatives de la fonderie et à plus de 150 km de cette dernière, mais les émissions de métaux de la fonderie qui sont déposées à cette distance sont si faibles et tellement mélangées à des métaux d'autres sources qu'il devient impossible de les distinguer d'après ces données.

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INTRODUCTION

Metal smelters are point sources of dust and aerosols to the atmosphere. The studies undertaken as part of the Point Sources Project of the Geological Survey of Canada's Metals in the Environment Initiative (1997–2002) examined various surficial geological materials in the vicinity of the Horne smelter at Rouyn-Noranda in order to investigate the deposition of smelter-emitted metals. Four interrelated regional survey studies looked at metal distributions in snow, soil, peat, and lakes (water and sediment). This paper provides a comparison of spatial distributions of metals in these sampling media, as related to the objectives of the project.

Two important objectives of the studies around the Horne smelter were to determine (1) distance of transport of metals from the smelter and (2) source apportionment of metals, distinguishing the smelter emissions from other sources. From the outset, the goal was to integrate the diverse data from these studies so as to obtain a consistent picture of the extent of the area affected by the smelter (the smelter 'footprint') and to determine the distance from the smelter at which smelter-emitted metals became indistinguishable from metals from other sources. For some of the sampling media it was hoped to estimate the amount of metal (say copper or lead) of smelter origin deposited per unit area per unit of time (the depositional 'loading' or depositional flux). By integrating the loading for a radial area around the smelter, the amount of metal of smelter origin could be totalled and expressed in tonnes/year. This tonnage might then be compared with known emission tonnages reported for the smelter for the same time period, thereby determining the proportion of the emissions accounted for by local deposition within the smelter footprint. If metal cannot be fully accounted for by this mass balance, it would suggest that long-range atmospheric transport occurs beyond the footprint. Source apportionment is difficult, because metals from non-smelter sources occur in all these sampling media, and the chemical composition of the metals can be the same whether or not the metal originated from the smelter. Isotopic tracing would be an ideal approach for source apportionment, but is problematic for fingerprinting recent emissions. The Horne is a custom smelter. Its feed comes from a wide variety of sources, including recycled materials, making an identifiable isotopic signature complex. However, as is shown here, distinctive multi-element patterns are recognized in the geochemical data from the various sampling media and these can be used to compare the sampling media with one another and trace the mixing and dilution of smelter-emitted metals with metals from non-smelter sources, even though the distance of tracing is limited.

The sampling media reveal different kinds of information. Snow samples provide a picture of metal deposition from the atmosphere over a few winter months (Kliza et al., 2000, 2002). Because the time since the first snowfall is known, and the cross-sectional area of the snow-sampling tube and volume of meltwater are known, the data can be expressed not only as concentrations (units of mass/volume), but also as the depositional loading or flux (with units of mass/area/time). The time interval of deposition captured by snow is short — restricted to a few winter months.

Depositional loading per unit time, over a time interval of about one year, can be estimated from actively growing *Sphagnum* (peat) hummocks. Samples taken from the surfaces of peat hummocks allow an estimate of deposition flux of metal to be made, given the growth rate and bulk density of the peat (Kettles and Dion, 2000; Bonham-Carter and Kettles, 2001; Kettles and Bonham-Carter, 2002). This is because the hummocks are ombotrophic — that is, they receive their nutrients from the atmosphere, not through a root system. The time resolution is at best annual for the most recent hummock growth. These two sampling media, snow and peat, are important because they yield the geographic distributions of both metal concentrations and metal loadings. This is essential for comparing the emission tonnages to deposition tonnages in a mass balance calculation, thereby estimating the long-range transport of metals outside the immediate smelter footprint.

Dating of metal deposition is not possible with soil or lake data (the lake sediments sampled in this survey were not well enough resolved with respect to time, c.f. the more detailed cores described by Alpay et al., 2005). Data from the soils are complex because there is no time horizon that would allow an estimate of annual deposition flux. Nevertheless, soil is an important sampling medium, because it provides corroborative information about the geographical extent of the smelter footprint (mainly from the humus, or organic-rich A-horizon) and about the vertical transport of smelter metals into the B and C horizons (*see* Henderson et al., 2002; Henderson and Knight, 2005). The great bulk of smelter metals deposited from the atmosphere is held in the humus layer, and metal concentration measurements provide a picture of metal deposition integrated over time.

The regional survey of lakes (Kliza and Telmer, 2001) provides data about the concentration of metals and other elements in lake water and lake sediment. The Kliza-Telmer survey (nearly 100 lakes within 80 km of the Horne smelter) provides another spatial view of the smelter footprint (Bonham-Carter et al., 2001). At each site, lake water was sampled and a short sediment core was collected. Sediment from the uppermost 2 cm of the core and a second sample from the core bottom (usually about 15 cm below the sediment–water interface) reflect sediment deposition during post- and pre-industrial time, respectively. The difference between top and bottom metal levels can be mapped, and the smelter influence examined, although the processes involved in how the metals arrived in the water and sediment are complex (i.e. not simply direct deposition from the atmosphere, but also transport from lake catchments and vertical movements in response to various processes within the sediment column). The time resolution of metals in the lake water is mostly related to the residence time of water in the lake, probably on the order of weeks for these small lakes, but because much of the metal is also derived from local catchments, the time resolution and metal loading rate of smelter metals are unknown. Similarly, the timing of deposition in the sediment core tops is unknown (although definitely postindustrial), so

the information is restricted to data on metal concentrations, not loading rates. Nevertheless, the lake water and sediment data provide another useful and corroborative piece of evidence about the spatial extent of the smelter footprint. A much more comprehensive study of two selected lakes addresses questions about the vertical distribution of metals in sediment cores from many lines of evidence (Alpay et al., 2005).

Previous work involving integrated multimedia surveys around smelters in other areas has been carried out in various parts of the world. However, the study around the Horne smelter is exceptional because of the variety of sampling media and because Rouyn-Noranda is relatively remote and not greatly affected by atmospheric pollution from other industrial sources. The most comprehensive study of this type to date was undertaken during a multinational, multi-participant project during the 1990s in the Kola Peninsula. Soil (Niskavaara et al., 1996; Boyd et al., 1997; Reimann et al., 1998), snow (Gregurek et al., 1999), moss (Ayras et al., 1997), stream water (de Caritat et al., 1996a, b), lake water (Reimann et al., 1999), groundwater (de Caritat et al., 1998), overbank sediments (Volden et al., 1997), and other surveys (e.g. Reimann et al., 2001) were undertaken to investigate the spatial distributions of metals from industrial sources in various environmental media. The Rouyn-Noranda area is more remote than the Kola region. The Rouyn-Noranda data are less comprehensive than the Kola data, but because there are fewer local anthropogenic sources of metals, the source apportionment and mass balance of smelter-emitted metals is less complex.

Data

The data for this paper have been published in various Open File reports of the Geological Survey of Canada. For each sampling medium, a regional picture of element concentrations was obtained by sampling within a 50 to 250 km radius of the city of Rouyn-Noranda, depending on the survey (Fig. 1). Some preliminary results based on a comparison of the surveys were presented by Bonham-Carter et al. (2002).

Prevailing wind directions, an important factor in the atmospheric dispersal of smelter emissions, are mainly toward easterly directions, particularly to the north, northeast, and southeast. Winds blowing toward westerly directions are less frequent. Summary wind roses, based on data from the Rouyn-Noranda airport, are shown in Henderson and Knight (2005) and Kliza et al. (2005).

Snow

Two snow surveys were conducted, one in March 1998 (Kliza et al., 2000) and a second in March 2001 (Kliza et al., 2002). The sampling and analytical protocols are given in these two publications. Telmer et al. (2004) discussed and interpreted the 1998 snow data, with special emphasis on a multi-element interpretation. A comparison of the two snow surveys by Kliza et al. (2005) demonstrates that most elements show a similar spatial pattern and have similar concentration levels for the two years. Both Telmer et al. (2004) and Kliza et al. (2005) demonstrate that the ratio of soluble:particulate metal changes with distance from the smelter and from one metal to another, an important observation when considering the potential availability of deposited metals to biota.

Peat

A peat survey was carried out in September 1997; the data along with sampling and analytical protocols are given in Kettles and Dion (2000). The data include information from profiles through peat hummocks and data from ‘hollows’. Kettles and Bonham-Carter (2002) and Bonham-Carter and Kettles (2001) investigated the spatial distribution of smelter-derived metals in the hummocks and compared the predicted tonnage of metals (Cu, Zn, Pb) deposited in one year to actual emission tonnages reported from the smelter during the same period, a topic revisited in this paper.

Humus

A comprehensive soil survey was carried out in 1997 and 1998. Henderson et al. (2002) provide a full description of field and analytical protocols. Only data from the organic-rich humus horizon are used in this paper. An analysis of data from all the soil horizons is described in Henderson and Knight (2005).

Lake sediments

A regional survey of lake water and short sediment cores was undertaken in 1997. The data and methods are given in Kliza and Telmer (2001). A preliminary analysis of the data was reported by Bonham-Carter et al. (2001). This suggested that the influence of the smelter outweighed factors such as catchment and lake geometry, the geology of the lake basin, and proximity to roads.

Emission data

Emission data (annual mean tonnages) for the metals Pb, As, Cu, Cd, and Zn for the period 1990–2001 were provided by Noranda, Inc. (Table 1a). Emission data are described in greater detail and for a longer time interval by Bonham-Carter (2005, Table B1, B2). For the winter periods corresponding to the two snow surveys, monthly data for the same metals (also supplied by Noranda, Inc.) are shown in Table 1b.

The annual emission data show that changes in the smelter operation introduced to control emissions have been effective in reducing amounts of emitted metals. For example, between 1990 and 2001, both lead and zinc emissions were reduced by 77%, cadmium emissions, by 50%, and copper emissions, by 30%. Arsenic levels decreased by 50% in the early 1990s, then increased in the late 1990s. The tonnage for arsenic emitted in 2001 is actually 150% greater than for 1990, which is counter to the main trends for the other metals.

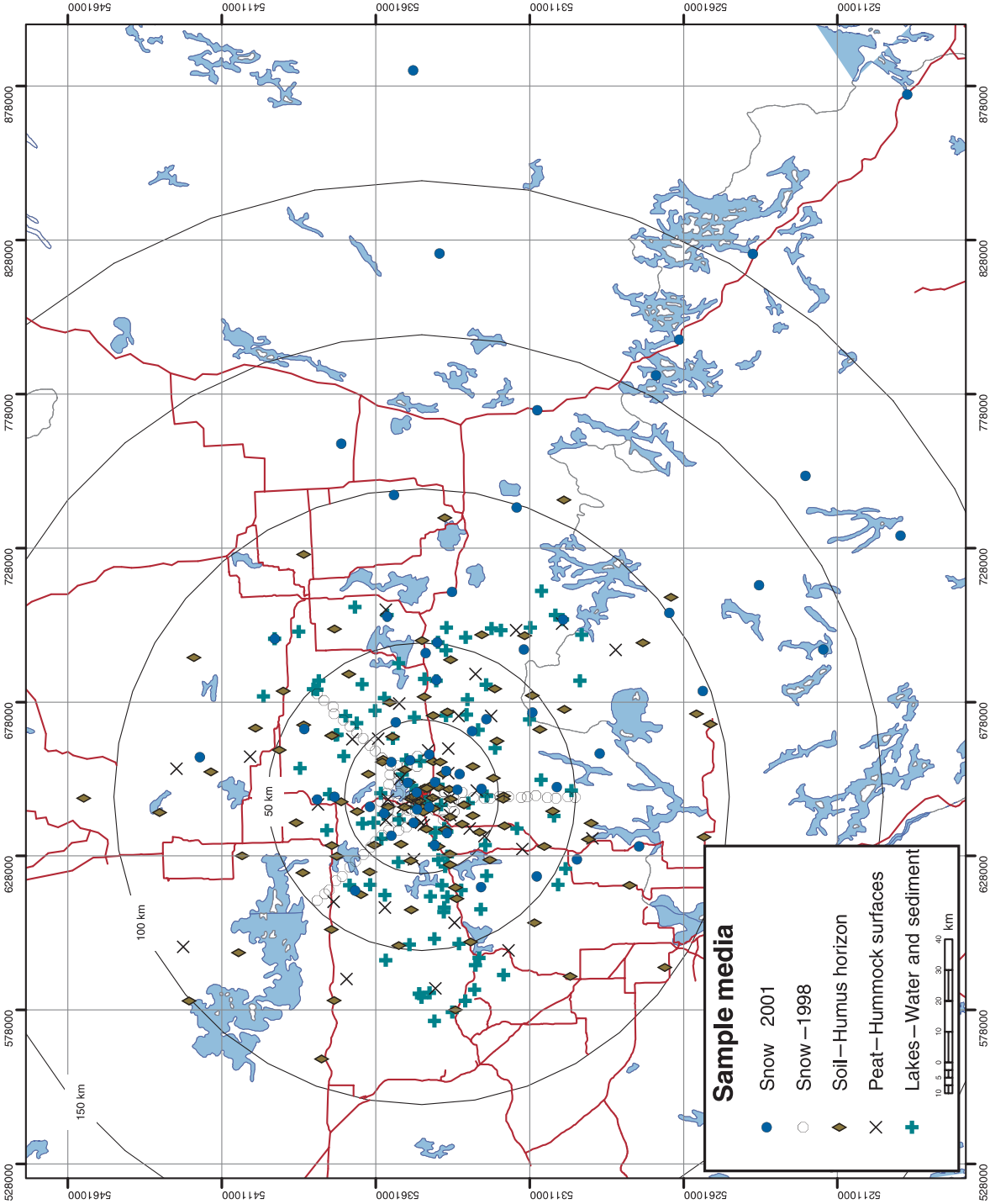

Figure 1. *Map showing the study region around Rouyn-Noranda, Quebec. Sample sites for snow (surveys in 1998 and 2001), peat hummocks, humus horizon in soil, and lakes (surface water and top 2 cm of sediment cores) are shown. The Horne smelter is in the town of Rouyn-Noranda at the centre of the plot.*

Table 1a. Annual emissions from the Horne smelter (tonnes/a for the period 1990–2001.

Year	Particulates	Pb	Zn	Cd	As	Cu
1990	1000	280	80	5	40	60
1991	820	190	60	4	20	90
1992	810	160	70	6	24	130
1993	720	195	70	4	18	73
1994	770	260	62	3	19	70
1995	940	340	85	3	29	58
1996	1200	300	85	2	63	65
1997	870	197	55	1.4	55	50
1998	920	150	39	2.4	78	70
1999	720	100	23	1.6	64	69
2000	620	80	19	2.2	59	59
2001	595	65.3	17.8	2.5	97.9	41.7

Table 1b. Monthly emissions for winter 1997–1998 and 2000–2001 (tonnes/month). Data supplied by Noranda, Inc. Monthly winter data are for two periods of snow sampling.

Month	Particulates	Pb	Zn	As	Cd	Cu
11/1/1997	60.17	22.00	6.17	5.57	0.15	4.02
12/1/1997	51.45	25.31	3.79	7.06	0.07	4.57
1/1/1998	49.56	15.53	3.67	5.80	0.07	4.69
2/1/1998	64.07	14.94	4.19	4.38	0.06	5.82
3/1/1998	78.13	13.22	3.90	7.08	0.06	7.16
Mean	**60.68**	**18.20**	**4.34**	**5.98**	**0.08**	**5.25**
St. dev.	11.46	5.19	1.04	1.13	0.04	1.25
RSD	0.19	0.29	0.24	0.19	0.50	0.24
Wt. mean[1]	**75.00**	**14.06**	**3.78**	**5.73**	**0.17**	**5.17**
Comp.[3]	**-1.25**	**0.80**	**0.54**	**0.22**	**-2.25**	**0.06**
11/1/2000	61.57	8.07	2.14	5.95	0.09	5.90
12/1/2000	61.75	3.23	0.69	5.27	0.03	8.95
1/1/2001	59.77	5.03	1.11	5.01	0.03	7.45
2/1/2001	52.42	4.47	0.99	7.63	0.10	5.33
Mean	**58.88**	**5.20**	**1.23**	**5.97**	**0.06**	**6.91**
St. dev.	4.40	2.06	0.63	1.18	0.04	1.63
RSD	0.07	0.40	0.51	0.20	0.67	0.24
Wt. mean[2]	**50.63**	**6.05**	**1.53**	**6.54**	**0.20**	**4.20**
Comp.[3]	**1.88**	**-0.41**	**-0.48**	**-0.48**	**-3.50**	**1.66**

[1] Weighted mean value based on annual tonnages in a) using two months in 1997 and three months in 1998
[2] Weighted mean value based on annual tonnages in a) using two months in 2000 and two months in 2001
[3] Comparison = (Weighted mean/Mean)/ Standard deviation.

Emissions are difficult to measure and vary greatly over time, even on a daily basis. This is due to several factors, notably the changes in composition and volume of the feed materials. The Horne is a 'custom' smelter, taking concentrates with a variety of compositions from more than 100 suppliers and from many parts of the world (Bonham-Carter, 2005, Appendix B). Accordingly, it is not surprising that the composition of emissions is also highly varied. An indication of this is provided by the data in Table 1b (and Fig. 2), which show how monthly tonnages can fluctuate markedly from annual averages.

Monthly values illustrate both variability with respect to the mean of the four or five adjacent months (precision), but also bias with respect to the annual means. For example, the precision of the monthly data for the 1997–1998 months, as indicated by the RSD (=standard deviation/mean), is 20 to 30% for Pb, Zn, As, and Cu, and 50% for Cd, whereas the RSD values for the 2000–2001 data are generally greater, i.e. 40% for Pb, 51% for Zn, and 67% for Cd. If these RSD values are typical, then if a confidence band around the annual emissions curve were added, it would be broad. An indication of the bias present in the monthly data, as compared with the annual data, can be obtained by calculating the difference between the monthly mean value and a monthly mean estimated by taking a weighted average of the two adjacent annual figures, and dividing by the monthly standard deviation (*see* Table 1b for clarification). Absolute values less than 1.0 indicate that the monthly mean value is within one standard deviation of the estimate based on annual values, i.e. the bias is relatively small. Values greater than 1.0 suggest that the monthly values are biased (either upward or downward), presumably because of a change in composition of the feed. For the 1997–1998 data, Pb, Zn, As, and Cu show little bias,whereas the Cd monthly value is more than two standard deviations lower than the weighted value from annual data. For the 2000–2001 data, Pb, Zn, and As monthly mean values are within one standard deviation of the weighted mean values, but both Cd and Cu values show bias. Cadmium values in the winter data are also lower than predicted from the annual values. Copper is considerably 'richer' in the winter emissions for that year, compared to the weighted mean from annual data.

Any conclusions based on comparing emission tonnages with tonnages of metal deposited within the smelter footprint must therefore recognize the presence of this variability and bias, and be tempered accordingly.

DATA ANALYSIS METHODS

Spatial patterns of metal concentration in these sampling media are similar in that they all show an elevated 'bull's-eye' centred on the smelter for metals emitted from the smelter. This is clear from the papers in this Bulletin (e.g. Kliza et al., 2005; Henderson and Knight, 2005), from several journal articles (e.g. Henderson et al., 2002; Kettles and Bonham-Carter, 2002), and in various GSC Open Files (e.g. Kettles and Dion, 2000; Kliza et al., 2000, 2002; Kliza and Telmer, 2001; Henderson et al., 2002) that contain many maps that illustrate the spatial distributions of metals around the smelter. Although the maps show that the pattern of metal deposition is not perfectly radial, the sample density is generally insufficient to be certain about the deviations from a radial pattern. It may be expected that the prevailing wind direction would produce an anisotropic pattern, asymmetrical and elongated in the dominant downwind direction. In this paper, part of the data analysis is confined to

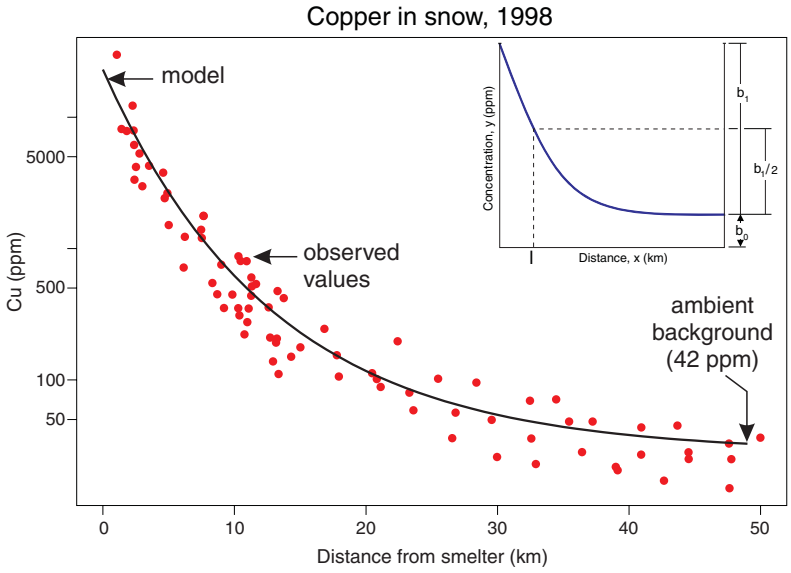

Figure 2.

Copper concentration versus distance from smelter for snow samples collected in 1998. Inset is a diagram of the three-parameter non-linear model (equation 1) fitted to data. The model approaches an asymptotic value at large distances from the smelter, equal to the ambient background level.

one spatial dimension, looking only at the behaviour of the metal values in the various media as a function of distance from the smelter. As discussed later, the effect of anisotropy due to wind has also been investigated, by using subsets of sample locations with particular directions from the smelter.

Two methods have been used to model the metal distributions. The primary objective of the modelling is to characterize the spatial patterns of metal distribution and predict the rate of metal deposition (loading) as a function of distance from the smelter. From the snow and peat data, the amount of metal of smelter origin deposited within a radius of about 150 km can be determined, using the model, and compared to the emissions from the Horne smelter. The second objective is to characterize the smelter influence by means of a multi-element ratio that helps to discriminate between smelter-derived material and material from other sources.

The first type of analysis involves the fitting of an empirical, three-parameter model to the data on metal concentration versus distance (or metal loading rate versus distance in some instances). These plots are usually isotropic (ignoring orientation from the smelter), but in some cases, they are anisotropic, as can be determined by using data subsets, based on direction. A comparison of the parameters of these models facilitates a comparison between surveys, and provides measures of the size (and to some extent the shape) of the smelter footprint. In the situation of snow and peat data, this is followed by transforming concentrations to loading rates (metal deposition rates in µg/cm^2/a) and calculating the amount of each metal in the smelter-centred anomaly by integrating the model over a circular area round the smelter. The anomaly tonnages for each metal are then compared among sampling media and with the reported emissions for the period considered in a mass balance, thereby estimating what proportion of the emissions can be accounted for within and somewhat beyond the smelter footprint.

The second type of analysis involves a multivariate approach, considering the combined effects of more than one metal (and/or element) at a time. Using results from a previous principal-component analysis of the snow data (Kliza et al., 2005; Telmer et al., 2004), and constrained by which elements are reported in the smelter emission data, a multi-element ratio is proposed that effectively discriminates between smelter emissions and materials from other sources, providing a source apportionment tool.

Empirical model

Assuming that metal deposition from the atmosphere occurs symmetrically around the smelter, values of metal concentration can be modelled as a function of radial distance from the smelter. In practice, wind direction distorts this picture, but a model provides an average representation of the data, and some of the spread around the model can be attributed to variability due to the effects of the prevailing winds. Various models have been proposed in the literature for modelling metal dispersal around a smelter (e.g. de Caritat et al., 1997; Čeburnis, 1999). Here we use an empirical model (Fig. 2) that has no physical basis, but is convenient because it fits the data well and has three parameters that can be readily interpreted. The model (Bonham-Carter and McMartin, 1997; Bonham-Carter and Kettles, 2001) satisfies the relationship

$$y = \beta_0 + \beta_1 2^{\frac{-x}{\lambda}} + \varepsilon \qquad (1)$$

where y is the natural logarithm of metal concentration (parts per million or other units) in the medium being considered, x is the distance from smelter (km), β_0 is the natural log of the metal concentration at an infinite distance from the smelter, $(\beta_0 + \beta_1)$ is the natural log of concentration very close to the smelter (at $x = 0$), λ is the 'half distance' at which the natural log of concentration has dropped to $\beta_0 + \beta_1/2$, and e is the error term. The modelled metal concentration is then equal to the inverse transform

$$\hat{c} = \exp(y) = \exp(\beta_0 + \beta_1 2^{\frac{-x}{\lambda}}). \qquad (2)$$

This is biased downward because of the effect of fitting equation (1) to logarithmically transformed concentration values. The effect is minor, except when computing the integration

(*see* next section), and in this situation the modelled concentration is multiplied by the ratio of the mean observed concentration divided by the mean predicted concentration. This 'adjustment factor' is not entirely satisfactory, because the bias caused by the logarithmic transform is not constant with concentration, but it does guarantee that the mean of the observed values at the data points will equal the mean of the predicted values at the same locations, and this is important for estimating the total amount of metal in the anomaly.

The same model in equation (1) can also be fitted directly to loading rates (μg/cm^2/a) for media where these can be estimated from concentration values. For either concentration or loading rate values, these three fitting parameters (β_0, β_1, and λ) and their standard errors are obtained by an iterative non-linear least squares method (using the nls function in S-Plus, Mathsoft (1999)). It is assumed that the model approaches an asymptotic value β_0 with increasing distance from the smelter. This value, after exponentiation to return to concentration or deposition rate, can be termed the 'ambient background' level. In practice, the ambient background will be affected by geological and other factors such as the influence of air masses containing metal particulates from a variety of natural and industrial sources, but it appears from the data that the concept of a constant background works well for these data. The background may be 'noisy' with a large variance, but it appears that there is no clear spatial trend in its value, at least for the data studied here.

Radial footprint distance

It is also convenient to define a distance from the smelter that can be used to characterize the 'footprint' radius. This is not the final distance travelled by airborne smelter emissions: it is an arbitrary distance of (x_1) (in kilometres) at which the modelled concentration (or loading) value reaches the background value plus one standard error of the background. (Because the background is obtained as a fitted parameter in a non-linear regression model, the variability of the parameter is expressed as a standard error by the regression program.) At this distance (x_1) from the smelter, values are close enough to the ambient background that the influence of the smelter is uncertain. Because the model approaches an asymptote at an infinite distance from the smelter, the model never quite reaches background, and picking a distance on the basis of the uncertainty of the background is a logical choice for the footprint radius. The expression for distance to background (footprint radius) is given by

$$x_1 = -\lambda \log_2 \frac{SE(\beta_0)}{\beta_1} \qquad (3)$$

where SE(β_0) is the standard error of β_0. The choice of using one standard error (rather than, say, two standard errors) is arbitrary. It should also be noted that $\exp(\beta_0 + \beta_1)$ is the concentration very close to the smelter. This value is often poorly defined in practice, because it is difficult to collect samples of these media near or within the city of Rouyn-Noranda without their being contaminated by road and other local dust. The half-distance parameter, λ, is also useful for comparing the shapes of the concentration curves from different surveys

Anisotropy

In order to account for the effect of anisotropy caused by the prevailing wind directions (in this area, winds generally blow from westerly, infrequently from easterly, directions), the following modelling procedure was used. First, an isotropic model was fitted to all data points. Values of β_0 and β_1 were then assumed to be constant for all wind directions, and different values of λ were determined by refitting equation (1), allowing only λ to change, to subsets of points based on their directions from the smelter. This has the effect of anchoring the modelled values at distance zero and infinity, but allowing the shape of the curve to change so as to accommodate change in wind direction. This is justified on the grounds that the ambient background deposition value (far from the smelter) can be assumed to be the same in all directions, and at the smelter itself the deposition value (notional because it cannot actually be measured) will also be the same in all directions. We note that the model of de Caritat et al. (1997) differs in that it allows maximum deposition to occur at some distance from the smelter, with a shadow zone close to the smelter, in order to account for the physical effects of stack height. At the scale used here, we judge this effect to be minor, and even if it does occur, we have no data from close enough to the smelter to prove or model the effect.

The total number of samples is not large for any of these sample media, so the number of subsets for determining the degree of anisotropy is restricted. In this paper, the points were divided into an 'upwind' group comprising all samples west of the smelter (azimuthal directions from the smelter between 180° and 360°), and a 'downwind' group comprising all points east of the smelter (0°–180° azimuth). Therefore three values of λ were calculated, one for all points and one each for an upwind subset and a downwind subset, respectively. In principle, a larger number of orientation subsets could be used, but in practice the number of subsets is limited by the need to have a large enough sample for the regression. It should be noted that unlike many orientation problems that involve line features in geology (lineaments, faults, etc), these data are truly directional, so that a northeast direction, for example, is not the same as southwest.

Another check on the degree of anisotropy was made using a statistical test. The residuals (observed minus predicted) values from the isotropic model (equation 1) were used to allocate observations to two groups, those with positive residuals and those with negative residuals. If the spread of values around the modelled line is strongly affected by the directions of the sample sites with respect to the smelter, one would expect that the positive residuals would be predominantly downwind sites and negative residuals, upwind sites. This would occur because the plume would be orientated in the dominant 'downwind' directions more often than the less frequent 'upwind' directions, and more deposition would occur at all distances downwind from the smelter than upwind. Therefore the mean direction of sites with positive residuals was compared with the mean direction of sites with negative residuals, and an F-test was used to test the null

hypothesis that the two mean directions are the same. Given the orientation of the *i*-th sample site as θ_i, the mean direction of $i = 1, \ldots, n$ sites is (e.g. Davis, 2002, p. 319):

$$\theta_i = \tan^{-1}(Y_r / X_r) \quad (4)$$

$$\text{Where } Y_r = \sum_{i=1}^{n} \cos\theta_i \text{ and } X_r = \sum_{1=1}^{n} \sin\theta_i .$$

The resultant length, *R*, a measure of direction that incorporates information about the spread of the vectors, is then

$$R = \sqrt{X_r^2 + Y_r^2} \quad (5)$$

and the standardized resultant length is $\overline{R} = \frac{R}{n}$ where n = the number of sample sites. The equality of two sets of directional vectors can be tested by calculating

$$F_{1,n-2} = \frac{(n-2)(R_1 + R_2 - R_p)}{(n - R_1 - R_2)} \quad (6)$$

where R_1 and R_2 are the resultant lengths of groups 1 and 2, respectively, and R_p is the resultant length of the pooled groups (e.g. Davis, 2002, p. 327). The greater is the difference between the resultant lengths, the larger is the value of F. The probability that the different groups of directions could occur due to chance can then be determined from the calculated F-value by comparing it with tabled values for particular probability levels. This provides a measure of whether the positive and negative residuals have significantly different average directions, and an inspection of the mean directions of the positive and negative residuals indicates whether the differences are consistent with prevailing wind directions. Ideally, the positive residuals are expected to have an orientation downwind and the negative residuals, upwind, if the wind direction does indeed explain at least some of the spread around the isotropic model, and therefore does play a role in the metal distribution pattern.

Integrated model

For snow and peat, metal concentration values can be transformed to loading rates (µg/cm^2/a). Then the total mass of metal within the anomaly caused by deposition of smelter emissions is equal to the total mass of metal in the medium considered, minus the mass of metal that can be attributed to ambient background levels. This assumes, of course, that metal deposition from the atmosphere is occurring everywhere and that the sample sites (snow or peat) are analogous to rain gauges, i.e. they provide estimates of deposition rate at the sample locations. Using the model, the deposition rate can be predicted for any location at a given distance (and possibly direction) from the smelter, irrespective of whether suitable peat hummocks (or suitable snow sampling sites) are available or not. With this assumption, we can then calculate the total amount of metal deposition occurring within a given radial distance from the smelter by integrating the product of metal loading rate and area, both functions of distance from the smelter.

The equation for the total mass of metal deposited in one year within the anomaly (I_A in tonnes/a) is

$$I_A = k[2\int_0^{x_{max}} cxdx - \exp(\beta_0)x_{max}^2], \quad (7)$$

where x_{max} (in kilometres) is the distance from the smelter over which integration is carried out. For peat, $k = 10^{-2}\,\rho t\pi$, where ρ is the bulk density of the surface peat material (g/cm^3), t (cm/a) is the thickness of peat accumulated in one year, and c is concentration in parts per million (or µg/g). For snow, the concentration units are also parts per million (or µg/mL), $k = 10^{-2}\bullet(365/n)\bullet(V/r^2)$, where V = volume of melted snow sample (mL), n = number days of snowfall, and r = inner radius of the snow sampling tube (in centimetres). Here it is assumed that no snow melts during the snowfall period (about three months for the 1998 and 2001 surveys, *see* Kliza et al., 2000, 2002) and that metal deposition during this period of continuous snow cover is representative of the whole year. In this way, the peat and snow data can be compared using similar units, either metal loading in µg/cm^2/a or metal mass deposited from the smelter in tonnes/a.

Multi-element ratio for source apportionment

From a multivariate statistical analysis of the snow geochemical data (Telmer et al., 2004; Kliza et al., 2005), it is clear that copper and arsenic are two metals that are typical of smelter metals, whereas iron and aluminium are typical of elements that, although present in the emissions, characterize the ambient background deposition at a large distance from the smelter. This can be shown by both a principal components analysis of geochemical data and a multiple linear regression using distance from the smelter as the response variable and the geochemical elements as explanatory variables. Telmer et al. (2004) also demonstrated this by ranking elements by univariate correlation coefficients of each element with distance from the smelter.

The problem with making comparisons among sampling media using multivariate statistical models is that the choice is restricted to elements that were analyzed in common, and that multivariate coefficients determined using data from one sampling medium are not suitable for use with data from other media. Furthermore, it would also be beneficial to use elements reported in the smelter emission data to determine whether samples can be expressed as mixtures of smelter materials and materials of non-smelter origin. Fortunately, Cu, As, Fe, and Al geochemical data are available from all the sampling media. Iron and aluminium data were not available on the list of smelter emissions, but Noranda, Inc. kindly supplied data on these two elements for 2001. Finally, by expressing the element combination as the ratio (Cu+As)/(Fe+Al) with common units for each element from a particular sampling medium, the resulting dimensionless quantity allows direct comparison of smelter emissions, the various sampling media, and a value based on crustal abundance, on the same graph.

RESULTS

Concentration model and effect of wind on metal distribution

The results of fitting equation (1) to Cu values in five different sampling media are shown in Figure 3; the model parameters and related quantities are summarized in Table 2 for Cu, Pb, and Zn. For these plots, snow data from both years were combined into a single data set. The lake-sediment values are for the topmost 2 cm of the core.

Copper

Copper concentration in snow (Fig. 3a) decreases about three orders of magnitude from the smelter to an ambient background level of about 14 ppm. The distance x_1 at which the modelled value equals the background plus one standard deviation is 63 km for the isotropic model. Holding β_0 and β_1 values constant from the isotropic model, and determining λ for the east- and west-of-smelter subsets, give modified λ values of 60 km and 67 km, respectively. These distances define the extent of the smelter footprint as determined by Cu values in snow.

The separation of sample sites into positive and negative groups on the basis of residuals from the isotropic model results in the positive residuals having a mean direction of 163° azimuth (i.e. about south-southwest from the smelter) and the negative residuals having a mean direction of 328° azimuth (about northeast from the smelter). The F-value is 13.54, which is significant at $\alpha = 0.01$, so despite the short mean resultant lengths — the resultant length is inversely related to the degree of dispersion or scatter of the individual directional vectors (*see* Fig. 3a, inset) — the two groups are statistically different with respect to direction from the smelter. These directions are generally consistent with positive residual sites being downwind (prevailing winds dominantly from westerly directions) and negative residual sites being upwind from the smelter.

Copper values in humus (Fig. 3b) decrease from about 5000 ppm close to the smelter to a background value of 25 ppm, again a drop of nearly three orders of magnitude. The isotropic value of x_1 is 64 km, with upwind distances equal to 58 km and downwind distances equal to 73 km. The mean directions of sites with positive and negative residuals are 102° and 244°, respectively, and the F-value is significant at $\alpha = 0.01$, indicating that the spread of points around the isotropic model is again at least partly related to wind direction.

Copper values in peat hummocks (Fig. 3c) drop from about 100 ppm close to the smelter to about 4 ppm at background. The isotropic model gives an x_1 of 52 km, with distances of 42 and 63 km for upwind and downwind values, respectively. Again the positive and negative residuals are consistent with downwind and upwind directions and have a large F value to support the significance of these groupings.

Copper values in lake water (Fig. 3d) drop from about 10 ppm to about 0.3 ppm at background. The effect of wind, as seen from both the deviations from the isotropic model and the very large value of F, is more marked for this medium than for the others. However, the data are noisy, as indicated by the wide variation of concentration and the lack, at least within about 70 km of the smelter, of an obvious approach to an asymptotic value. Nevertheless, the isotropic x_1 value is 72 km, with upwind and downwind values of 62 and 81 km, respectively, generally consistent with the other media. Note that the standard error of β_0 is much larger for this medium than for the others, reflecting a greater degree of uncertainty in the estimation of background levels.

Copper values in the upper layer of lake sediment (Fig. 3e) are also relatively noisy, dropping from about 5000 ppm near the smelter to a background level of 43 ppm, i.e. over two orders of magnitude. The effect of anisotropy is very weak, as seen from short mean resultant lengths, and relatively small F value (still just significant at a = 0.01). The mean directions for positive and negative residuals are consistent with downwind and upwind directions. Distances to background values, both isotropic and anisotropic, are close to 52 km.

Lead

Lead values (Table 2, not illustrated as a figure in this paper) follow a pattern similar to that for copper values. In general, the data are noisier than the Cu data. For Pb in snow, the effect of the wind is not significant, as seen from the F-test, although the resultant directions are still consistent with upwind and downwind directions. The x_l values for snow, peat, and humus range from 56 to 69 km, the upwind values, from 66 to 73 km, and the downwind values, from 48 to 68 km. The lake-sediment and lake-water distances to background are much shorter, however, about 31 km, although for Pb in lake water, the effect of the wind is very marked, giving an upwind distance of 10 km and downwind distance of 81 km.

Zinc

Zinc values (Table 2) are also noisy compared to copper values and show shorter distances to background (isotropic x_l is in the range of 39–53 km). The effect of anisotropy due to the wind is significant for snow and peat samples, but not for humus or lake-sediment samples. The mean directions for positive and negative residuals in humus are actually reversed from what would be expected for the effects of the prevailing wind, but the F value is also very low, indicating that the directions of positive and negative residuals are not significantly different. The lake-water values are too noisy for the model (equation 1) to converge.

Metal tonnages in the smelter anomaly

Numerical integration of equation (7) (as illustrated in Fig. 4) for the snow and peat data provides estimates of the tonnages of metal deposited in one year (*see* Table 3, 4, and Fig. 5). Bonham-Carter and Kettles (2001) used the same peat

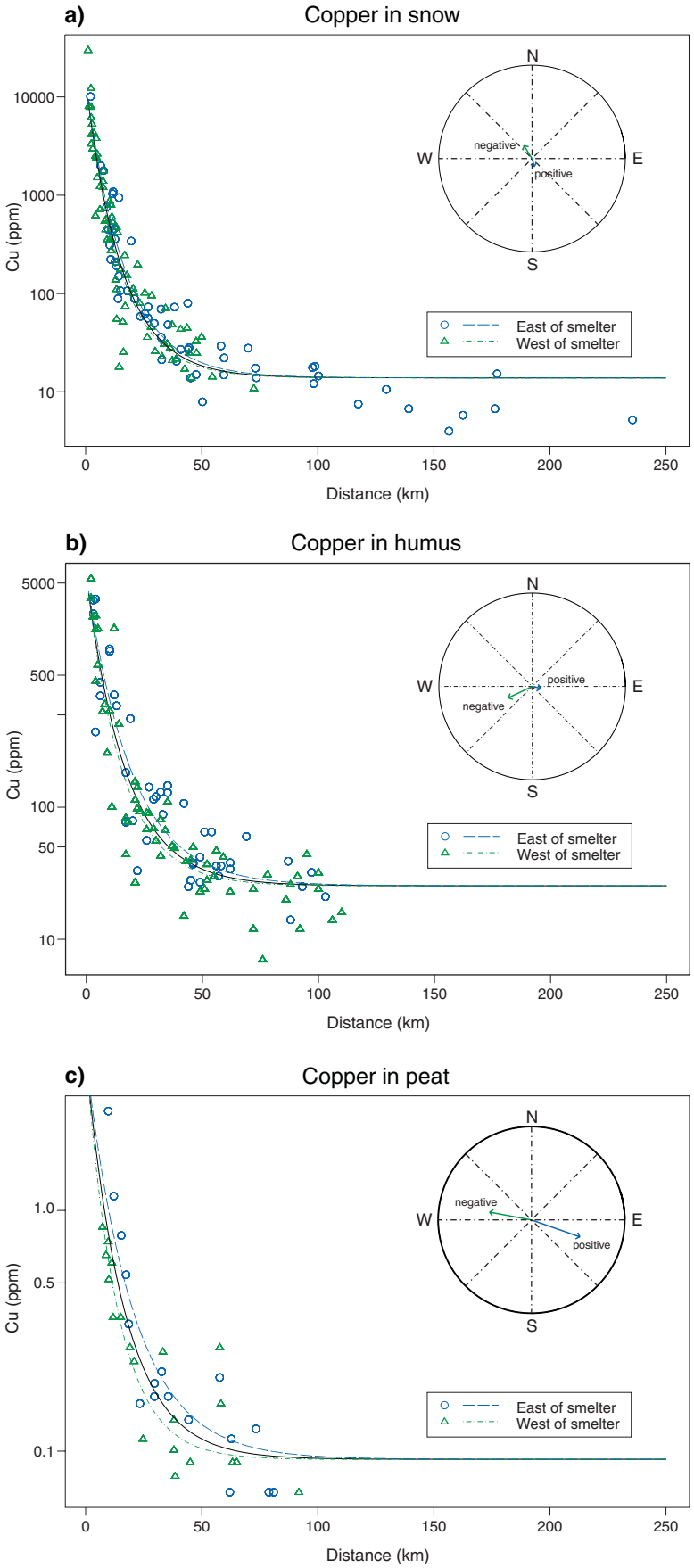

Figure 3.

Comparison of Cu concentration versus distance from smelter in various sampling media, and the effect of sample site direction from smelter (see *text for explanation*). ***a)*** *Snow (1998 and 2001 combined);* ***b)*** *humus;* ***c)*** *peat.*

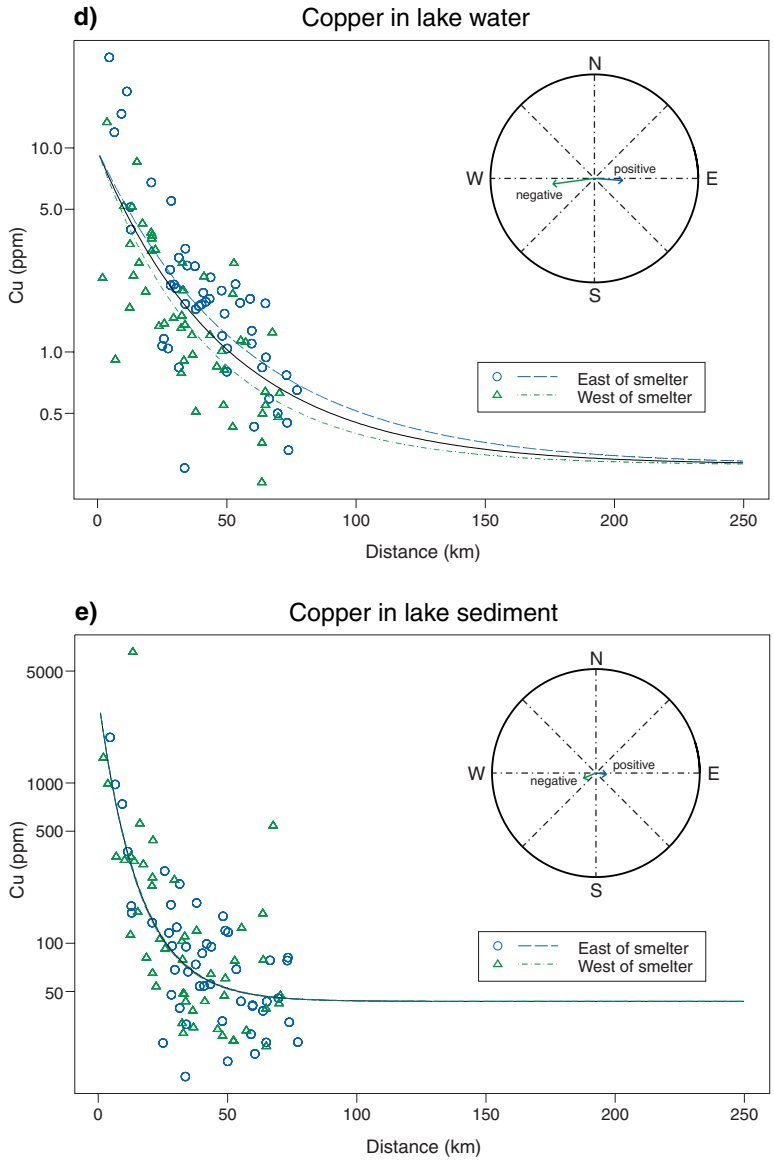

Figure 3. (Cont.)

d) *lake water;* ***e)*** *lake sediment (top 2 cm).*

Table 2. Comparison of model parameters for equation (1) fitted to metals in five sample media. Values of x_l-d and x_l-u are based on λ values fitted to points east of the smelter (downwind) and west of the smelter (upwind), respectively. The last three columns are for determining whether the mean resultant directions of positive and negative residuals (θ_1 and θ_2 respectively) are significantly different from one another, using an F-test. F-values have (1, n-2) degrees of freedom (df), where n = number of samples. n = snow, 132; humus, 104; peat, 37; lake water, 45; lake sediment, 57. Values with an asterisk are significantly different at $\alpha = 0.01$.

Element units	β_0 ln(ppm)	SE(β_0) ln(ppm)	β_1 ln(ppm)	SE(β_1) ln(ppm)	λ km	SE(λ) km	x_l km	x_l -d km	x_l -u km	exp(β_0) ppm	F-test[1] --	θ_1 deg	θ_2 deg
Cu-snow	2.63	0.13	6.94	0.21	10.86	0.77	62.74	67.35	59.86	13.87	13.54*	163	328
Cu-humus	3.23	0.13	5.41	0.25	11.96	1.25	64.14	73.02	58.36	25.28	10.80*	102	244
Cu-peat	1.41	0.18	3.82	0.56	11.61	3.04	51.58	62.95	42.46	4.11	31.59*	109	281
Cu-lake water	-1.28	0.85	3.56	0.68	34.64	16.74	71.62	81.37	62.26	0.278	42.27*	94	262
Cu-lake sediment	3.77	0.17	4.42	0.50	11.00	2.21	51.57	50.68	52.19	43.38	8.37*	98	247
Pb-snow	2.13	0.22	6.63	0.29	14.02	1.57	68.94	70.48	67.87	8.41	6.45	100	294
Pb-humus	3.95	0.15	4.61	0.29	11.78	1.71	58.47	72.94	49.54	51.94	19.96*	102	244
Pb-peat	0.26	0.44	5.45	0.71	15.47	5.30	56.16	65.59	48.18	1.29	10.08*	119	280
Pb-lake water	-1.73	0.40	2.05	0.81	13.40	11.30	31.52	81.14	10.03	0.18	64.67*	86	260
Pb-lake sediment	4.30	0.11	3.56	0.82	6.15	1.75	30.85	33.12	29.26	73.70	14.25*	50	223
Zn-snow	3.41	0.11	4.90	0.24	7.88	0.77	43.60	57.04	39.51	30.27	17.87*	171	336
Zn-humus	4.36	0.12	3.15	0.25	11.29	2.04	52.92	53.89	51.93	78.26	3.45	262	182
Zn-peat	2.97	0.12	2.16	0.63	9.40	3.88	38.72	55.45	28.14	19.55	16.27*	135	298
Zn-lake sediment	4.58	0.10	2.40	0.28	11.39	2.48	51.54	44.55	57.17	97.51	6.35	166	301

[1] Tabled F values for $\alpha = 0.01$ for snow, df = (1, 130) is 6.83; humus, df = (1, 102) is 6.90; peat, df = (1,35) is 7.40; lake water, df = (1, 43) is 7.30; lake sediment, df = (1, 55) is 7.12.

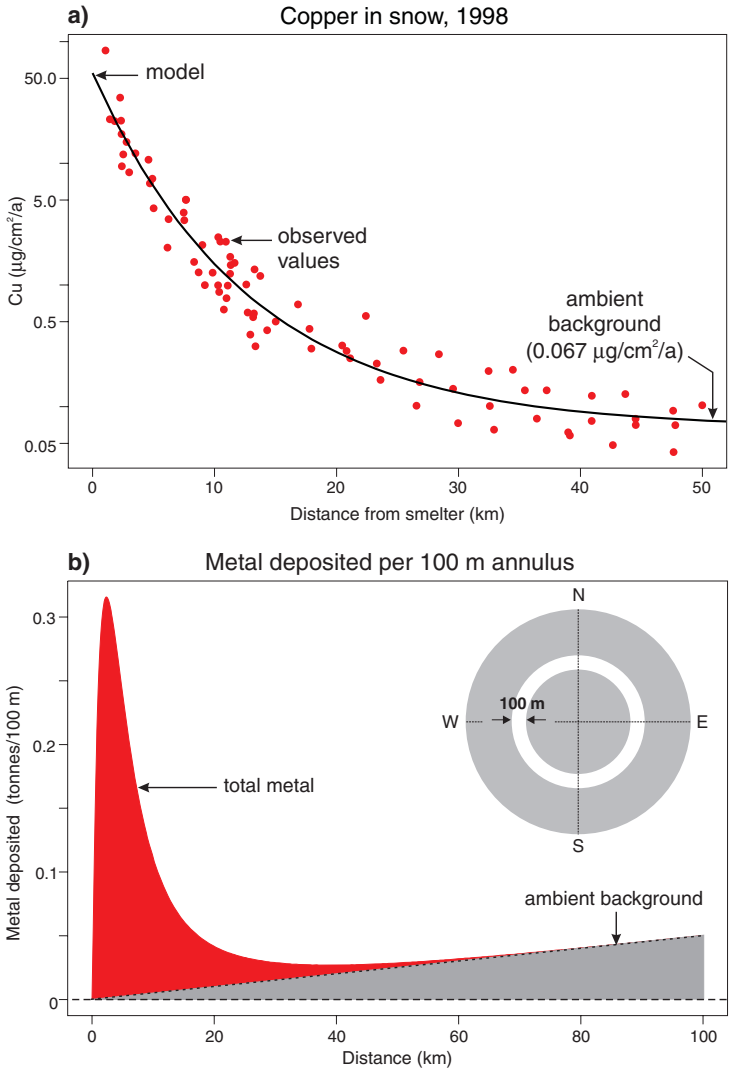

Figure 4.

a) *Model fitted to Cu loading rates (µg/cm²/a).* ***b)*** *Integration of loading rate times area at successive distances from the smelter to determine the total metal tonnage in the smelter anomaly. Diagram inset illustrates (not to scale) the idea of calculating the amount of metal in successive annuli (rings) 100 m wide, starting at the smelter and continuing outward until the difference between the total tonnage and background tonnage is negligible. Note that the background tonnage increases with distance, because although the background concentration is constant, the area of each annulus increases with radial distance from the smelter. In this example, about 31 tonnes of Cu are contained in the anomaly. The shape of the anomaly tonnage curve reflects the combined effect of area of annuli increasing with distance and metal concentration decreasing with distance. The distance at which a 100 m annulus contains the greatest amount of metal peaks at about 5 km from the smelter.*

Table 3. Model parameters fitted to metal loading rates (µg/cm²/a) for snow (1998), snow (2001), and peat (1997). The value of ω is a correction factor to account for the inverse logarithmic transformation.

Element	β_0	SE(β_0)	β_1	SE(β_1)	λ	SE(λ)	x_l	exp(β_0)	ω
units	*	*	*	*	***km***	***km***	***km***	**µg/cm²/a**	--
Cu-snow-1998	-2.70	0.14	6.71	0.18	8.96	0.65	49.60	0.0672	1.18
Cu-snow-2001	-3.11	0.19	6.65	0.64	11.30	1.89	57.78	0.0446	1.62
Cu-peat-1997	-2.38	0.18	3.83	0.56	11.61	3.04	51.57	0.0926	1.14
Pb-snow-1998	-2.55	0.26	5.94	0.25	10.92	1.42	49.42	0.0781	1.09
Pb-snow-2001	-3.51	0.16	5.85	0.68	8.78	1.53	45.78	0.0299	1.52
Pb-peat-1997	-3.54	0.44	5.45	0.71	15.47	5.30	56.16	0.0291	1.21
Zn-snow-1998	-2.28	0.14	4.77	0.21	7.76	0.82	39.74	0.1023	1.18
Zn-snow-2001	-2.25	0.16	4.84	0.86	6.64	1.57	32.95	0.1054	1.75
Zn-peat-1997	-0.82	0.12	2.16	0.63	9.39	3.87	38.70	0.4404	1.09
As-snow-1998	-3.85	0.17	5.52	0.22	8.83	0.94	44.09	0.0213	1.10
As-snow-2001	-4.45	0.17	5.81	0.75	8.35	1.59	42.77	0.0116	1.42
Cd-snow-1998	-5.89	0.16	3.73	0.23	8.08	1.26	36.58	0.0028	1.16
Cd-snow-2001	-5.36	0.12	4.11	0.77	5.38	1.26	27.71	0.0047	1.20

*units are natural logarithms of µg/cm²/a

Table 4. Comparison of the amount of metal in the smelter anomaly and the amount of metal emitted from the Horne smelter, using snow and peat data. The last column shows the amount of non-smelter metal deposited from the atmosphere within a 100 km radius of Rouyn-Noranda.

Element	Smelter anomaly	Reported emissions	Proportion[4]	Background loading rate[5]	Tonnage in background[6]
units	*tonnes/a*	*tonnes/a*	*%*	*µg/cm²/a*	*tonnes/a*
Cu-snow-1998	31.1	63.0[1]	49	0.0793	25.0
Cu-snow-2001	43.1	82.9[2]	52	0.0723	22.6
Cu-peat-1997	14.3	53.7[3]	27	0.1055	33.1
Pb-snow-1998	31.6	218.4[1]	14	0.0851	26.8
Pb-snow-2001	10.4	62.4[2]	17	0.0454	14.3
Pb-peat-1997	20.1	222.7[3]	9	0.0351	11.1
Zn-snow-1998	12.1	52.1[1]	23	0.1207	37.9
Zn-snow-2001	13.9	14.8[2]	94	0.1844	57.6
Zn-peat-1997	16.7	62.5[3]	27	0.4801	151.1
As-snow-1998	4.5	71.7[1]	6	0.0234	7.4
As-snow-2001	3.4	71.6[2]	5	0.0166	5.2
Cd-snow-1998	0.20	0.98[1]	20	0.0032	1.0
Cd-snow-2001	0.19	0.78[2]	24	0.0056	1.8

[1] Emission value for comparison to snow-1998 (survey done in March 1998) is mean monthly emission value for November 1997, December 1997, January 1998, February 1998, March 1998 multiplied by 12 (*see* Table 1b).
[2] Emission value for comparison to snow-2001 (survey done in March 2001) is mean monthly emission value for November 2000, December 2000, January 2001, February 2001, March 2001 multiplied by 12 (*see* Table 1b).
[3] Emission value for comparison to peat-1997 (survey done in October 1997) is a weighted average of annual emissions equal to ((9 x 1997 emissions)+ (3 x 1996 emissions))/12 (*see* Table 1A).
[4] Proportion of reported annual emissions accounted for by smelter anomaly
[5] Equal to $\exp(\beta_0) \bullet \omega$.
[6] Tonnage ascribed to deposition of metal from non-smelter sources within a radial distance of 100 km from the smelter.

hummock data and compared the estimated metal tonnages with the annual emission data shown by the lines in Figure 5. Later, after the publication of the peat paper, monthly emission data were obtained for the Horne smelter for the two snow-sampling periods. These show that considerable short-term variability occurs in the emissions data and that monthly emission rates may diverge considerably from annual rates, as discussed earlier. In Figure 5, estimates of anomaly tonnages are shown with error bars. The error bars are based on evaluating the upper and lower concentrations, using the standard errors of the three fitted parameters as follows:

$$\hat{c}_u = \exp(y_u) = \exp\{(\beta_0 + SE(\beta_0)) + (\beta_1 + SE(\beta_1))2^{\frac{-x}{\lambda + SE(\lambda_0)}}\} \quad (8)$$

and

$$\hat{c}_l = \exp(y_l) = \exp\{(\beta_0 - SE(\beta_0)) + (\beta_1 - SE(\beta_1))2^{\frac{-x}{\lambda - SE(\lambda_0)}}\}. \quad (9)$$

Then equation (7) is integrated using equation (8) to estimate an upper value for the tonnage error bar, and using equation (9) to estimate the lower value of the tonnage error bar, for each data set. These values give error bars that are larger than would be expected for one standard deviation either side of the mean tonnage estimate, because β_0, β_1, and 1 are not uncorrelated with one another. They do, however, give some idea of the sensitivity of the tonnage estimates to the spread of the data values about the model (equation (1)), and this spread also includes the effect of anisotropy due to prevailing wind directions. We have not repeated here the Monte Carlo estimates made by Bonham-Carter and Kettles (2001), which included errors due to analytical precision and errors in estimates of peat growth rate and bulk density. The conclusion from that study was that the spread of points around the model (much of which can be accounted for by wind direction) was the dominant source of error, compared with other factors. The Monte Carlo estimates also assumed that β_0, β_1, and λ are uncorrelated, which again leads to error bars that are too wide, but give an idea of the sensitivity of the results to errors due to residuals from the model.

For comparison, the amounts of metal in these sampling media due to deposition at ambient background levels (i.e. from non-smelter sources), from the smelter out to 100 km from the smelter, are shown in the final column of Table 4.

For example, Cu values in the 1998 snow background were 25 tonnes within 100 km of the smelter, which is roughly the same amount as in the smelter anomaly (31 tonnes).

Copper

The 1998 snow data gave an estimate of 31 tonnes in the metal anomaly, which is 49% of the mean reported emission tonnage (Table 4). The 2001 snow data gave an estimate of 43 tonnes, which is 52% of the mean reported emission value. The peat data gave an estimate of 14 tonnes, or 27% of the mean reported emission value. However, Figure 5a illustrates that these percentages should be treated with caution, because of the amount of variability in both the emission data and the anomaly estimates. Nevertheless, even allowing for the various sources of uncertainty, these results show that between 30 and 50% of the copper emitted from the smelter can be accounted for by deposition within about 100 km of the smelter (integration of equation (7) is continued beyond the footprint, statistically defined by the x_l values, although the amount of metal accounted for in the zone outside the footprint but within 150 km of the smelter is small, less than 5% of the anomaly total).

Lead

The mass of Pb in the snow anomaly for 1998 is 32 tonnes, which is 14% of the mean reported emissions (Table 4). The emissions decreased drastically between 1998 and 2001 (from 218 to 62 tonnes/a), and the mass of Pb in the 2001 snow anomaly also decreased by about the same proportion from 32 tonnes to 10 tonnes, which is 17% of the reported emissions. The peat estimate accounts for only 9% of the emissions. Figure 5b shows that the error bars on the Pb anomaly estimates are relatively small compared to the tonnage error bars for Cu. The estimated proportion of lead emissions accounted for in the snow and peat anomalies is between 9 and 17%, i.e about one third of the proportion of Cu emissions.

Zinc

The estimates of Zn anomalies (Fig. 5c) in the three surveys gave comparable results (12, 14, and 17 tonnes for 1998 snow, 2001 snow, and 1997 peat, respectively). However, the emission data show a substantial drop over this period from 63 tonnes to 15 tonnes, which was not reflected in the anomaly calculations, in contrast to the results for Pb. The proportion of emissions accounted for by the 1997 peat values and 1998 snow values is about 25%, whereas the 2001 snow survey accounted for 94% of emissions. The reason for the large value in 2001 is not understood.

Arsenic

As shown in Figure 5d, arsenic emissions increased from about 20 tonnes/a in the mid-1990s to nearly 100 tonnes/a in 2002. The As values in peat were too unreliable to be used, but the two snow surveys gave estimates of about 4 tonnes/a in the anomaly, accounting for only 5 to 6% of the emissions, much lower than for Cu, Pb or Zn.

Cadmium

Since 1990, cadmium emissions have decreased from 10 tonnes/a to 2 tonnes/a or less (Fig. 5e). The monthly winter emission rates appear to be substantially lower than the annual rates, possibly because the feed in the two sampling winters was lower than normal during those months. The proportion of the emissions accounted for is about 20% for both years.

Multi-element ratio for source apportionment

Figure 6 summarizes the behaviour of the element ratio (Cu+As)/(Fe+Al) with increasing distance from the smelter for all the sampling media. The horizontal dashed line near the top of Figure 6 represents the value of the ratio (= 4.23) for the 2001 smelter emissions, based on the reported annual tonnages of Cu = 41.7, As = 97.9, Fe = 15, and Al = 18. The horizontal solid line near the bottom represents the average value for the crust of 0.4×10^{-3}, using crustal abundance values (Cu = 50 ppm, As = 2 ppm, Al = 81×10^3 ppm, Fe = 46.5×10^3 ppm) from Taylor (1964). The ratio for C-horizon soils in this vicinity has a median value of 0.5×10^{-3} (P. Henderson, pers. comm., 2002), close to the crustal abundance value.

The results shown in Figure 6 are consistent with the hypothesis that smelter emissions are progressively diluted with increasing distance from the smelter, by mixing of emitted material and airborne dust and aerosols from non-smelter sources. This is indicated for example in the snow data by values close to the smelter of about 2 (i.e. close to the smelter emission value of 4). The ratio decreases by a factor of about 100 to a background value of 0.015 at a distance greater than about 80 km from the smelter.

The background values for peat and lake water are a little lower than for snow, but in the same general level. However, close to the smelter, the ratios for peat and lake water are generally not as high as the value for snow.

The lake sediment values shown in Figure 6 are interesting because there is a clear distinction between the 'top' lake-sediment values and the 'bottom' lake-sediment values in samples taken close to the smelter. Values for (Cu+As)/(Al+Fe) in the core-bottom samples have no relationship with distance from the smelter, whereas values from the core-top samples decrease with distance, in a manner similar to values from humus and the other media, as might be expected.

Although the ratio (Cu+As)/(Al+Fe) is complex in several of the sampling media (for example, several confounding factors affect the Al and Fe values in lake sediments and soils), it is useful for comparing the degree of mixing of smelter emissions with materials from sources unrelated to

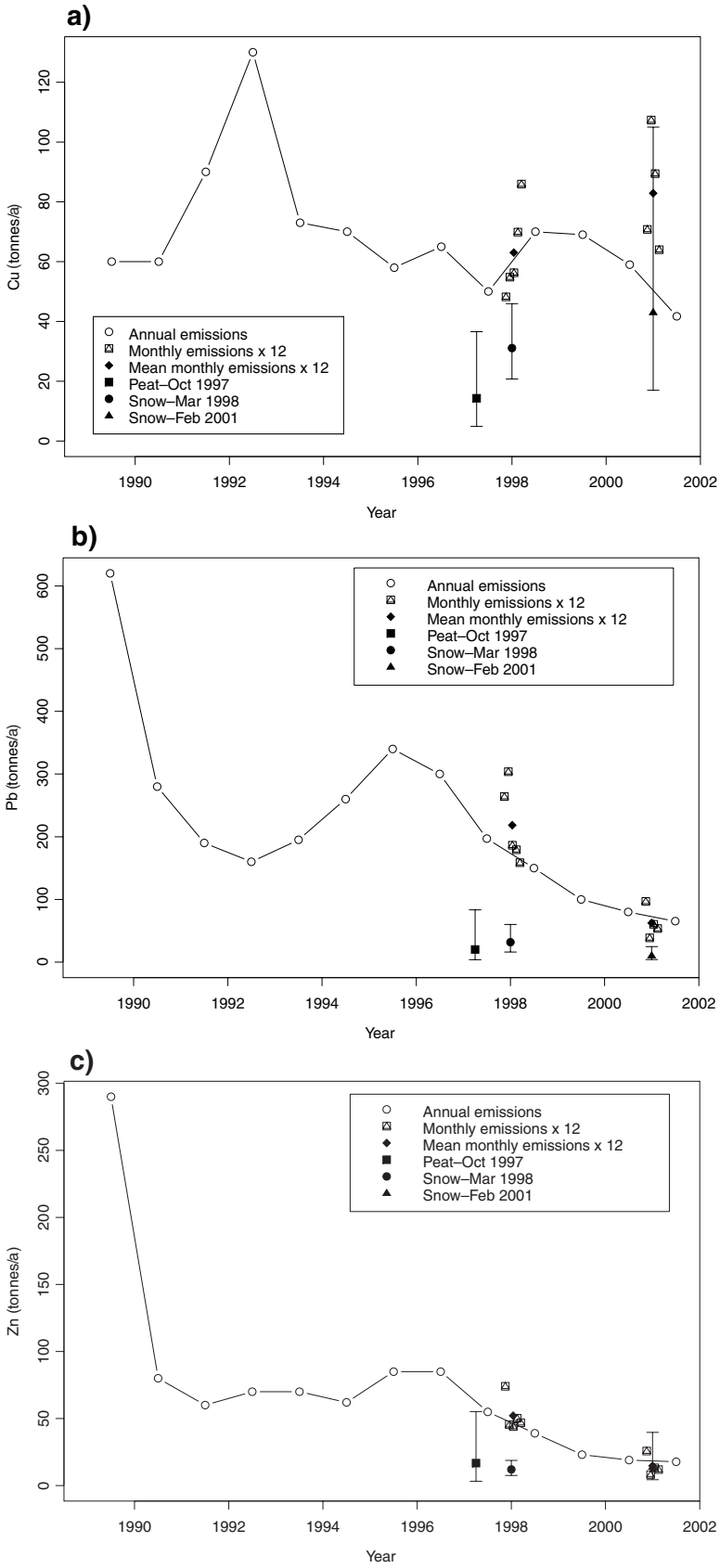

Figure 5.

Comparison of emission data reported for the Horne smelter with estimates made of metal in the smelter anomaly. Annual tonnages are shown for the whole period, joined by lines, with symbols to indicate monthly tonnages (x 12 so they plot on the same scale) for two snow sampling periods (Table 1b). ***a)*** *Copper;* ***b)*** *lead;* ***c)*** *zinc.*

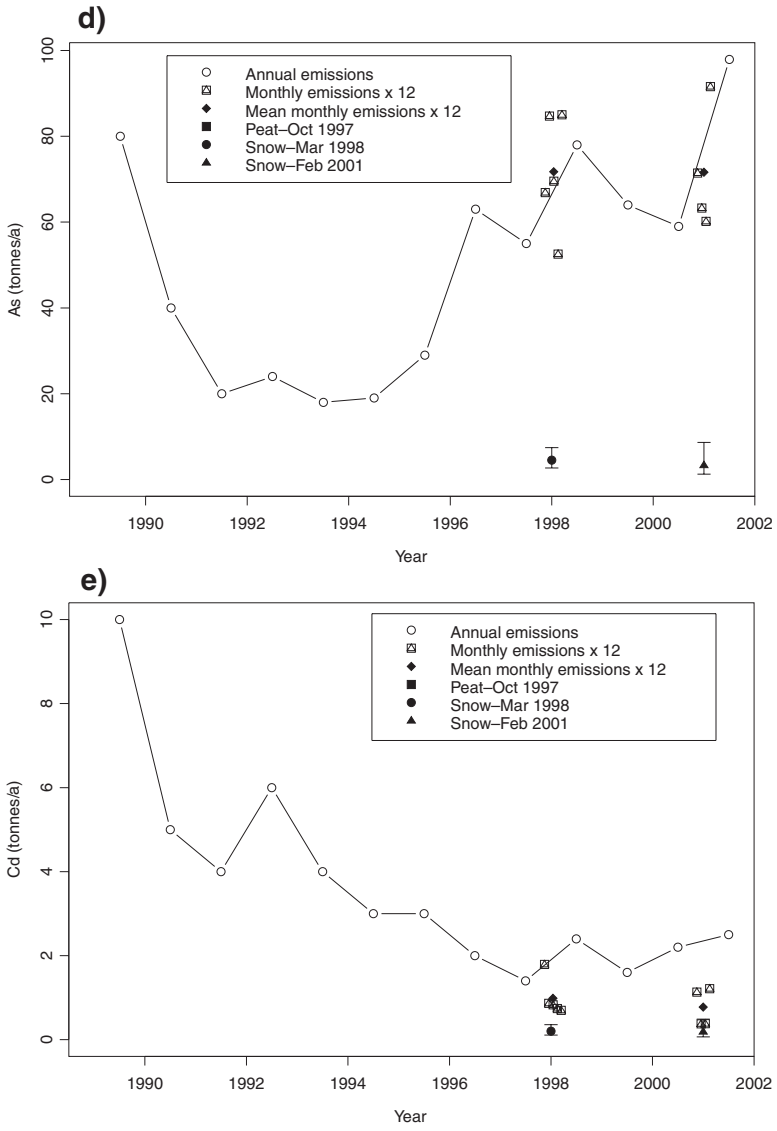

Figure 5. (cont.)

d) *arsenic;* ***e)*** *cadmium.*

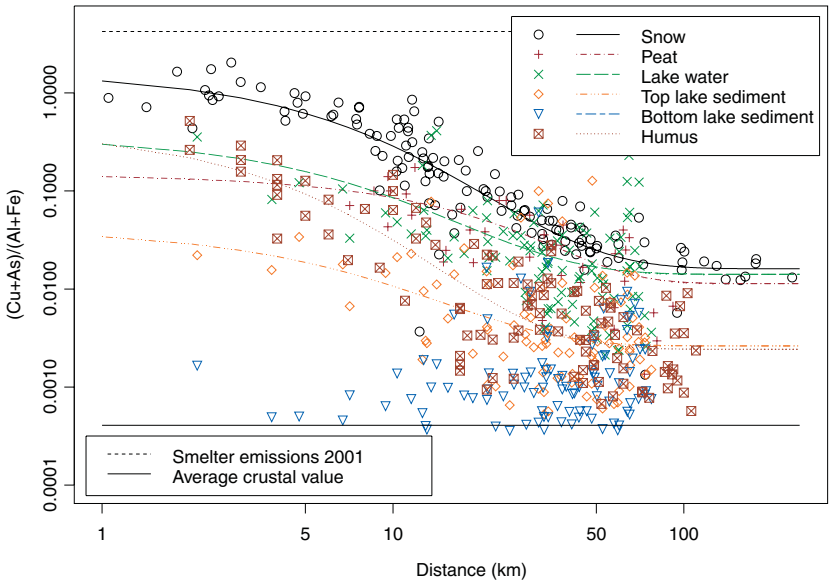

Figure 6.

Ratio (Cu+As)/(Fe+Al) plotted for various sampling media. Also shown is the ratio for reported smelter emissions (2001) and the crustal average value. Modelled values are shown as lines for snow (combined years), peat, humus, lake water, and lake sediment (top 2 cm). Although no line is fitted, note that bottom ('pre-industrial') lake-sediment values show no trend with distance from the smelter. Horizontal lines for smelter emissions and crustal abundance figures are for reference, with no dependence on or change with distance from the smelter.

the smelter. The shape of the peat curve is different from that of the curves for other media, although the distance to background is generally similar.

DISCUSSION AND CONCLUSIONS

The smelter footprint is probably best defined by values of Cu in snow, because snow sampling extended more than 200 km from the smelter (combining both sampling years), the source of the metals in snow is the atmosphere, and copper is an important metal in the Horne emissions. Copper seems to be the best indicator of smelter influence, partly because the emissions are relatively rich in copper and partly because copper 'behaves' in a more predictable manner in the sample media described here. If the smelter footprint is defined statistically as the zone within which the modelled Cu value is greater than the background value plus the standard error of the background, the footprint is between 60 and 67 km from the smelter, with the larger distance downwind toward the east. Although a large proportion of the smelter emissions are carried beyond this distance, the smelter-derived metal becomes indistinguishable from background levels once deposited from the atmosphere due to dilution with metals from non-smelter sources.

Snow, peat, humus, lake water, and lake sediment all provide a generally similar picture of enrichment within the smelter footprint of about the same size and shape. The prevailing winds cause deposition downwind from the smelter to be greater than deposition upwind, but the effect is not as large as might first be expected.Using the model parameters in Table 2 and equations (1) and (2), the deposition flux in $\mu g/cm^2/a$ can be determined for any metal given the distance (and if desired the direction) from the smelter. This is useful for studies involving the impact of smelter deposition on the environment (Environment Canada and Health Canada, 2001; Bonham-Carter, 2005).

The proportion of smelter-emitted copper that is accounted for by deposition within about 150 km from the smelter (the amount deposited between the footprint as defined previously (i.e. 60–67 km) and 150 km is generally less than 5% of the total anomaly) is in the range of 27 to 52% of stack emissions, depending on the year and whether snow or peat is used for the calculation. The range for Pb is 9 to 17%. Discounting a very large (unexplained) estimate based on 2001 snow sampling, the range for Zn is 23 to 27%. The range for As is 5 to 6% and for Cd, 20 to 24%.

These results indicate that emissions not accounted for by deposition within the smelter footprint must be transported by the atmosphere more than this distance. Because the proportion of smelter-emitted metal to metal from other sources in the atmosphere decreases progressively with increasing distance, the 'unaccounted for' emissions may travel hundreds of kilometres from the smelter, but are impossible to detect on the ground using ordinary geochemical methods. Stable isotope methods, for example the tracing of Pb and Sr from different sources (e.g. Simonetti et al., 2000a, b) in snow and other media, cannot easily be applied to fingerprint emissions, because in recent years the Horne smelter has become a custom smelter, processing a mixture of feed sources that changes almost daily.

Samples of particulates settling from the air on to ground filters taken in January and February 2000 near the Horne smelter had an equivalent diameter between 0.6 and 16 µm, with an average diameter of 3 µm (Paktunc et al., 2001). Plume sampling from an aircraft (Banic et al., 2001) during the same time period gave the range of particle sizes as 0.6 to 27 µm equivalent diameter, with an average size between 1.6 and 2.7 µm. Most dust and aerosol particles emitted from the smelter are therefore less than 10 µm in equivalent diameter and a substantial proportion are less than 2 µm. Gravitational settling of particles <2 µm under dry conditions is so slow that particles in this size range behave essentially like a gas. Such small particles are dispersed by the atmosphere and are deposited mainly during precipitation events. Whatever the transport and deposition mechanism in the atmosphere, the

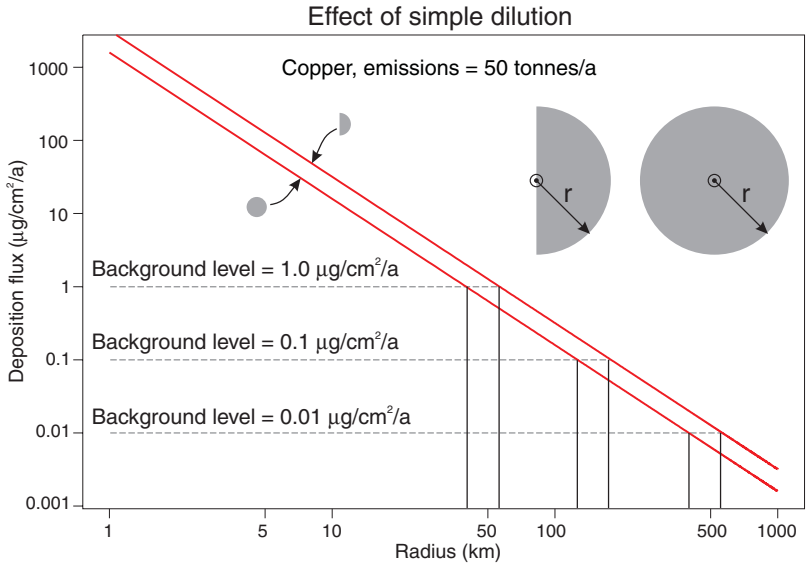

Figure 7.

Deposition flux for copper for a simple model of dispersal from a point source, such that 50 tonnes of metal are deposited evenly in a circle (and half-circle) of increasing radius. The effect of dilution is so great from a point source that the size of the smelter footprint, as seen by deposition on the ground, is restricted to a relatively small distance from the source. The effect is strengthened by non-smelter sources of metal in the atmosphere as seen in the ambient background levels.

dominant process affecting the concentration of deposited metal as a function of distance from the smelter is dilution from a point source. Because of the geometric increase in circular area surrounding the smelter with increasing radial distance, dilution occurs relatively rapidly, even under the influence of prevailing winds.

For example, consider a simple situation in which 50 tonnes/a of copper (actual value for Horne smelter in 1997, *see* Table 1) are emitted radially from a point source (Fig. 7). If the emissions are spread evenly (clearly an unrealistic situation) over a circle of radius r km, then the deposition rate at any location within a circle with r = 50 km is about 0.63 μg/cm^2/a; this decreases to 0.1 μg/cm^2/a for a circular area with r = 126 km and to 0.01 μg/cm^2/a for r = 400 km (Fig. 7). If the emissions are spread over a half-circle (all metals carried downwind only, for example), the deposition rate is 0.1 μg/cm^2/a for r = 178 km and 0.01 μg/cm^2/a for r = 564 km. The actual deposition rates for ambient background levels of Cu are 0.106 μg/cm^2/a for 1997 (peat), 0.0793 μg/cm^2/a for 1998 (snow), and 0.0723 μg/cm^2/a for 2001 (snow). Thus it is not surprising that the smelter footprint, as seen in all these sample media, is less than 100 km from the smelter.

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