Contents

Author Index

Geochemistry of snow around the copper smelter at Rouyn-Noranda, Quebec: comparison of 1998 and 2001 surveys

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Abstract: Two snow surveys were conducted (1998 and 2001) in the region surrounding the copper smelter at Rouyn-Noranda, Quebec.

Total loading rates of metals per year (ng/cm²/a) were determined for a large suite of elements, of which 13 (Cu, Pb, Zn, Cd, As, Sb, S, Ag, Ni, Al, Mg, Fe, Mn) are reported on here. The spatial distributions of loading rates of smelter-derived metals from both survey years show a bull's-eye pattern centred on the smelter, skewed northeast and southeast of the smelter as a consequence of the prevailing wind directions. Most element patterns can be divided into two parts, a proximal part close to the smelter with high loading rates dominated by deposition of smelter-emitted metals and a distal part in which loading rates approach an ambient background level and metals are predominantly from non-smelter sources. The radius of the area obviously affected by metal emissions is usually about 50 km. The differences in deposition rates for smelter-derived metals (Cu, Pb, Zn, As, Cd) between the two sampling years may be explained in part by changes in reported emissions between 1998 and 2001.

All samples were thawed and filtered. Dissolved and particulate fractions were analyzed separately. The proportion of total metal in dissolved form provides an indication of potential bioavailability. It differs among elements, between years for the same element (due to changes in filter size), and, for some elements, with distance from the smelter.

Résumé : Deux études portant sur la neige ont été respectivement menées en 1998 et en 2001 dans la région de la fonderie de Rouyn-Noranda (Québec).

On a calculé les taux de charge totaux annuels (ng/cm²/a) d'un grand nombre d'éléments, dont 13 (Cu, Pb, Zn, Cd, As, Sb, S, Ag, Ni, Al, Mg, Fe et Mn) font l'objet du présent article. Du point de vue spatial, les taux de charge en métaux émis par la fonderie et établis pendant les deux études susmentionnées sont répartis concentriquement depuis la fonderie, mais en biais vers le nord-est et le sud-est en raison des vents prédominants. La plupart des éléments ont pu être répartis en deux groupes, un à proximité de la fonderie, où les taux de charge élevés se rattachent surtout à des métaux émis par la fonderie, et un autre à une plus grande distance de la fonderie, où les taux de charge se rapprochent des concentrations de fond et se rattachent principalement à des métaux qui ne sont pas issus de la fonderie. Le rayon de la zone où il est évident que des émissions de métaux ont été déposées mesure dans l'ensemble environ 50 km. Les différences de taux de dépôt de métaux émis par la fonderie (Cu, Pb, Zn, As et Cd) relevées entre les deux années d'échantillonnage peuvent s'expliquer en partie par des variations d'émissions rapportées de 1998 à 2001.

Tous les échantillons ont été dégelés et filtrés. Les fractions dissoutes et particulaires ont fait l'objet d'analyses distinctes. La proportion de métaux dissous est un indice de leur biodisponibilité potentielle. Elle varie selon les éléments, d'une année à une autre pour un élément donné (en raison de l'utilisation de filtres de différentes dimensions) et, dans le cas de certains éléments, selon la distance par rapport à la fonderie.

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BACKGROUND

In certain environments, snow is an excellent sampling medium for studies of metals and other substances transported in the atmosphere. In many parts of Canada, precipitation falls as snow during the winter, usually November to April. Barring the occurrence of melting periods, the resulting snowpack records a sequence of precipitation events (wet deposition) and dry atmospheric fallout (dry deposition), thereby providing a sample of atmospheric deposition integrated over the time from first snow until the time of collection. Consequently, chemical and mineralogical investigations of regional snowpack (and ice) are becoming widely used in regions with sufficiently cold winters as a medium to characterize emissions from industrial, urban, and other sources (e.g. Barrie and Vet, 1984; Dick and Peel, 1985; Shewchuk, 1985; Wolff and Peel, 1985; Chan and Lusis, 1986; Philips et al., 1986; Gorzelska, 1989; Grosch and Georgii, 1989; Landsberger et al., 1989; Jickells et al., 1992; Wolff, 1992; Lazareva et al., 1993; Malakov and Senilov, 1993; Hinkley, 1994; Ayras et al., 1995; Niskavaara et al., 1996; Reimann et al., 1996; Viklander, 1996; Hinkley et al., 1997; Viskari et al., 1997; Yakhnin et al., 1997; Gregurek et al., 1998; Hudson and Golding, 1998; Šakalys et al., 1999; Ingersoll, 2000; Kaasik et al., 2000; Rosman et al., 2000; Sherrel et al., 2000; Simonetti et al., 2000a, b). The chemical composition of snow changes both spatially and temporally due to various factors such as the local sources of material emitted to the atmosphere (including anthropogenic and natural sources), weather conditions, topography, forest cover, redistribution by wind, and others (Colbeck, 1981; Wolff, 1992; Reimann et al., 1996). In order to determine the extent of contamination of the environment around a point source, it is necessary to determine the ambient background of atmospheric fallout (i.e. the loading rate in the absence of the smelter) in the study area. Once this ambient background is established, the spatial patterns of chemical elements deposited in snow (corrected for ambient background) provide information about the influence of the point source, the distance of transport of emissions deposited during the winter months, the loading rates of metals with distance and direction from the smelter, and the availability of smelter-derived metals in readily soluble form.

As part of the Geological Survey of Canada's Metals in the Environment (GSC MITE) initiative, two snow surveys (1998 and 2001) were completed around the Horne smelter, a copper smelter that has been operating since 1927 in the Quebec town of Rouyn-Noranda (Fig. 1). Their purpose was to characterize the chemical footprint of smelter emissions transported by the atmosphere. The winter 1998 snow survey successfully defined the size of the footprint around the Horne smelter and provided a comprehensive picture of metal distribution in the snow — how metal levels change with distance from the source and what processes controlled metal deposition (Telmer et al., 2004). The 1998 sampling distribution was restricted mainly to samples along three radial traverses (northwest, northeast, and south), and the farthest sample was 50 km from the smelter. This left some uncertainties about the spatial representivity of the survey. Would a second survey provide a similar pattern? Is 50 km a great enough distance to reach ambient background levels? If samples were not restricted to radial traverses, would the radial deposition pattern observed in the 1998 survey change shape?

In addition to changes in the sampling pattern, some minor changes were made to the site selection and laboratory protocol used in 1998. The 2001 sites were restricted mainly to locations on frozen lake surfaces to avoid the possibility of contamination from the soil surface and 'wicking' of metals from the ground upward into the snow by capillary action. The 1998 samples were thawed and filtered using 0.45 µm filter paper, whereas the filter size for the 2001 samples was 0.1 µm. Thus the proportion of 'soluble' to 'particulate' fractions differs to some degree between the two years due to this change in filter size, and this must be considered in the interpretation.

MATERIALS AND METHODS

Regional snowpack

Two snow surveys (1998, 2001) involved collecting 160 samples over approximately 75 000 km² of the area surrounding the Horne smelter (Fig. 1). The sample density was higher close to the smelter and decreased with increasing radial distance from Rouyn-Noranda. All samples were collected before mid-March to avoid the spring melt. Ideally, sampling in mid-March in this region of Quebec provides a measure of total wintertime accumulation. Details of both surveys have been documented in Kliza et al. (2000, 2002).

In 1998, snow was collected between March 10 and 12 within a 50 km radial area around the smelter (Fig. 1). A total of 82 sites were sampled and at every tenth site, a field duplicate was collected, giving a total of 93 samples. Where practical, sampling was done on a 9 km² grid close to the smelter, and along three radial traverses, with a sample spacing of about 3 km. Samples were collected by helicopter or truck. Sites were not restricted to lake surfaces or type of location, except that sample locations were always at least 25 m from a road.

The snowpack in the 1998 survey incorporates about 129 days of atmospheric metal accumulation from November 5 to March 12. The mean snow depth was 81 cm, and the snow was typically dry and heterogeneous, and composed of two types of snow. Generally, the top section was made up of soft 'fluffy' snow whereas the bottom section was composed of hard granular snow crystals. A total of 183.7 mm of snow precipitation was reported at the Rouyn-Noranda airport weather station, with rare days of wet precipitation mixed with snow not accumulating more than 2 mm. The wind direction for these four winter months was dominantly to the south and southeast as demonstrated by the wind rose for that time period (Fig. 2).

The 2001 snow survey used a different radial sampling scheme designed to fill in some gaps in the 1998 coverage, and in particular to provide information about the area farther than 50 km from the smelter. A total of 57 sites were sampled, out to a distance of approximately 275 km from Rouyn-Noranda (Fig. 1). The samples were concentrated in

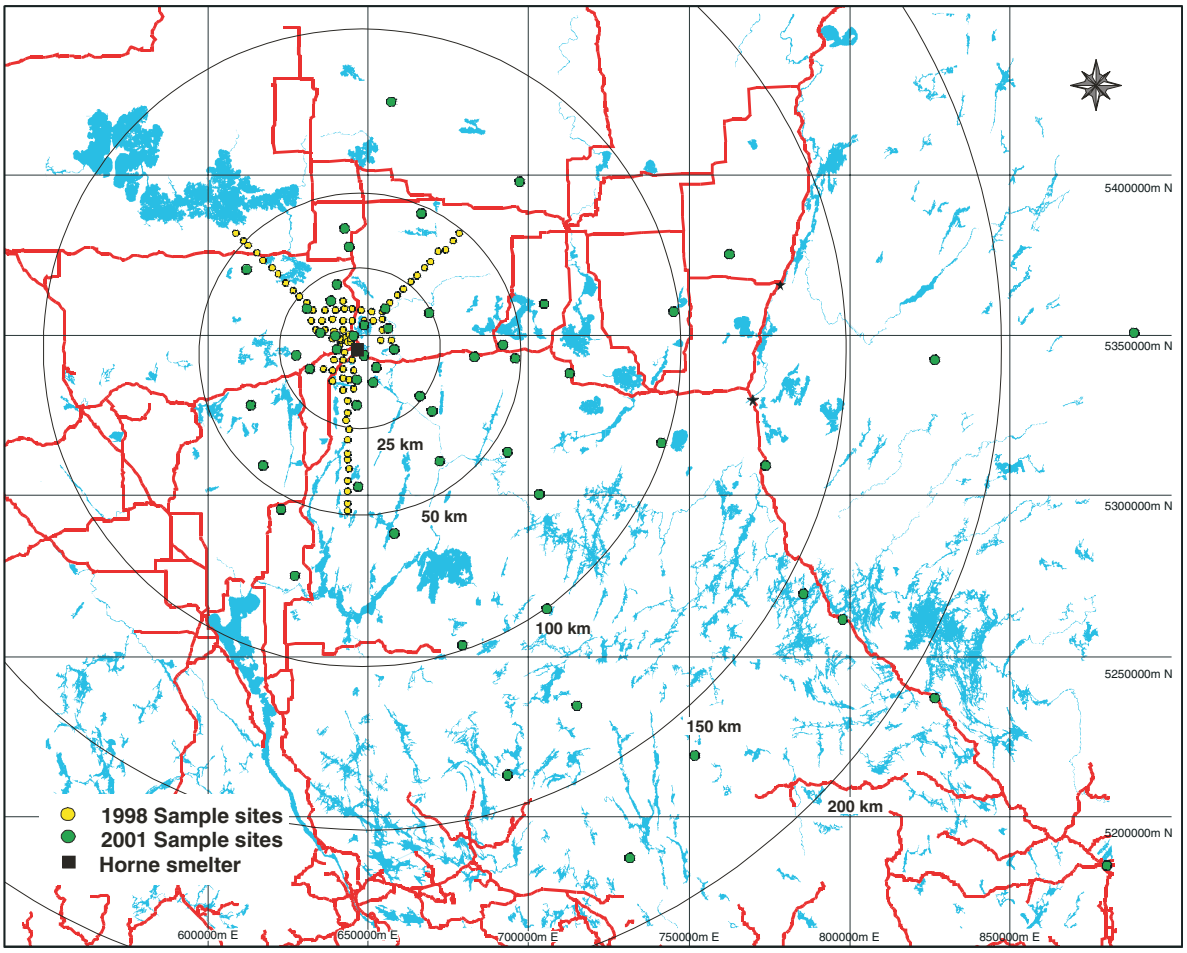


Figure 1. *Location map showing sample sites for 1998 and 2001 surveys. Note that the 1998 survey was restricted to a maximum distance of 50 km from the Horne smelter and concentrated on three radial traverses, whereas the 2001 survey extended to 275 km from the smelter and provided more coverage east and southeast of the smelter.*

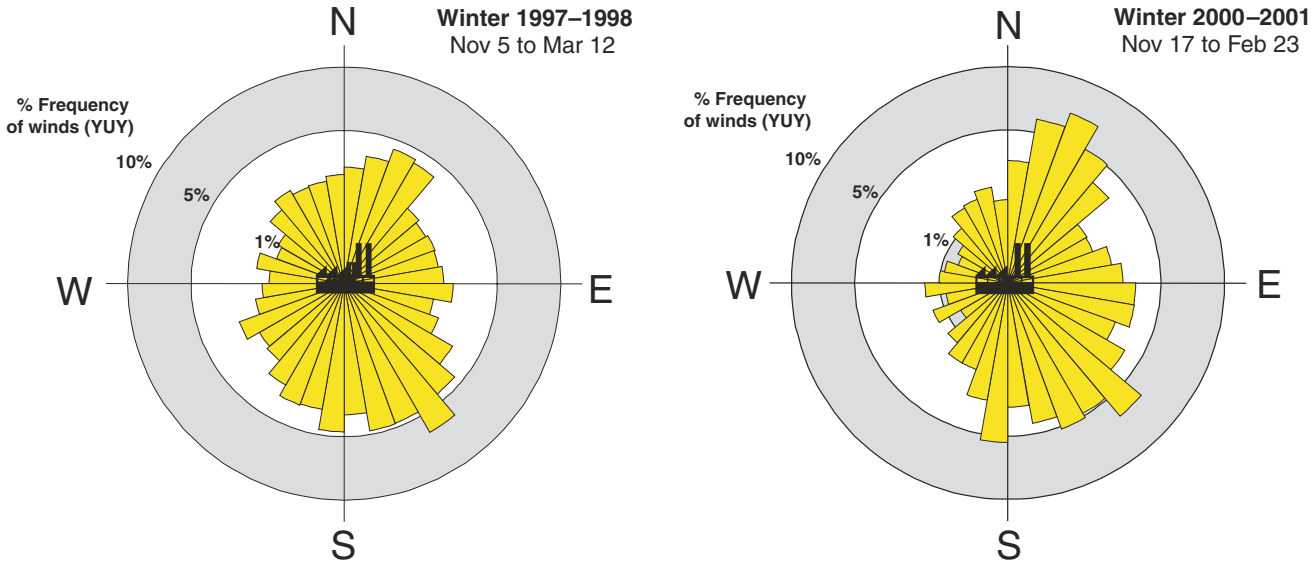


Figure 2. *Wind roses for winter 1997–1998 and 2000–2001. The length of each 10° sector shows the proportion of time that wind was blowing toward that direction. The roses were drawn using the program by Baas (2000). Data from Rouyn-Noranda airport (YUY).*

the southeast quadrant in the dominant wind direction for the winter months, as established from historical wind records. Most samples were collected by helicopter, using preselected sites on the surfaces of relatively small frozen lakes, thus eliminating contamination by soil and minimizing effects of ground vegetation. Any slush existing at the lake–snow interface was excluded. At most stations, samples were taken about 10 m from the landing point in undisturbed, relatively clean snow. At 11 of the 57 sites, a duplicate sample was taken, giving a total of 67 samples.

The 2001 snow was dry and light and visually homogenous. Pack depth varied from 19 to 96 cm, averaging 64 cm depth. A total of 142.5 mm of snow was reported at the Rouyn-Noranda airport. Snowpack samples represented three months (about 99 days) of snow accumulation. For this period (November 17 to February 23), temperatures remained at or below freezing with no melting events. Figure 2 illustrates that the dominant winds were from the northwest (37.8 %) and southwest (33.5%).

Sample handling and processing methods

Procedures for sampling snow are described in detail *in* Kliza et al. (2000, 2002). At each sample site, snow depth was measured with a plastic measuring stick. Samples were collected using an 8.26 cm outer diameter, clear Lexan (polycarbonate) tube approximately 1 m in length. The inner diameter of the tubes changed slightly between the two surveys (1998 = 8.9 cm, 2001 = 8.8 cm), and this difference was considered in computing deposition loading rate per unit area of ground. The snow tube was cleaned at each site by dipping it into the snowpack three times to remove any contaminating dust or moisture. The tube was then pressed through the snow to the ice of the frozen lake surface, forcing the snow up into the tube. For samples taken on a soil surface, the tube was stopped approximately 3 cm from the surface, the depth predetermined by a preliminary probe. A polycarbonate plate was used to plug the bottom of the core tube so as to ensure that no sample was lost during withdrawal. Each snow sample was put into a clear, 0.1 mm thick polyethylene bag measuring 30 cm by 46 cm. The plastic bag was then folded over, rolled, and sealed with white plastic electrical ties to make the bag airtight and prevent contamination during storage. Sample bags were packed around with snow in Styrofoam coolers for transport to the laboratory and then transferred to a freezer unit.

All processing was carried out in a 'Class 100' clean room at the Geological Survey of Canada in Ottawa. Samples were brought out to thaw approximately 24 h before the day of preparation. The outside of each sample bag was thoroughly washed with deionized water and checked for any punctures or cracks. Samples were weighed to determine the total mass of snow. Each sample bag was placed into another unused bag in order to contain the snow meltwater in case the sample bag leaked. To begin melting, samples were placed on a countertop until slushy (approximately 6 h). Partly melted samples were subsequently moved to a refrigerator to continue melting at temperatures of approximately 4°C for 12 h.

Sample preparation involved the separation of dissolved and suspended particulate matter using a vacuum filter apparatus. The 1998 samples were filtered through preweighed Durapore® membrane filters at the conventional boundary (0.45 µm) for dissolved material. The 2001 samples were filtered through stacked 0.45 and 0.1µm Durapore® membrane filters to ensure the collection of fine atmospheric dust, metals bound in colloids, metal organic complexes, inorganic complexes, and free inorganic ions. The membranes were stacked to prevent clogging of the 0.1 µm filter by straining off the coarse fraction first. The stacked membranes were dried and analyzed in combination, as the sample was too small to analyze the 0.1 to 0.45 µm fraction separately. The volume of filtrate was recorded to provide a measure of the amount of snow in the sample. The filtered meltwater was separated into aliquots. One aliquot was preserved by acidification with 0.4% HNO_3. The filter membranes were placed in a covered Petrie dish to dry, then weighed. Tables 1 and 2 summarize the list of elements, instrumentation, and detection limits.

The filtered meltwater contains the fraction of the deposited material that occurs in dissolved, rather than particulate, form, and therefore provides an estimate of the most readily available metals (potentially important for impact studies). However, the particulate fraction may also contain metals in a relatively available form (particularly in the 0.45 to 2 µm, for example), so the total loading values (combining the two fractions) may give a more reliable picture of metal deposition for use in impact studies. The total load provides an estimate of the total dry and wet deposition of material (including aerosol particles) accumulated since the first snowfall of the winter.

Table 1. List of elements analyzed in meltwater, showing analytical method and detection limit.

Symbol	Element	Method	Units	Detection limit
Ag	Silver	ICP-MS	ppb	0.05_1, 0.005_2
Al	Aluminium	ICP-MS	ppb	$2_{1,2}$
As	Arsenic	ICP-MS	ppb	$0.1_{1,2}$
Ca	Calcium	ICP-ES	ppm	$0.02_{1,2}$
Cd	Cadmium	ICP-MS	ppb	0.05_1, 0.02_2
Cr	Chromium	ICP-MS	ppb	$0.1_{1,2}$
Cu	Copper	ICP-MS	ppb	$0.1_{1,2}$
Fe	Iron	ICP-MS	ppb	$5_{1,2}$
Mg	Magnesium	ICP-ES	ppm	$0.005_{1,2}$
Mn	Manganese	ICP-MS	ppb	$0.1_{1,2}$
Na	Sodium	ICP-ES	ppb	$50_{1,2}$
Ni	Nickel	ICP-MS	ppb	$0.2_{1,2}$
Pb	Lead	ICP-MS	ppb	$0.01_{1,2}$
S	Sulphur	ICP-ES	ppm	0.15_1, 0.05_2
Sb	Antimony	ICP-MS	ppb	$0.01_{1,2}$
Zn	Zinc	ICP-MS	ppb	$0.5_{1,2}$

[1]1998 snow samples (<0.45 µm)
[2]2001 snow samples (<0.1 µm)

Table 2. List of elements analyzed in particulate fraction, showing analytical method and detection limit.

Symbol	Element	Method	Units	Detection limit
Ag	Silver	ICP-MS	ppb	0.001_1, 0.0001_2
Al	Aluminium	ICP-MS	ppb	0.04_1, 0.1_2
As	Arsenic	Hydride-ICP-MS$_1$, ICP-MS$_2$	ppb	0.004_1, 0.2_2
Ca	Calcium	ICP-ES	ppb	$0.4_{1,2}$
Cd	Cadmium	ICP-MS	ppb	0.001_1, 0.0004_2
Cr	Chromium	ICP-ES	ppb	$0.02_{1,2}$
Cu	Copper	ICP-MS	ppb	$0.002_{1,2}$
Fe	Iron	ICP-ES	ppb	$0.1_{1,2}$
Mg	Magnesium	ICP-ES	ppb	$0.1_{1,2}$
Mn	Manganese	ICP-MS	ppb	$0.002_{1,2}$
Na	Sodium	ICP-ES	ppb	$1_{1,2}$
Ni	Nickel	ICP-MS	ppb	$0.004_{1,2}$
Pb	Lead	ICP-MS	ppb	$0.0002_{1,2}$
S	Sulphur	ICP-ES	ppb	$1_{1,2}$
Sb	Antimony	ICP-MS	ppb	0.0002_1, 0.002_2
Zn	Zinc	ICP-MS	ppb	$0.01_{1,2}$

[1]1998 snow samples (> 0.45 µm)
[2]2001 snow samples (> 0.1 µm)

Laboratory methods

Table 1 lists the elements determined by inductively coupled plasma (ICP) emission and mass spectrometric methods on filtered meltwater, after preservation with 0.4% nitric acid. Detection limits for some elements differ a little between the two years. Table 2 lists the elements determined by the same methods, after dissolution of the filtered particulates with a hydrofluoric acid-aqua regia mix. Again, detection limits for some elements differ between survey years. Dissolved organic carbon values were determined for the filtered but unpreserved aliquots and pH was determined on unfiltered samples. These results are not shown here, but are available in Kliza et al. (2000, 2002).

Concentration data (ppb) were recalculated to total mass of metal deposited per unit area of ground per year (ng/cm²/a) using the sampling tube cross-section area and sample volume and annualized assuming that the deposition rate is constant over a year at each location. In this way, the two years can be compared even though the period of deposition represented by the samples, and the tube cross-sections, differ between years. Combined total-load data are given for each year (Table 3, 4), with a '% soluble' field following each element field to indicate the proportion of the total that is either less than 0.45 µm (1998) or less than 0.01 µm (2001).

RESULTS AND DISCUSSION

The results are summarized for four aspects of the work, as follows: 1) maps showing spatial patterns observed in the metal-loading data; 2) summary statistics from fitting models to the data for both years; 3) comparison of metal concentration values with those reported in the literature and their classification according to a published scheme; and 4) information on metal solubility and how this changes with distance from the smelter.

Spatial and multivariate patterns

Figure 3 shows a series of maps for the 1998 and 2001 surveys by element, with the sample locations superimposed. Spatial interpolation was carried out using an inverse-distance weighting method (an option in Vertical Mapper™; an add-on program to MapInfo® GIS; *see* Northwood Geoscience, 1999, p. 24–28), to convert the element values known at the sample locations to a continuous geochemical surface. These surfaces were then colour-coded using a colour ramp ranging from blue (low values) to red (high values), controlled by percentiles of deposition rate for each element, as shown in Figure 3. Thus, the 90th percentile is shown approximately by the transition from yellow to green and the 50th percentile is approximately at the blue–green transition. Although the interpolation error on these maps differs from place to place depending mainly on the local sample density, the maps give a graphical representation of the main spatial patterns present in the data. Dot plot maps (requiring no spatial interpolation) are also available *in* Kliza et al. (2000, 2002).

Although a radial bull's-eye pattern centred on Rouyn-Noranda is prominent for most elements (the top 10% of the data loading rates usually occur within 10 km of the smelter), some exceptions exist. For example, many elements have elevated rates about 40 km east of the smelter where a sample was taken close to the main east-west road (*see* for example, Zn values in the 2001 survey in Figure 3). This sample was taken close to a road and was almost certainly contaminated by road dust. The interpolation procedure produced a large 'high' on the geochemical surface simply because there were no other nearby samples to constrain the estimation procedure. Had interpolation been carried out by kriging, the kriging variance in this area would have indicated great uncertainty, because the interpolated values were affected by a single point only.

The effect of prevailing wind direction on these maps is not as great as might be expected. There is some suggestion on certain maps (Sb for example) of a southeastward elongation of the contours. However, this is uncertain and may be controlled at least in part by the uneven sampling distribution pattern

As described by Telmer et al. (2004), three spatial patterns describe the distribution of elements in snow around the Horne smelter. First, a strong to moderate smelter-centric pattern exists for some metals that normally occur in low concentrations in snow (e.g. Pb, Cu, As) and are known to be at significant levels in the smelter emissions. A second pattern presents little or no relationship to the smelter, but is governed more by other sources of variation such as weathering of rocks, dust, road dust, urban emissions, highway emissions, and others (e.g. Al, Mg). A third pattern represents a mixture of both factors. This inference is supported partly by single element patterns, but also by multi-element patterns derived by multivariate statistical analysis.

A principal-components analysis of 13 elements in the 2001 data (log transformed to stabilize the variance) shows that the first two principal components define two major factors (Fig. 4). Samples can be considered in terms of mixtures

Table 3. Summary of analytical results for 1998 samples, expressed as total (soluble + particulate) loading rate per year. % soluble column allows data to be broken down into soluble and particulate fractions.

Sample	Distance from smelter	Ag 1998		Al 1998		As 1998		Cd 1998		Cu 1998		Fe 1998		Mg 1998		Mn 1998		Ni 1998		Pb 1998		S 1998		Sb 1998		Zn 1998	
Units	km	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble
RN98-08	1.1	252.20	0.4	31665	2.3	5084	26.6	211.6	74.0	84494	58.9	69173	0.5	7053	25.4	625	34.0	958.1	34.3	18011	54.5	63017	55.6	896.3	11.3	20172	34.0
RN98-09	1.4	130.32	0.8	8699	2.1	1972	22.4	38.9	56.7	22998	38.8	26242	0.4	1734	24.6	199	31.1	411.7	16.5	8992	45.8	10213	32.4	385.5	10.9	5081	27.1
RN98-03	1.8	42.96	11.2	4447	4.2	2697	71.1	52.2	78.5	22243	64.9	10666	2.2	1007	37.9	90	48.1	209.3	26.5	9940	76.6	7494	44.2	188.6	36.8	4045	56.7
RN98-10	2.3	107.36	9.6	6870	7.4	4335	43.2	131.1	75.4	34625	61.6	29578	0.9	2228	36.0	167	36.6	558.9	22.4	27745	63.3	30596	76.1	1329.4	16.6	11519	52.4
RN98-02	2.3	60.73	10.3	8114	4.9	2229	41.1	75.4	67.6	22437	67.3	18043	0.6	2145	36.0	153	45.7	233.3	29.0	21917	76.1	21726	58.0	498.3	18.3	8381	39.5
RN98-07	2.4	76.33	10.5	3229	3.8	1277	51.8	31.7	70.9	17425	72.1	7469	3.2	891	29.8	67	42.2	167.5	30.4	7345	61.4	8228	70.5	224.9	15.9	2702	55.5
RN98-01	2.4	55.48	15.5	4900	3.8	974	49.1	32.1	74.7	9454	72.0	7411	4.1	1065	29.0	85	55.9	135.4	23.1	9670	70.9	5138	64.5	275.7	17.1	2462	53.6
RN98-05	2.5	60.31	12.9	4767	5.1	1693	60.0	34.8	69.2	11845	69.7	9858	2.7	1356	31.6	104	43.7	193.7	28.4	8660	68.3	7106	65.7	299.7	19.9	3646	54.8
RN98-04	2.8	53.14	34.3	3492	8.4	1786	75.4	48.7	86.8	14994	86.0	4737	6.2	988	53.1	77	68.0	132.4	45.3	11270	79.8	17769	92.5	188.6	34.0	3240	79.5
RN98-35	3.0	32.69	24.6	2932	5.9	1042	79.4	26.8	84.7	8423	77.4	4403	15.9	736	46.1	61	64.1	83.9	36.3	5366	75.3	15459	92.0	139.2	27.0	1712	69.6
RN98-34	3.5	82.70	10.6	3741	4.7	2800	59.1	59.1	77.6	12095	69.6	9282	2.0	1063	40.4	100	54.7	178.7	26.3	19083	59.2	19119	88.1	611.5	19.1	4737	66.3
RN98-82	4.6	82.45	7.3	4222	5.5	1884	62.6	70.2	78.1	10720	63.4	8415	5.6	1140	32.7	82	51.5	147.4	30.0	14946	68.9	19036	87.7	412.6	21.8	4084	67.3
RN98-79	4.7	35.89	21.5	4265	4.0	936	58.5	37.7	80.1	6852	74.8	5522	5.0	968	30.0	74	59.1	81.9	28.6	7759	70.4	10287	88.4	167.2	23.3	2288	64.1
RN98-06	4.9	39.03	27.7	6505	3.9	1155	55.9	25.1	64.7	7486	77.2	7593	1.5	1773	21.9	128	45.8	98.9	32.9	6112	69.4	9064	82.3	172.1	21.5	2409	53.9
RN98-36	5.0	21.68	34.9	2706	6.1	730	78.2	23.9	88.7	4279	80.8	2705	4.1	611	49.4	53	70.4	47.1	41.1	4836	79.8	10637	93.2	95.3	30.3	1392	76.7
RN98-33	6.1	8.64	22.2	2167	4.6	383	79.5	13.4	86.8	2030	70.3	2010	11.1	789	65.7	168	87.3	25.6	46.1	1871	72.5	8337	90.8	37.5	34.2	712	71.0
RN98-78	6.2	22.52	13.2	3019	5.8	601	72.9	22.1	81.7	3474	76.4	3764	10.3	1134	64.6	93	78.1	57.4	26.9	4083	71.1	11604	93.5	138.4	25.5	1438	67.8
RN98-80	7.5	22.66	15.2	4073	3.8	534	75.1	28.6	86.6	3935	73.5	4167	10.4	1203	51.9	152	78.4	57.6	28.9	4691	79.2	9029	90.9	99.0	32.3	1303	69.9
RN98-52	7.5	20.86	23.3	3501	3.8	510	63.1	28.7	87.7	3404	68.1	4714	3.9	845	38.1	65	59.4	62.8	25.5	5723	77.4	13813	89.2	150.1	20.7	1663	65.9
RN98-27	7.6	22.46	27.0	3791	5.1	788	77.4	24.0	83.4	5027	80.4	4449	14.4	1209	54.0	162	80.8	42.2	10.4	4776	74.2	15603	93.0	146.8	28.4	1626	63.7
RN98-81	7.7	32.09	14.3	3687	4.9	1063	75.2	52.3	85.9	5010	69.1	4744	8.4	875	45.8	71	58.0	82.8	30.6	6937	74.9	15730	91.9	192.0	28.9	2227	69.4
RN98-32	8.3	6.29	17.6	2624	6.1	240	83.2	14.8	82.1	1549	68.8	2051	11.1	4021	88.8	602	84.8	46.1	60.2	1545	55.5	17811	95.6	32.0	37.8	659	76.2
RN98-77	8.7	6.30	17.5	3372	3.8	206	80.6	14.9	90.0	1272	73.0	2389	4.6	877	47.7	66	68.7	29.3	34.5	1805	70.0	17013	96.7	33.9	36.3	712	77.4
RN98-53	9.0	18.33	6.0	8877	3.5	419	60.2	30.6	54.2	2136	60.9	16297	2.4	2495	41.8	390	78.9	39.9	26.2	3321	72.6	24404	53.4	95.9	27.1	3908	18.2
RN98-28	9.2	6.18	17.9	3078	4.9	250	78.4	10.0	85.2	998	69.3	2397	10.8	752	48.4	67	71.4	19.9	22.1	1159	70.8	13876	95.0	29.5	36.1	479	68.2
RN98-57	9.8	5.47	20.2	2121	4.9	218	76.3	10.6	88.7	1263	79.4	1951	8.8	517	46.4	43	68.5	22.4	35.2	2033	84.8	13717	95.6	36.6	37.0	629	70.0
RN98-76	10.3	6.38	17.3	4143	4.2	143	75.7	7.8	80.4	994	74.2	3059	15.1	905	34.2	72	59.3	27.0	30.3	1060	71.5	6610	93.4	30.3	32.3	476	66.3
RN98-74	10.3	13.95	25.0	2663	6.5	405	79.0	19.2	90.4	2468	77.7	2680	15.1	1091	69.6	286	93.9	39.1	36.3	3444	76.7	12879	95.6	61.0	43.6	1043	78.4
RN98-54	10.4	5.95	18.6	2871	3.1	159	70.6	9.4	67.9	877	68.1	2216	5.0	624	37.2	59	70.0	17.9	24.6	1218	65.7	11808	93.3	27.2	33.4	468	59.1
RN98-73	10.5	13.01	8.5	3220	4.7	477	80.2	30.3	83.9	2279	64.3	3043	9.9	5026	88.4	571	92.9	42.8	34.4	3596	59.1	21139	95.2	88.8	41.7	1285	71.5
RN98-56	10.8	6.17	17.9	2664	3.6	172	76.6	13.8	83.5	628	69.5	1997	8.6	1050	63.6	56	68.6	18.3	43.2	1271	66.8	13162	95.1	24.6	41.4	477	68.2
RN98-25	10.9	10.05	23.9	2450	6.3	395	78.4	18.7	80.2	2266	80.9	2510	17.1	743	54.1	85	81.0	32.6	44.8	2869	81.0	10153	94.6	51.9	37.4	937	70.5
RN98-31	11.0	3.48	31.8	5251	4.5	168	83.7	10.5	77.4	778	75.4	3088	8.5	1126	33.8	95	60.3	30.9	50.7	1129	78.7	14252	96.6	23.2	38.3	692	59.6
RN98-29	11.1	4.34	25.5	2136	5.3	147	80.9	6.7	83.4	989	58.9	1769	11.1	700	64.8	107	87.6	15.6	28.2	798	75.2	11890	94.2	17.8	42.7	467	66.0
RN98-51	11.3	6.32	41.4	1884	7.0	198	77.7	29.5	95.7	1236	80.9	1646	16.1	536	56.5	53	79.1	27.3	33.3	2249	86.1	13457	96.9	28.9	42.9	754	83.4
RN98-24	11.3	7.74	14.3	2307	5.8	381	83.2	9.4	86.8	1707	73.4	2426	13.3	770	58.8	96	82.1	33.1	32.0	1907	76.9	11059	94.9	42.7	43.1	737	72.0
RN98-50	11.3	10.57	26.2	3519	5.5	321	70.1	21.8	84.8	1459	75.6	4479	7.2	764	35.6	67	69.8	27.0	35.0	3470	83.4	15382	86.4	65.8	28.3	1419	57.1
RN98-75	11.6	6.94	15.9	3154	5.0	230	82.8	18.0	90.6	1520	76.1	2418	13.7	2183	81.0	131	86.3	33.7	40.4	2304	76.0	17787	97.1	39.7	52.1	886	82.5
RN98-49	12.6	6.77	16.3	2293	5.2	270	71.4	11.3	78.8	1009	71.7	2852	9.4	780	64.5	116	86.4	18.8	23.5	1548	76.4	10183	86.5	46.8	36.6	733	49.9
RN98-55	12.7	4.23	26.1	2028	4.1	154	75.4	7.5	84.0	594	74.9	1449	7.6	449	45.1	43	73.0	13.7	32.2	1061	73.5	3769	87.9	26.1	38.3	346	67.9
RN98-23	12.9	2.94	37.6	2290	5.9	103	72.3	3.7	86.6	392	69.1	1645	6.7	1750	80.8	79	82.3	19.3	22.9	473	78.5	3619	91.5	14.9	37.8	243	75.2
RN98-58	13.2	3.91	28.3	1982	5.2	121	74.0	6.2	84.1	544	68.3	1817	6.1	483	51.5	55	79.0	15.7	28.1	932	76.1	10294	94.4	20.8	34.7	354	68.0
RN98-30	13.2	2.88	38.5	2356	6.1	105	84.6	5.8	83.9	583	75.8	1483	7.5	562	48.9	53	74.2	14.4	30.6	563	74.4	15254	97.1	11.5	42.1	283	69.5
RN98-72	13.3	9.02	24.4	2398	4.7	240	77.7	15.7	75.1	1344	68.4	2207	13.5	542	44.7	47	69.1	29.2	30.6	2406	76.3	9352	94.6	43.9	38.1	672	70.1
RN98-26	13.3	3.05	36.2	1333	3.3	50	70.0	3.0	79.8	314	64.0	1086	9.4	292	40.4	34	76.7	10.9	40.4	296	62.9	3584	92.5	9.1	21.3	129	54.5
RN98-71	13.7	8.01	21.6	3890	3.8	226	73.8	13.7	81.0	1187	66.7	2611	8.7	763	36.6	67	63.7	30.2	35.6	1569	70.2	10491	95.4	32.4	37.5	510	72.7
RN98-48	14.3	3.20	34.6	2020	4.4	118	79.1	6.6	86.5	425	71.8	1562	7.1	519	49.3	37	67.5	12.2	36.1	679	71.9	8912	94.4	20.3	36.4	315	67.4
RN98-22	15.0	2.63	42.0	1501	6.3	66	77.9	3.7	80.4	501	58.2	1326	18.6	376	48.8	37	77.8	12.7	34.8	351	82.5	7689	95.8	9.7	43.9	225	67.5
RN98-70	16.8	5.83	19.0	2341	4.7	170	83.6	17.0	84.1	693	60.2	1838	13.4	2035	84.9	1644	97.0	19.3	22.9	1030	61.1	9601	94.9	25.5	55.3	447	76.2
RN98-21	17.8	2.42	45.8	1695	7.5	51	76.6	3.1	79.5	437	58.5	1325	17.0	456	55.4	55	82.1	10.5	42.1	269	80.6	10014	96.4	8.3	46.0	229	72.8
RN98-47	17.9	2.79	39.7	2152	2.0	70	75.2	3.6	75.7	301	64.7	1564	7.1	435	25.5	42	68.5	11.5	38.2	429	64.6	10539	96.2	14.1	37.3	185	61.0
RN98-69	20.5	4.17	26.5	2322	1.9	82	73.6	5.2	67.1	319	39.3	1506	7.3	381	29.0	22	41.7	17.0	40.5	432	52.1	4451	92.7	11.5	35.8	173	54.4
RN98-20	20.8	2.17	51.0	1815	5.8	34	74.9	3.8	86.7	287	50.8	1401	17.0	417	45.1	46	76.4	11.0	40.1	176	75.6	5604	94.5	4.5	40.5	165	69.0
RN98-46	21.1	2.75	40.2	2250	5.5	63	83.0	9.0	92.4	250	69.6	1369	8.1	862	65.4	500	96.1	10.8	40.7	379	67.5	14103	98.1	11.5	41.7	253	79.8
RN98-68	22.4	5.09	21.7	2855	4.5	150	84.6	7.1	81.5	557	57.3	1893	12.9	2326	84.4	3053	96.0	21.1	21.0	1068	60.1	18108	96.3	21.7	61.3	400	75.1

Table 3. (cont.)

Sample	Distance from smelter	Ag 1998		Al 1998		As 1998		Cd 1998		Cu 1998		Fe 1998		Mg 1998		Mn 1998		Ni 1998		Pb 1998		S 1998		Sb 1998		Zn 1998	
Units	km	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble	ng/cm²/a	% soluble
RN98-19	23.3	1.85	59.8	1493	6.8	28	75.5	2.6	84.6	226	51.2	1089	17.3	421	56.1	48	82.3	12.6	34.9	132	76.2	8903	97.1	4.0	44.2	188	75.2
RN98-45	23.6	4.37	25.3	2127	4.5	46	75.3	3.5	83.1	166	52.6	1256	8.8	2886	84.3	942	92.5	11.9	37.1	256	58.2	14916	96.8	9.3	27.5	151	65.6
RN98-67	25.5	3.13	35.3	2407	3.2	54	78.5	3.7	70.7	289	54.3	1566	11.2	616	53.2	108	86.2	18.7	23.6	419	64.0	11079	97.2	9.4	50.7	175	62.5
RN98-18	26.6	2.25	49.2	1849	5.7	22	80.1	7.0	74.8	102	50.5	1106	17.5	1521	84.6	149	93.0	21.5	71.8	80	68.9	3609	91.8	3.5	56.7	123	79.3
RN98-44	26.8	1.85	59.8	2056	4.5	32	75.8	4.4	75.2	159	64.2	1368	8.1	567	41.6	63	77.5	9.8	45.2	195	71.7	11337	97.2	5.0	49.9	115	77.9
RN98-66	28.4	2.88	38.4	3232	3.9	130	90.7	8.8	87.8	270	59.4	3025	43.3	709	48.6	121	84.5	20.9	51.7	466	70.9	15154	97.8	10.0	61.9	251	74.6
RN98-43	29.6	1.72	64.4	2009	4.8	39	76.8	2.7	83.3	140	62.4	1263	8.8	540	52.8	57	79.2	10.4	42.3	181	63.0	12284	96.9	5.9	48.6	128	80.1
RN98-17	30.0	1.40	79.0	1431	4.7	12	71.0	1.7	75.0	73	54.1	843	13.1	554	69.3	27	74.3	9.2	47.8	49	61.2	3504	94.6	1.5	54.9	68	67.4
RN98-65	32.5	2.33	47.4	3113	3.9	103	92.7	6.4	82.3	196	60.4	2828	44.2	660	44.9	71	72.9	19.8	49.8	305	66.5	9594	96.9	6.7	62.5	321	87.3
RN98-42	32.6	1.73	64.0	2543	3.3	44	80.7	2.7	86.0	101	55.9	1450	7.6	397	27.9	50	71.7	11.1	39.7	167	67.5	15339	98.0	5.0	42.6	107	76.8
RN98-16	32.9	1.41	78.5	1757	2.5	12	75.2	1.3	83.2	65	41.7	1051	10.5	697	72.0	68	84.7	9.4	46.7	51	62.0	3548	93.4	1.3	55.5	63	70.1
RN98-64	34.5	2.42	45.7	3374	4.9	60	84.8	6.0	83.3	201	60.9	1882	5.9	1115	64.7	366	88.7	16.2	27.3	373	61.4	12421	95.3	9.0	66.0	216	76.0
RN98-41	35.4	2.43	45.6	2431	5.9	64	71.1	3.5	75.9	136	52.4	1602	6.9	865	60.7	719	93.3	15.8	28.0	299	58.5	13928	96.8	7.6	43.5	164	73.1
RN98-15	36.4	1.35	82.2	1439	6.6	18	48.6	1.5	74.9	80	59.0	986	23.1	350	53.4	31	79.3	11.1	39.9	76	83.3	3496	94.8	1.3	46.8	95	79.9
RN98-63	37.2	1.99	55.6	2826	3.3	36	82.6	3.7	74.1	136	63.3	1565	7.1	537	44.7	68	79.2	14.2	31.0	252	72.7	12233	97.6	5.1	64.8	142	75.6
RN98-14	39.0	1.35	81.9	1952	4.6	16	81.3	2.8	80.5	62	56.9	1208	9.2	492	47.9	42	76.2	11.9	37.0	71	74.2	3582	92.5	1.6	59.8	114	83.4
RN98-40	39.1	1.50	73.6	1907	4.9	37	87.1	3.3	33.1	58	52.1	1208	9.2	486	47.9	57	79.7	9.1	48.7	102	70.6	11717	97.8	2.6	51.9	95	81.4
RN98-39	40.9	1.63	67.9	1664	7.3	40	87.4	4.1	86.8	76	69.2	1071	10.3	596	63.5	106	90.2	9.0	49.2	143	80.6	19822	98.5	3.8	62.2	129	86.8
RN98-62	40.9	1.78	62.0	2407	4.4	38	86.2	3.0	67.9	123	64.3	1143	9.7	430	51.5	46	77.4	12.2	36.3	200	80.9	13544	98.5	4.3	61.9	116	76.2
RN98-13	42.7	1.31	84.2	1636	6.0	13	81.7	2.4	87.6	48	57.9	1067	19.7	658	69.9	273	95.8	11.8	37.5	60	74.5	7233	96.5	1.4	61.1	119	87.0
RN98-61	43.7	2.10	52.6	3781	10.7	39	80.9	5.6	86.0	127	64.6	1819	6.1	671	44.3	70	75.0	15.6	28.4	232	74.9	15327	98.4	5.5	60.6	169	81.0
RN98-38	44.5	1.43	77.4	2285	5.6	30	83.2	3.0	87.8	80	71.8	1177	9.4	496	49.9	53	80.0	10.2	43.2	140	77.9	16471	98.5	3.6	56.3	100	85.6
RN98-12	44.5	1.40	78.9	1825	7.5	15	79.6	7.9	34.3	71	68.6	1300	24.4	518	58.2	103	90.4	13.2	33.4	81	82.4	3558	93.1	1.9	58.3	107	86.7
RN98-60	47.6	1.68	65.9	3558	3.0	36	84.2	4.0	76.8	93	63.2	1765	6.3	1128	65.3	250	90.5	13.0	33.9	182	72.5	13233	98.1	4.8	66.3	111	80.9
RN98-37	47.6	1.31	84.6	1605	5.2	17	84.4	1.5	73.8	42	60.1	911	12.1	650	73.0	109	91.7	7.9	55.9	72	86.5	7805	96.5	1.8	63.4	95	86.6
RN98-11	47.8	1.34	82.8	1509	10.2	10	75.0	1.5	75.8	71	68.6	1017	23.2	4357	94.6	149	93.2	11.5	38.5	86	89.3	3598	92.1	2.1	62.5	87	82.4
RN98-59	50.0	1.67	66.1	3218	3.3	32	80.2	4.6	91.2	103	47.6	1977	13.4	1227	67.8	967	96.2	10.4	42.5	158	66.3	10874	97.1	4.2	47.9	150	72.3

of two end members — a smelter end member and a geological end member. The elements lie along a general trend between these two extremes, as shown on a plot of PC-1 versus PC-2 (Fig. 4). For example, As, Sb, Cu, Ag, Pb, and Cd lie close to the smelter end member, whereas Al, Mg, Mn, and Fe are associated with the geological end member. Sulphur, zinc, and nickel lie somewhere between these two groups, with some influence from both factors. Sulphur appears to lie off the main trend, possibly indicating a somewhat different chemical behaviour. This interpretation is similar to the one made by Telmer et al. (2004) on the basis of the 1998 snow survey and confirms that the 2001 data behave comparably to the 1998 data.

Summary statistics

Because of the strong radial pattern in the element maps, two-dimensional plots of each element versus distance from the smelter provide good summaries of the spatial distributions and models fitted to the data values give useful summary statistics about key parameters that help to characterize the distance of transport of emissions from the smelter. For example, the plot for copper (Fig. 5a) shows that Cu values decrease rapidly by three orders of magnitude within a distance of about 40 km from the smelter. Note that the 1998 and 2001 surveys show good agreement where they both overlap (within 50 km from the smelter), but the 2001 values taken beyond 50 km indicate that deposition rates continue to decrease and therefore the ambient background levels from the 1998 data are somewhat biased upward.

Background values shown on the plot and 'distance to background' values are derived from a model fitted by nonlinear least squares to the data (Bonham-Carter and McMartin, 1997; Bonham-Carter and Kettles, 2001). The model satisfies the relationship

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

where y is the natural logarithm of the metal deposition rate (µg/cm²/a; please note that Tables 3 and 4 and Figure 3 show metal loading rates in ng/cm²/a, whereas the modelling and statistical results are reported in µg/cm²/a), x is the distance from smelter (km), β_0 is the natural log of the deposition rate at an infinite distance from the smelter, $(\beta_0 + \beta_1)$ is the natural log deposition rate very close to the smelter (at x = 0), λ is the 'half distance' at which the natural log deposition rate has dropped to $(\beta_0 + \beta_1)/2$, and ε is an error term. By fitting this model to the data, estimates of the three parameters and their standard errors can be obtained. The estimated metal concentration, $\hat{c}$, is then

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

The ambient background deposition rate toward which the model tends with increasing distance from the smelter is $\exp(\beta_0)$ µg/cm²/a. The distance to background can be arbitrarily defined as the distance (x_1) km at which the modelled value reaches the background value plus one standard error of

Table 4. Summary of analytical resluts for 2001 samples, expressed as total (soluble + particulate) loading rate per year.

Sample	Distance from smelter	Ag 2001		Al 2001		As 2001		Cd 2001		Cu 2001		Fe 2001		Mg 2001		Mn 2001		Ni 2001		Pb 2001		S 2001		Sb 2001		Zn 2001	
Units	km	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble	ng/cm^2/a	% soluble
RN01-49	2.0	113.49	1.7	12029	6.4	3044	35.1	175.9	90.6	37139	43.8	80181	0.9	4887	27.5	423	33.5	507.0	23.9	10298	42.3	29634	60.8	1462.1	8.6	14704	19.0
RN01-29	4.2	29.08	19.6	3917	13.8	855	75.1	40.5	78.5	9291	76.0	11756	5.1	1177	40.9	94	56.0	87.8	31.8	2163	67.0	13285	83.1	206.6	16.0	3407	19.0
RN01-30	4.3	7.00	3.7	2851	14.3	298	78.2	17.5	93.8	2289	78.1	2122	13.0	2400	82.9	204	93.2	18.3	45.3	672	75.0	7113	94.2	37.5	27.0	311	68.8
RN01-50	6.4	30.66	14.9	56648	3.4	632	44.3	51.3	85.8	10562	63.4	56614	3.0	11993	13.6	1192	45.1	179.7	37.0	2274	60.8	29419	66.1	224.7	15.6	4152	41.2
RN01-47	6.5	24.91	2.7	2620	4.7	428	69.5	34.7	71.8	7334	42.3	7100	10.3	11144	94.8	1566	96.7	43.3	42.0	954	27.7	17514	89.3	76.7	23.3	1040	34.4
RN01-48	8.8	5.76	2.9	3273	11.9	145	90.3	32.0	94.8	2104	73.8	2887	16.2	2207	78.6	197	89.8	26.6	25.2	499	67.3	12612	95.5	26.7	36.2	375	62.0
RN01-46	11.6	10.90	38.4	2184	22.9	238	84.7	18.8	95.3	3817	79.1	2558	16.7	805	67.5	80	87.0	44.2	37.4	648	79.2	10976	95.2	39.5	30.8	485	51.9
RN01-44	11.8	12.88	35.9	2258	23.6	420	80.8	32.7	95.2	4006	78.4	4566	9.1	708	51.3	47	65.3	43.4	41.3	1114	75.4	9923	93.6	80.2	22.9	850	35.9
RN01-41	12.3	7.88	2.2	181945	0.04	174	26.4	15.9	23.6	1680	16.7	321120	0.1	27130	1.7	2708	0.7	262.7	2.6	912	10.2	13621	72.8	37.9	7.1	2257	2.4
RN01-38	13.3	0.50	25.1	1934	15.7	26	80.8	5.9	94.9	203	75.1	1129	11.2	2019	86.4	74	83.1	13.0	38.9	119	86.0	11129	97.6	3.8	55.6	374	91.2
RN01-41a	14.0	2.58	6.1	2605	2.4	21	36.4	17.4	96.4	327	28.1	2245	25.4	3516	89.0	605	96.9	42.5	75.8	68	12.7	26773	98.3	13.1	32.2	4112	98.2
RN01-45	14.4	9.25	15.9	2643	15.9	292	83.3	20.0	91.3	3483	70.4	4759	8.8	1061	63.7	163	75.2	39.5	45.0	796	65.3	11083	89.8	79.1	27.6	899	33.0
RN01-27	14.4	0.24	42.5	2065	16.6	10	58.3	4.5	93.8	66	74.6	1318	28.2	658	60.2	39	79.6	19.9	43.5	32	75.5	5630	96.0	1.7	48.4	62	74.8
RN01-40	14.9	0.95	14.7	2102	37.2	42	64.0	5.9	93.5	394	77.9	1011	13.8	1501	87.0	284	96.8	11.2	49.9	76	78.9	11769	97.2	4.0	37.3	133	62.6
RN01-39	16.0	0.81	44.6	2778	15.1	49	86.8	5.5	92.7	191	76.1	1416	11.4	773	58.3	63	77.2	16.7	38.6	103	81.4	12129	97.7	4.3	51.0	116	78.9
RN01-28	16.2	0.58	15.1	1652	8.7	9	66.7	1.7	87.8	94	57.4	1119	3.4	357	37.4	25	64.2	13.1	11.5	30	53.1	3035	88.1	2.5	18.1	59	45.9
RN01-37	17.0	0.84	16.6	2422	19.6	22	75.0	3.2	88.5	275	70.9	1986	36.5	2717	88.3	277	95.0	14.6	38.3	74	65.8	10305	97.0	5.0	32.4	126	64.5
RN01-43	19.6	3.94	20.6	3005	17.6	154	81.9	18.7	96.1	1255	71.1	2507	12.5	672	49.9	49	74.4	36.2	43.4	349	75.7	10522	96.2	26.1	29.1	326	50.1
RN01-31	25.5	1.17	31.1	2440	13.5	43	83.9	3.7	86.8	230	71.3	1399	12.5	754	59.5	56	79.0	17.8	39.3	81	72.1	10741	96.7	5.4	44.0	174	55.1
RN01-42	27.0	1.19	28.9	1957	17.9	36	83.9	7.2	95.3	269	67.3	1362	21.0	359	39.9	33	76.0	15.3	37.4	93	70.5	8251	95.8	7.2	29.5	162	65.9
RN01-36	28.2	0.56	25.4	1939	11.8	21	73.0	2.4	91.5	169	73.0	1094	13.1	583	57.1	53	81.1	13.4	42.9	61	75.7	7414	96.0	3.0	42.2	96	70.2
RN01-22	32.8	0.63	25.0	1773	17.5	25	74.4	7.6	67.3	78	65.5	1404	36.0	795	69.2	47	80.0	36.6	58.7	54	79.0	8460	96.3	2.5	45.4	124	70.1
RN01-35	33.9	0.54	49.6	1368	20.9	25	56.0	2.9	95.7	113	70.4	732	16.8	515	70.7	44	85.4	12.3	39.9	53	82.8	8263	97.0	3.0	59.2	90	79.4
RN01-26	35.1	0.66	39.3	2757	10.7	19	80.8	6.6	93.1	114	64.1	1929	13.2	678	43.5	53	76.3	19.5	18.6	86	59.1	6432	93.9	8.7	17.5	154	51.7
RN01-21	38.2	1.03	44.2	2194	27.4	30	83.9	5.7	96.6	268	82.0	1559	24.7	624	63.9	43	79.6	22.3	47.5	110	72.0	11194	97.9	6.9	26.6	183	67.7
RN01-34	44.0	1.13	15.4	2851	21.7	59	88.2	10.6	69.2	294	76.2	2215	31.4	1221	71.7	83	83.6	21.9	31.7	133	81.6	13751	97.1	7.8	32.0	197	73.5
RN01-23	44.2	0.33	28.9	1801	15.9	23	83.3	4.1	96.5	99	65.3	1097	8.7	506	58.9	38	78.4	13.1	29.2	61	63.8	7213	96.9	6.4	20.8	112	56.9
RN01-20	45.3	0.17	46.9	1001	33.5	10	68.7	15.2	99.2	51	86.1	550	35.5	476	78.7	47	93.2	14.6	55.8	28	90.3	6575	98.6	1.3	79.6	101	91.7
RN01-25	45.5	0.47	54.1	2683	11.2	12	64.3	3.7	93.5	51	71.7	1327	7.9	543	44.7	38	75.4	19.4	45.2	29	76.9	7033	97.0	1.3	47.9	67	82.4
RN01-51	46.6	10.48	1.6	49675	4.4	37	21.0	60.2	19.1	1668	25.5	45027	4.5	12330	21.3	967	45.2	166.7	34.3	2098	52.7	31592	63.8	16.7	15.6	18493	8.8
RN01-10	50.3	0.18	30.8	1143	39.7	13	83.6	1.4	90.7	29	67.9	402	13.6	245	58.7	23	82.1	5.8	37.4	21	72.5	3853	94.6	1.0	47.5	64	57.5
RN01-24	54.5	0.21	39.6	1954	19.4	5	33.3	3.5	94.9	53	64.2	1095	20.8	1171	79.6	115	90.8	22.6	47.6	20	70.0	7871	96.9	1.4	37.9	78	81.9
RN01-09	58.3	0.43	27.1	2410	27.2	18	74.4	4.7	95.7	108	60.0	1201	9.8	701	64.6	41	75.9	20.4	46.1	44	76.2	8691	94.8	3.3	42.8	142	76.8
RN01-11	59.5	0.31	28.0	1674	17.0	17	78.7	4.3	94.5	55	65.0	807	10.9	464	53.1	34	74.6	9.0	39.3	23	68.1	4583	93.7	1.1	50.5	95	70.7
RN01-19	59.6	0.41	30.3	2889	12.9	12	60.0	5.3	94.6	81	55.7	1634	15.3	876	55.2	91	84.4	48.7	10.2	37	65.2	6499	95.1	2.3	43.5	106	72.0
RN01-52	67.2	1.73	24.8	8634	7.5	17	75.6	12.4	61.3	479	36.2	7238	7.6	3264	21.6	198	60.1	39.9	33.1	255	56.4	9928	91.3	5.0	25.7	2074	14.9
RN01-32	70.0	0.38	30.3	1929	14.6	61	92.4	4.0	93.7	102	66.8	1128	10.2	594	56.0	39	72.6	11.3	40.7	42	63.1	6675	96.3	3.9	35.7	111	64.7
RN01-18	72.5	0.20	36.8	1828	25.5	8	63.0	4.2	93.6	40	66.6	867	20.7	547	65.0	40	82.9	20.4	30.7	23	82.2	8650	97.5	1.0	82.6	57	81.3
RN01-33	73.2	0.40	34.6	1765	16.5	17	66.7	3.8	96.8	64	67.0	935	14.7	667	68.5	55	82.7	11.6	47.7	29	73.7	7719	97.1	1.7	45.0	77	78.3
RN01-08	73.6	0.38	35.2	33006	3.8	12	56.5	8.2	97.4	51	68.7	14573	0.9	5238	7.9	307	11.3	37.8	14.1	43	59.1	8048	94.8	4.6	21.1	136	70.8
RN01-17	94.7	0.27	47.0	7697	9.9	11	52.4	4.9	96.3	77	70.0	7680	19.4	2359	30.7	121	52.3	20.3	25.2	77	57.9	14373	97.1	1.8	69.8	207	90.5
RN01-12	97.7	0.25	38.8	1985	24.2	10	61.5	9.2	97.6	65	69.6	875	11.0	509	58.0	34	72.8	20.5	61.7	31	80.1	8739	96.6	2.5	55.7	139	90.9
RN01-04	98.3	0.56	15.8	2419	14.5	14	74.4	6.3	95.2	45	70.3	1326	6.7	1111	65.3	313	79.7	15.5	46.2	45	62.8	5960	94.7	2.6	43.6	509	91.2
RN01-05	98.8	0.40	33.9	3063	22.3	18	69.7	11.9	77.6	67	77.0	1453	9.3	1110	55.2	69	74.1	12.0	45.1	44	86.5	10826	96.6	2.2	54.0	193	89.3
RN01-07	100.3	0.28	65.2	1922	29.1	14	73.2	7.6	98.4	53	81.2	879	20.9	656	72.9	44	80.9	13.5	54.4	34	86.5	11923	98.1	2.1	76.5	140	92.2
RN01-03	117.5	0.18	44.2	1172	20.4	7	56.5	3.6	96.0	28	74.6	665	28.7	439	66.8	40	84.7	16.1	63.4	15	77.8	4535	94.8	2.2	30.9	109	90.7
RN01-13	129.5	0.23	62.0	1982	33.2	9	33.3	6.2	97.4	39	79.1	793	18.4	302	48.3	36	80.8	11.2	52.0	27	83.2	9781	97.7	1.9	67.5	134	91.4
RN01-53	130.9	0.53	63.5	5494	14.1	9	33.3	4.7	95.3	159	60.3	3183	13.8	1741	42.8	88	65.3	16.4	38.2	89	80.9	14558	97.5	3.3	52.6	201	80.3
RN01-16	139.2	0.34	42.5	1749	15.0	9	33.3	3.2	91.8	25	42.2	930	15.7	326	44.6	33	66.2	14.8	39.3	16	61.4	7026	94.4	1.0	28.1	46	73.5
RN01-06	156.6	0.09	71.5	992	26.5	3	50.0	1.7	95.3	15	75.1	407	7.9	269	62.4	20	78.5	5.1	62.6	12	82.5	3345	94.5	0.8	42.2	48	87.0
RN01-14	162.5	0.18	60.2	1416	19.9	6	33.3	3.4	93.0	21	69.9	655	16.3	468	69.1	79	56.8	9.0	47.4	14	73.8	7785	96.8	1.0	69.0	69	82.1
RN01-54	170.2	0.24	53.2	10760	8.3	8	33.3	67.8	12.1	144	88.1	5868	8.6	2779	26.7	129	45.0	59.5	19.6	114	80.3	9369	95.8	3.2	42.7	281	82.4
RN01-02	176.3	0.15	49.1	1290	33.2	8	63.0	8.4	98.5	25	78.7	499	14.6	318	64.1	20	77.1	11.5	60.9	19	83.7	6409	96.5	1.6	69.3	86	93.4
RN01-15	177.3	0.25	40.3	2219	25.7	10	60.0	2.9	95.9	56	71.3	1060	9.5	617	63.6	61	76.4	14.3	28.2	32	81.1	9840	97.0	1.2	75.4	88	83.7
RN01-55	206.3	0.70	51.5	136308	0.9	8	33.3	4.5	88.7	194	38.9	145342	0.5	28406	5.4	2903	6.7	105.0	10.0	690	59.3	12979	91.8	3.4	32.8	521	50.1
RN01-01	235.6	0.15	51.6	1274	28.0	5	33.3	3.9	96.9	19	78.7	537	14.3	345	63.2	25	75.4	8.9	68.8	15	82.4	5433	95.5	0.7	63.1	67	89.5
RN01-56	277.1	1.43	9.3	26798	5.6	8	33.3	13.8	96.3	164	68.3	18783	5.9	6911	34.3	483	46.3	50.2	56.0	755	71.6	18617	95.2	4.8	38.5	794	85.4

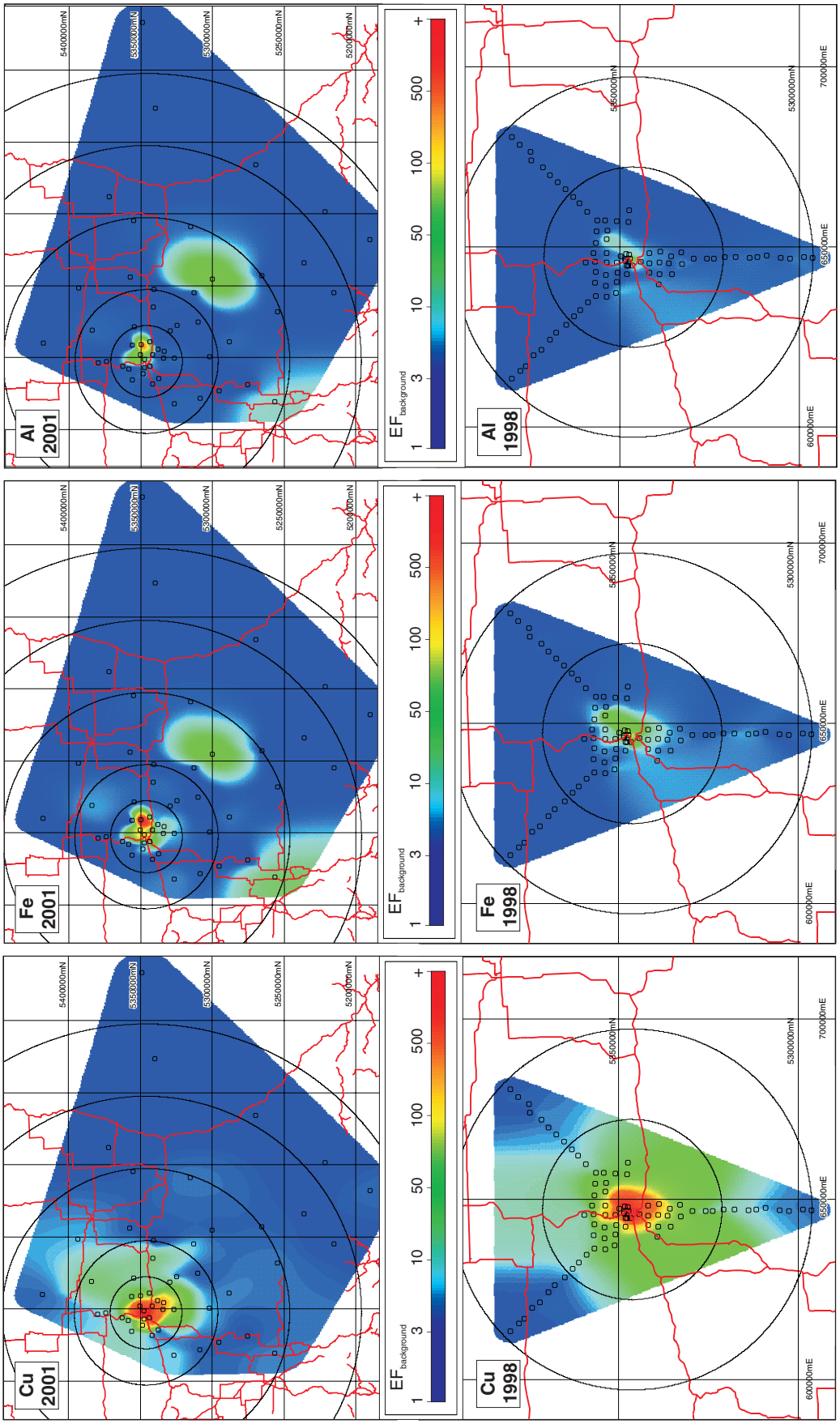


Figure 3. *Maps showing element deposition rates in ng/cm²/a, coloured by percentile values as indicated in the legend. Values were interpolated from sample locations to illustrate general patterns. In general, most elements show a strong smelter influence, with minor differences between years. A circular bull's-eye pattern predominates, moderated somewhat by the influence of the wind. A small group of samples taken along a road east of the smelter in the 2001 data set are characterized by high values, probably an effect of road dust. These samples have been removed from some profile plots showing fitted model (Fig. 5).*

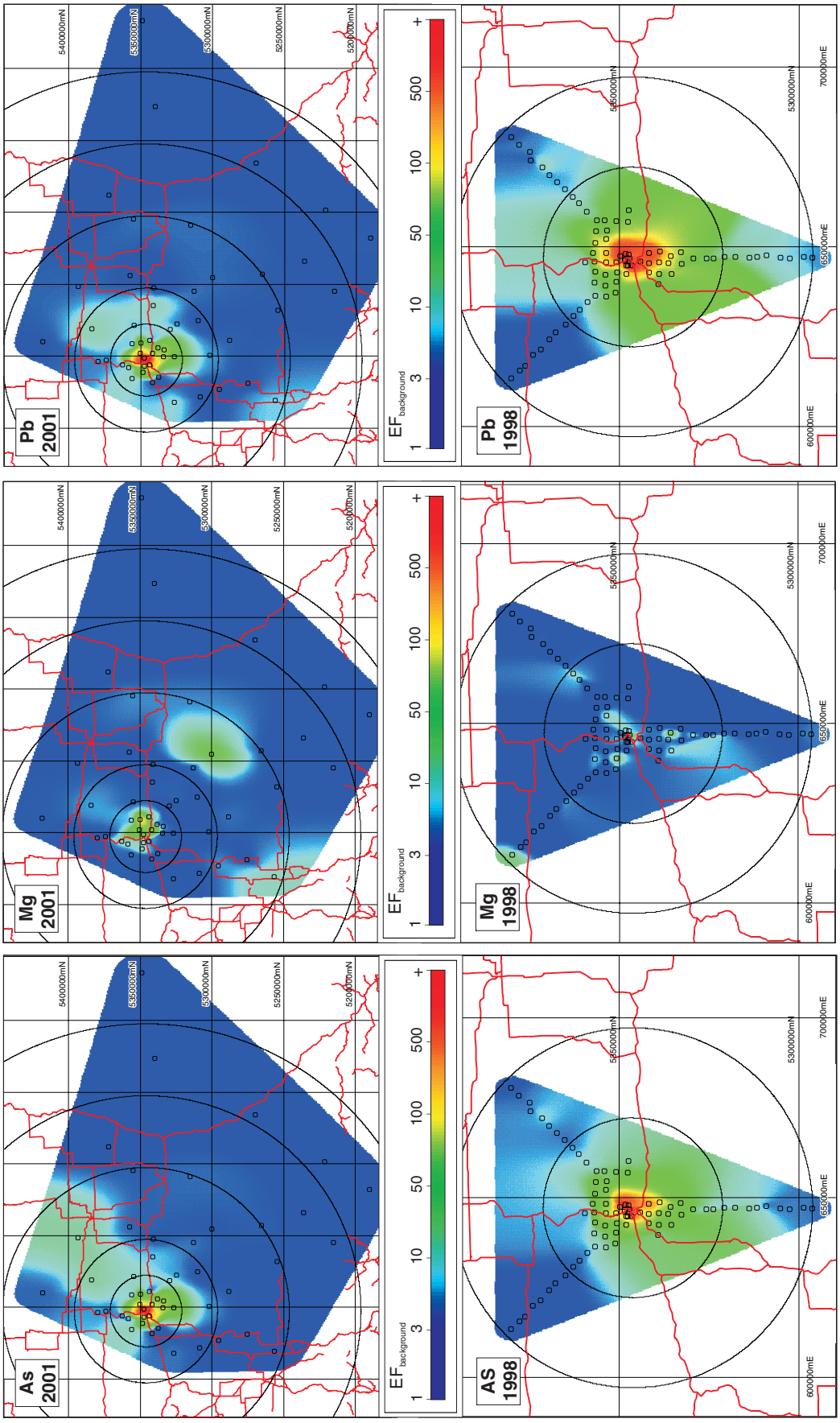


Figure 3. (Cont.)

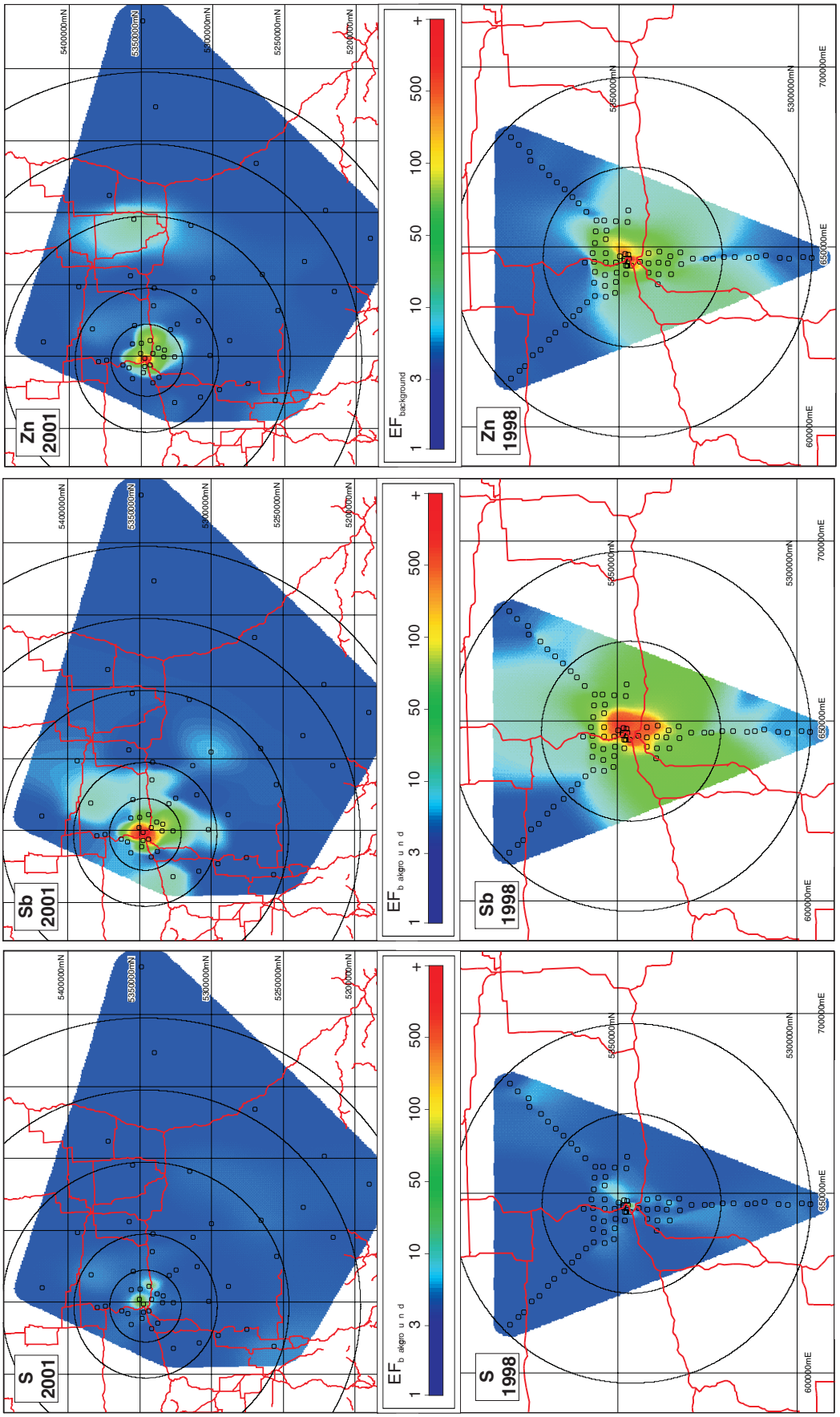


Figure 3. (Cont.)

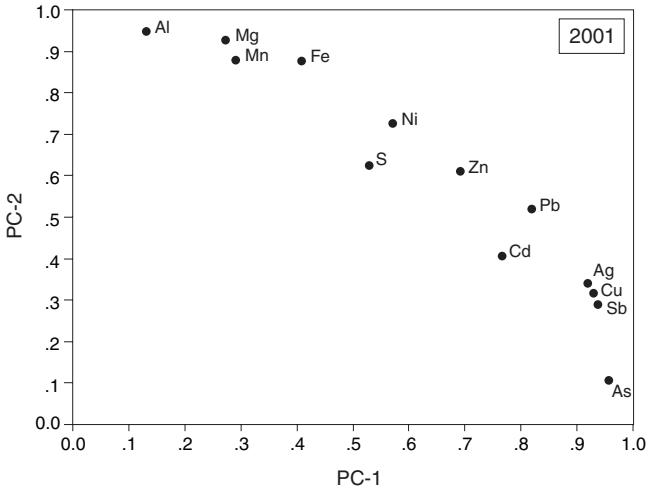


Figure 4. *Principal components scores based on an analysis of elements from 2001 snow data. PC-1 is dominated by smelter metals and PC-2, by elements associated with weathering of silicate minerals.*

the background (because this is an exponential model, the model value never actually reaches the background value until at an infinite distance from the smelter, but of course it approaches background much closer). The expression for this value is given by

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

where $SE(\beta_0)$ is the standard error of β_0 obtained from the fitting process. The value of x_1 is not the final distance travelled by elements from the smelter; rather, it is a relative measure for comparing element behaviour and is the distance beyond which the variability in the background effectively makes it statistically difficult to separate elements from a smelter from other sources of elements in the atmosphere. Undoubtedly a significant proportion of the smelter loading travels farther than this distance, as discussed by Bonham-Carter et al. (2005).

Table 5 summarizes the values of the model parameters generated by fitting equation (1) to the 1998 and 2001 data for each element. Figure 5 provides plots of element-loading versus distance with both years on the same graph, and models for both years superimposed. In both the table and plots, the samples close to the road running east of Rouyn-Noranda and suspected of being contaminated by road dust, have been excluded from the analysis (sample numbers RN01-50, RN01-51, RN01-52, RN01-53, RN01-54, RN01-55, and RN01-56). Table 6 summarizes the background and distance parameters, with the elements in the order of increasing distance of transport, based on 1998 data. A column for each year also shows the median values for samples collected within 50 km of the smelter. A comparison of 1998 and 2001 medians (more than 50 km), background, and distance values is shown as three columns of ratios.

The following paragraphs summarize the results for each element, beginning with the smelter-related elements. Note that in Table 6, the most 'smelter-centric' elements (Cu, Pb, Sb, As, Zn) are at the bottom of the table, because the travel distance (size of smelter footprint) is greatest for these elements. Elements such as Mg, Al, S, Fe, and to some extent Ni, Ag, and Cd have a smaller footprint size and the influence of the smelter gets 'lost' in background at shorter distances from the smelter.

Because the median values within 50 km may be affected by the different spatial distribution of samples between the two years, an inset in Figure 5 shows a plot of the median metal-loading rates for 10 km intervals, starting from the smelter and increasing to 50 km, between 1998 and 2001.

Copper

Perhaps not surprisingly, copper (Fig. 5a) has the largest smelter footprint (approximately 50 km for 1998, approximately 58 km for 2001), consistent with the fact that the Horne is a copper smelter (although lead emissions are much higher than copper emissions — *see* Table 7). Copper background value is approximately 0.067 µg/cm²/a (1998) but is lower at approximately 0.044 µg/cm²/a for 2001. This is because the distal samples taken in the 2001 survey at distances of more than 50 km from the smelter show that the background value is lower than what would be obtained from samples taken only out to 50 km from the smelter (as was the case in 1998). In fact, the data for samples taken within 50 km of the smelter are remarkably similar in both years, as is confirmed on the inset medians plot for Cu.

Lead

Lead (Fig. 5b) has the next largest smelter footprint (approximately 50 km for 1998, approximately 46 km for 2001). Major differences occur between the two years, with 1998 levels being higher than 2001 levels at every distance. For example, the median Pb loading rate for samples closer than 50 km from the smelter is 1.060 µg/cm²/a in 1998 and 0.103 µg/cm²/a in 2001, or 10 times lower in 2001. The inset medians plot shows that this difference is systematic, with consistently higher 1998 medians over each 10 km interval. The reason for this is uncertain. Lead emissions were 150 tonnes/a in 1998 and 65.3 tonnes/a in 2001, or 2.5 times lower in 2001; however, this difference appears to be insufficient to explain the differences in lead content in snow between the two years.

Antimony

The two Sb curves (Fig. 5c) give similar estimates of background (0.0022 µg/cm²/a vs. 0.0019 µg/cm²/a) and similar footprint radii (approximately 47 and 41 km), but the median values out to 50 km indicate a systematically larger loading in 1998. Emissions data were not available for this metal, but the reduction in loading rates in values is likely related to a decrease in emissions.

Table 5. Summary of model parameters fitted to element data for the 1998 and 2001 snow surveys.

Element /Year	1 β_0	2 SE(β_0)	3 β_1	4 SE(β_1)	5 λ	6 SE(λ)	7 exp($\beta_0+\beta_1$)	8 exp(β_0)	9 X_l	10 Res
unit					km	km	µg/cm^2/a	µg/cm^2/a	km	
Cu-1998	-2.699	0.144	6.710	0.180	8.96	0.65	55.2020	0.0673	49.6	0.432
Cu-2001	-3.146	0.197	6.635	0.629	11.46	1.90	33.4817	0.0430	58.2	0.837
Pb-1998	-2.552	0.258	5.935	0.252	10.92	1.42	29.4593	0.0779	49.4	0.601
Pb-2001	-3.547	0.162	5.752	0.648	9.23	1.62	9.0703	0.0288	47.6	0.750
Zn-1998	-2.282	0.137	4.775	0.207	7.76	0.82	12.0975	0.1021	39.7	0.477
Zn-2001	-2.265	0.158	4.801	0.848	6.79	1.62	12.6291	0.1038	33.5	0.809
Cd-1998	-5.894	0.162	3.728	0.231	8.08	1.26	0.1146	0.0028	36.6	0.541
Cd-2001	-5.356	0.116	4.109	0.772	5.39	1.27	0.2874	0.0047	27.7	0.629
As-1998	-3.846	0.173	5.522	0.220	8.83	0.94	5.3441	0.0214	44.1	0.527
As-2001	-4.449	0.169	5.844	0.756	8.27	1.58	4.0350	0.0117	42.3	0.816
Sb-1998	-6.113	0.221	6.020	0.242	9.87	1.15	0.9112	0.0022	47.1	0.587
Sb-2001	-6.266	0.175	6.564	0.820	7.88	1.42	1.3472	0.0019	41.2	0.858
Al-1998	0.792	0.061	1.734	0.272	3.11	0.76	12.5034	2.2078	15.0	0.354
Al-2001	0.713	0.170	1.311	0.740	8.54	7.21	7.5685	2.0401	25.1	0.815
Fe-1998	0.308	0.080	3.379	0.260	3.99	0.52	39.9249	1.3607	21.6	0.420
Fe-2001	0.043	0.198	3.710	0.978	7.45	2.75	42.6488	1.0439	31.5	0.988
Mg-1998	-0.353	0.113	1.180	0.364	4.04	2.14	2.2864	0.7026	13.7	0.594
Mg-2001	-0.563	0.177	2.371	0.636	10.30	4.56	6.0982	0.5695	38.5	0.789
S-1998	2.150	0.143	0.680	0.239	7.16	5.77	16.9455	8.5849	16.1	0.535
S-2001	1.977	0.088	0.977	0.311	10.39	5.50	19.1825	7.2210	36.1	0.389

Column 1. Background parameter (β_0) fitted in equation (1), units are in natural logarithms (µg/cm^2/a).
Column 2. Standard error of β_0 obtained by fitting, units same as in column 1.
Column 3. Source parameter (β_1) fitted in equation (1), units same as in column 1.
Column 4. Standard error of β_1 obtained by fitting, units same as in column 1.
Column 5. Half-distance parameter (λ) fitted in equation (1).
Column 6. Standard error of λ lobtained by fitting.
Column 7. Loading rate (µg/cm^2/a) close to smelter, i.e. modelled value at distance = 0 km from smelter.
Column 8. Ambient background loading rate (µg/cm^2/a) far away from smelter, i.e. modelled value at distance = ∞ km from smelter.
Column 9. Distance, x_l (km), at which modelled loading rate is within one standard error of ambient background loading rate.
Column 10. Residual standard error, with 79 degrees of freedom (1998) or 47 degrees of freedom (2001) as measure of fit, units same as in column 1.

Table 6. Median values less than 50 km from smelter, ambient background levels, and distance to background *(x_l)* summary, with elements sorted by increasing distance based on 1998 data.

Element	1998 Median <50 km (µg/cm^2/a)	1998 Background exp(β_0) (µg/cm^2/a)	1998 Distance x_l (km)	2001 Median <50 km (µg/cm^2/a)	2001 Background exp(β_0) (µg/cm^2/a)	2001 Distance x_l (km)	Ratio: 1998 value/2001 value Median <50 km	Background exp(β_0)	Distance x_l
Mg	0.767	0.7026	13.7	0.805	0.5695	35.1	0.95	1.19	0.39
Al	2.583	2.2078	15.0	2.605	2.0401	22.4	0.99	1.06	0.67
S	11.471	8.5849	16.1	10.976	7.2210	31.4	1.05	1.16	0.51
Fe	1.964	1360.7	21.6	1.986	1.0439	29.3	0.99	1.26	0.74
Ni	0.0195	0.0121	24.9	0.0203	-	-	0.96	-	-
Ag	0.0047	0.0016	35.7	0.0011	-	-	4.3	-	-
Cd	0.0088	0.0028	36.6	0.0076	0.047	27.7	1.2	0.60	1.31
Zn	0.457	0.1021	39.7	0.197	0.1038	32.9	2.3	0.97	1.21
As	0.152	0.0214	44.1	0.037	0.0117	42.8	4.1	1.83	1.03
Sb	0.0238	0.0022	47.1	0.0071	0.0019	41.5	3.4	1.15	1.13
Pb	1.006	0.0779	49.4	0.103	0.0288	45.8	9.8	2.60	1.08
Cu	0.661	0.0673	49.6	0.275	0.0430	57.8	2.4	1.52	0.86

*Model did not converge for Ni, Ag for 2001 or for Mn for either year.

Table 7. Summary of annual emissions from the Horne smelter from 1994 to 2001. Data supplied by Noranda, Inc.

	1994 (tonnes/a)	1995 (tonnes/a)	1996 (tonnes/a)	1997 (tonnes/a)	1998 (tonnes/a)	1999 (tonnes/a)	2000 (tonnes/a)	2001 (tonnes/a)
Feed	853 551	881 025	934 187	896 863	881 283	829 017	787 696	840 233
SO_2	154 000	172 000	148 000	144 000	112 500	94 000	90 000	---
Particulates	770	940	1200	870	920	720	620	595
Pb	260	340	300	197	150	100	80	65.3
Zn	62	85	85	55	39	23	19	17.8
Cd	3	3	2	1.4	2.4	1.6	2.2	2.5
As	19	29	63	55	78	64	59	97.9
Cu	70	58	65	50	70	69	59	41.7

Arsenic

Median As values (Fig. 5d) within 50 km of the smelter are about four times higher in 1998 than in 2001 (0.152 µg/cm²/a for 1998 versus 0.037 µg/cm²/a for 2001), although the footprint radius is about the same for both years (approximately 44 and 43 km). The inset medians plot shows that the higher values in 1998 occur at least up to the 40 to 50 km distance interval. The background estimate is definitely higher for 1998, although only by a factor of 1.8. The emission tonnages for this element actually increased over the sampling period, from 78 tonnes/a in 1998 to 98 tonnes/a in 2001, counter to the trends shown in the snow data. Annual arsenic emissions have likely been insufficiently resolved over time to be sure whether the drop shown in the snow data can be accounted for by the change in emission rates.

Zinc

Zinc values (Fig. 5e) in snow appear to be similar for both sampling years, as shown from the two curves and the background levels. However, the median values for distances less than 50 km are 0.457 µg/cm²/a in 1998 and 0.197 µg/cm²/a in 2001, a decrease by a factor of more than two. The medians plot shows that the higher 1998 Zn values occur within the first 20 km; beyond this point the differences are small. Notice that the footprint radius is somewhat less in 2001 (drop from approximately 40 km to approximately 33 km). Over the interval 1998 to 2001, zinc emissions decreased from 39 tonnes/a to 18 tonnes/a, consistent with the drop in median values from snow.

Cadmium

The median loading rates for Cd (Fig. 5f) in samples taken within 50 km of the smelter are similar in both sampling years (0.0089 µg/cm²/a in 1998 and 0.0076 µg/cm²/a in 2001), although background levels increased over this time interval from 0.0028 µg/cm²/a to 0.0047 µg/cm²/a; this can also be seen in the medians plot. The distal samples have a higher cadmium content in 2001 than would be expected from the 1998 data. Emission figures indicate essentially the same values for both years (2.4 tonnes in 1998, 2.5 tonnes in 2001). Increased background values could be due to an increase in cadmium in other air masses that controlled the ambient background, although no independent evidence exists to support this.

Silver

Median Ag values at less than 50 km from the smelter (not shown in Fig. 5) decreased from 0.0047 µg/cm²/a in 1998 to 0.0011 µg/cm²/a in 2001.

Nickel

Median Ni values (not shown on Fig. 5) remained essentially unchanged in 1998 and 2001.

Iron

Although background values for Fe (Fig. 5g) were lower in 2001 than in 1998, the median value at distances under 50 km from the smelter remained similar in both sampling years.

Sulphur

For some reason, S values between 25 and 50 km from the smelter are bimodal in the 1998 data, with modes of about 2 µg/cm²/a and 15 µg/cm²/a (Fig. 5h). Sulphur is erratic and its presence is not readily explained in terms of a smelter origin.

Aluminium

The Al data show a similar pattern and level for both 1998 and 2001 (Fig. 5i).

In summary, it is interesting to note (Table 6, final column) that the 1998:2001 footprint ratio is generally larger for the smelter-centric elements than for the non-smelter elements. The only exception is Cu. The loading rates for Cu, Pb, Sb, As, Zn, and Cd are all higher within 50 km of the smelter, and these elements have a somewhat larger footprint radius than Ni, Fe, S, Al, and Mg. Background levels are generally higher in the 1998 data than in the 2001 data (except for Cd and Zn), mainly because sampling was restricted to a 50 km radius in 1998, which proved to be too close to the smelter to obtain an unbiased estimate of background values.

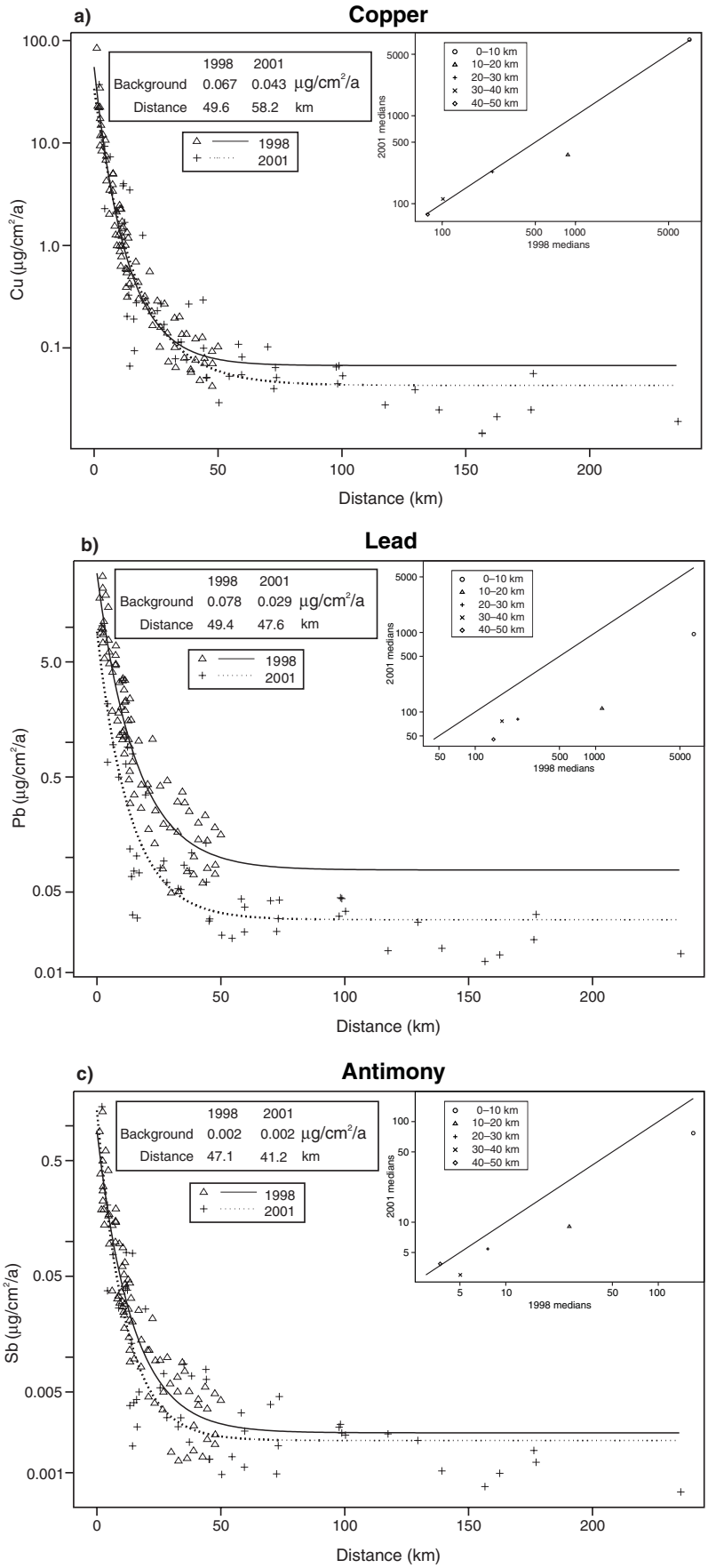


Figure 5.

Plots of metal-loading versus distance for elements in snow. Note the log scale for the y-axis. The model (equation (1)) fitted to the 1998 data is shown as a solid line and to the 2001 data, as a dotted line. Loading units are expressed as µg/cm²/a (cf. the ng/cm²/a units in Tables 3 and 4). 'Background' values are fitted ambient background values of the model at an infinite distance from the smelter. 'Background distance' values (equation (2)) reflect the distance at which the model value first reaches a level within 1 standard error of background. This distance is referred to as the 'footprint radius' and is not to be confused with the limit of transport of the metal. Inset diagrams summarize median metal levels at five distance intervals between 1998 and 2001 sampling years, and facilitate a comparison of the surveys. The straight line is for a 1:1 correlation.

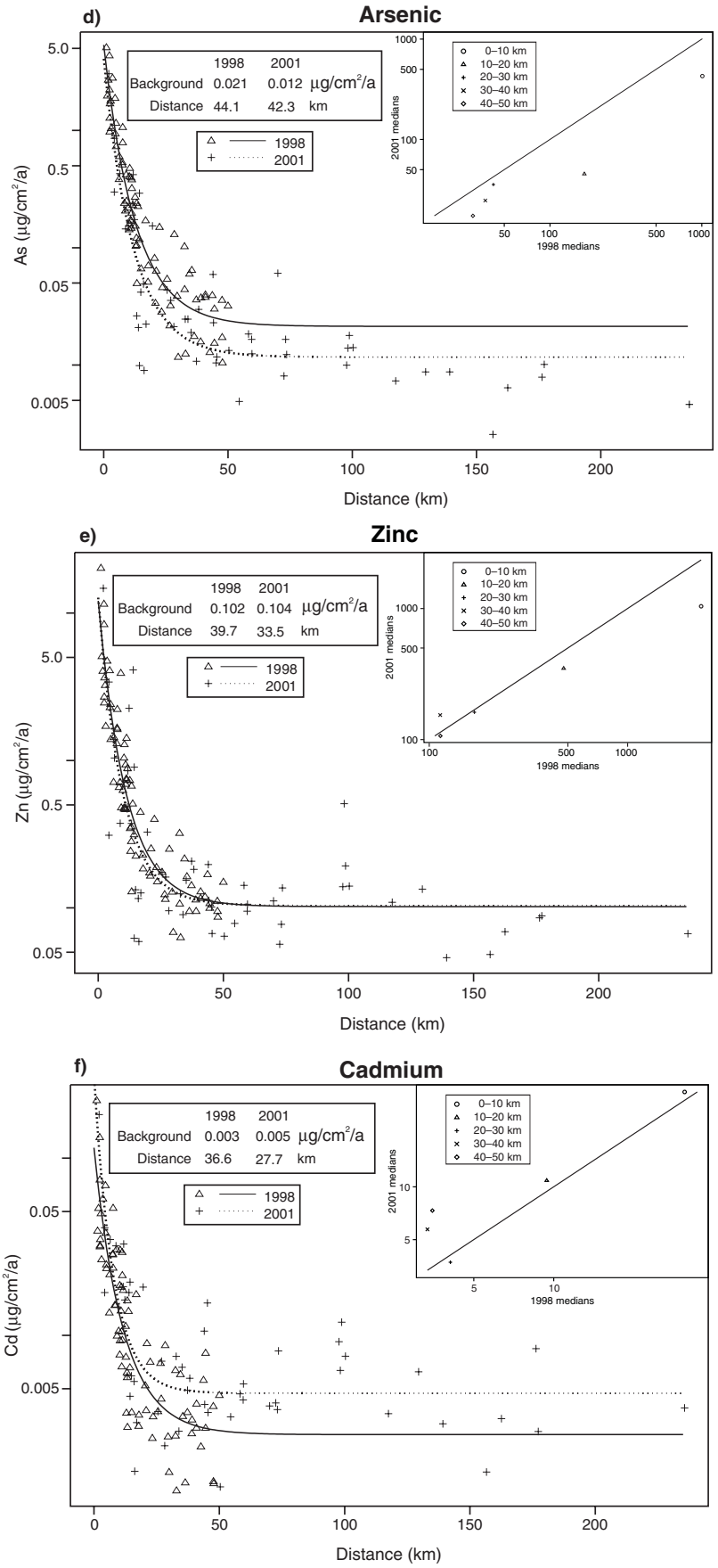
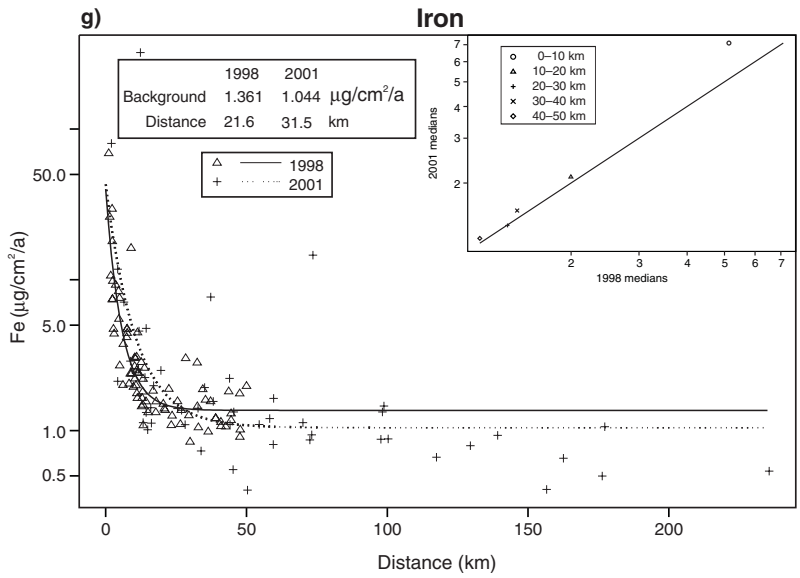
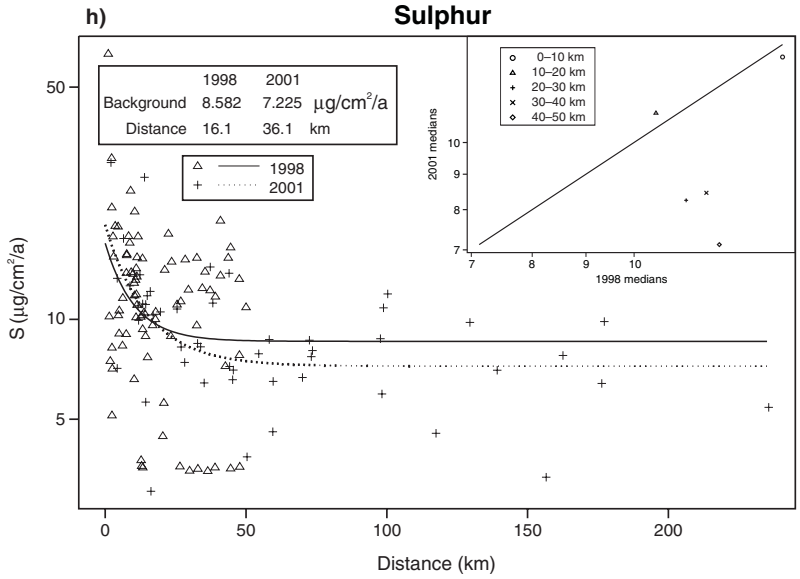


Figure 5. *(Cont.)*





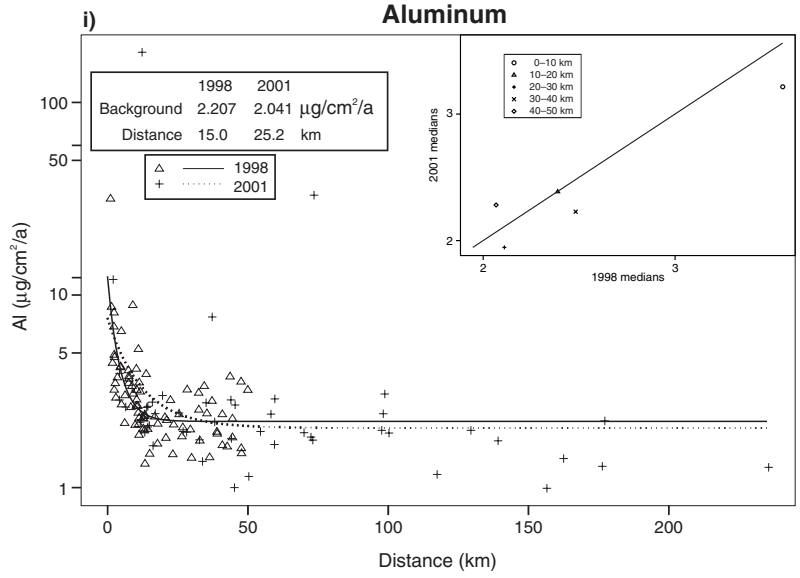


Figure 5. *(Cont.)*

Comparison of Rouyn-Noranda metal concentration values from snow with values reported in the literature

It is instructive to see how the snow chemistry around Rouyn-Noranda compares with results reported from other parts of the world. Table 8 summarizes metal levels from a variety of snow surveys and provides a comparison with values from this study. Note that the comparison is on the basis of concentrations, not loading rates, because of the insufficient number of published loading rates. Metal concentration levels in bulk precipitation were grouped by Galloway et al. (1982) into three classes, i.e. urban, rural, and remote, as shown in Table 8 and Figure 6.

In general, the class ranges of Galloway et al. (1982) overlap. For example, although Cu values can range from 6.8 to 120 ppb in his urban class, rural samples can range from 0.4 to 150 ppb, i.e. some rural values can even exceed the urban range. Similarly, remote samples can contain as much as 0.85 ppb or as little as 0.035 ppb, again demonstrating an overlap with the rural class.

In general, the Rouyn-Noranda snows have metal levels higher than the range typical of remote sites. On the other hand, the range of metal levels around Rouyn-Noranda are for the most part typical of those of the urban and remote classes of Galloway et al. (1982). Copper values within 25 km of the smelter are typical of urban values, except for samples from within about 12 km of the smelter, where levels can be higher than expected for an urban setting. Lead levels out to about 50 km from the smelter are typical of urban values, with most values exceeding the urban maximum, even close to the smelter. Cadmium levels in samples within 20 km of Rouyn-Noranda are also typical of an urban environment; beyond this distance, they are typical of rural environments. Zinc levels exceed the urban range within 10 km of the smelter, but are typical of rural values beyond 50 km.

We conclude that within 10 to 15 km from the smelter, some metal levels (Cu, Zn) in the Rouyn-Noranda surveys exceed values typical of precipitation in urban environments, being more characteristic of industrial sites such as smelters in the Kola Peninsula (Reimann and de Caritat, 1998) and the Belledune smelter in New Brunswick (Pilgrim and Hughes, 1994).

Metal solubility

One of the important questions for studies of metals being deposited around smelters is the proportion of the metal deposited that is bioavailable. Bioavailability is a complex and difficult factor to measure and is beyond the scope of this study. However, it is possible to examine the relative proportions of dissolved and particulate material for each element, because each sample was thawed and filtered, with the filtrate and residue being analyzed separately.

Figure 7 shows graphs of the dissolved/(dissolved + particulate) ratio for 12 elements as a function of distance from the smelter. A novel presentation of the solubility information is made by Telmer et al. (2004), using a more complete suite of elements than the one summarized here. The 2001 data were obtained using a finer filter than in 1998 (0.1 µm instead of 0.45 µm), so, as a general rule, one would expect a higher proportion of material to show up in the filtrate in the 1998 data, and therefore the 'solubility', as the term is used here, would normally be higher for the 1998 samples than the 2001 samples. This does not always occur, however. Median solubility ratios are summarized by year in Table 9.

In general, the solubility–distance curves have several different characteristics, depending on the element.

1. *Elements that are very insoluble*, with little change with distance from the smelter. Aluminum (Fig. 7a) is the least soluble element reported here, although for some reason the 2001 samples were often more soluble than the 1998 samples, despite the finer filter used for 2001 samples. Iron (Fig. 7b) is also mostly in the particulate fraction (i.e. very insoluble), with no obvious differences between years. There is a suggestion of solubility increasing with distance from the smelter, but this is not pronounced. Both Fe and Al usually have at least 80% of the total element in particulate form.

2. *Elements that are moderately soluble*, with little systematic change in solubility with increasing distance from the smelter; the solubility is usually within a characteristic range. This includes Ni (not shown), Pb (Fig. 7c), Cu (Fig. 7d), and As (Fig. 7e), with Ni being the least soluble of this group and As the most soluble.

3. *Magnesium* (Fig. 7f) behaves differently in that solubility can occur across a wide range of values from about 20 to 90%, with no obvious change with distance from the smelter.

4. *Elements that become more soluble with distance from the smelter.* These include Ag (Fig. 7g), Sb (Fig. 7h), Zn (Fig. 7i), and possibly Mn (Fig. 7j). The 1998 data show Mn solubility changing from about 40% close to the smelter to 90% at 50 km. However, solubility in the 2001 data at distances greater than 50 km appears to decrease again, or at least to become much more variable. For both 1998 and 2001, Ag shows a marked trend, with solubility in 2001 being less than in 1998, particularly at great distances from the smelter. Antimony and zinc (although noisier) show a similar trend.

5. Elements that are very soluble, with only a weak change in solubility with distance. Sulphur (Fig. 7k) is the best example of this (a few samples within about 5 km of the smelter have solubilities in the 40 to 80% range, but beyond 10 km, more than 90% of sulphur is in solution). Cadmium (Fig. 7l) also is highly soluble at all distances.

Table 8. Concentration values of metals in snow from various sources, including the classification of Galloway et al. (1982).

Reference	Sample type	Location	Designation	Zn ppb[1]	Pb ppb	Cu ppb	Ni ppb	Cd ppb
Bulk precipitation								
Galloway et al. (1982)	precipitation (wet & dry)		***urban***	18–280 (34)	5.4–147 (44)	6.8–120 (41)	2–114 (12)	0.48–2.3 (0.7)
Galloway et al. (1982)	precipitation (wet & dry)		***rural***	1–311 (36)	0.6–64 (12)	0.4–150 (5.4)	0.6–48 (2.4)	0.008–46 (0.5)
Galloway et al. (1982)	precipitation (wet & dry)		***remote***	0.016–0.32 (0.22)	0.02–0.41 (0.09)	0.035–0.85 (0.06)	<DL <DL	0.004–0.639 (0.008)
Snow			***Industrial and urban***					
this study	snowpack	10 km from Rouyn-Noranda, Quebec	industrial, urban	10.9	7.98	31.5		0.28
Kliza et al. (2000)	snowpack	10 km from Rouyn-Noranda, Quebec	industrial, urban	19.4	48.87	40.16		0.30
Reimann and De Caritat (1998)	snowpack	Kola Peninsula, Russia	industrial	17.3	8.43	690.50	853	315.095
Pilgrim and Hughes (1994)	snowpack	Belledune, New Brunswick	industrial	108.9	648.76			12.52
Gorzelska (1989)	snowpack	Inuvik (average), Nunavut	industrial	41.4	279.90	0.49	22	0.05
this study	snowpack	15 km from Rouyn-Noranda, Quebec	urban	5.6	3.28	11.66		0.17
Kliza et al. (2000)	snowpack	15 km from Rouyn-Noranda, Quebec	urban	9.6	20.58	14.70		0.17
Jonasson (1973)	fresh snow	Ottawa, Ontario	urban	18–192 (25)	55–410 (83)	15–69 (19)	17–21 (19)	0.1–1 (0.7)
Jeffries and Snyder (1981)	snowpack	Sudbury, Ontario	urban			52.00		
Simonetti et al. (1996)	snowpack	outside of Montréal, Quebec	urban	11.7–169 (18)	0.24–0.95 (0.59)	0.59–0.94 (0.92)		0.049–0.115 (0.084)
			Rural					
this study	snowpack	25 km from Rouyn-Noranda, Quebec	rural	3.2	1.34	3.6		0.12
Kliza et al. (2000)	snowpack	25 km from Rouyn-Noranda, Quebec	rural	4.6	6.99	4.80		0.09
Simonetti et al. (1996)	meltwater snowpack	western Quebec	rural	2.1–5.4	0.52–2.54	0.39–4.01		0.018–0.097
Simonetti et al. (1996)	meltwater snowpack	Lamothe (65 km east of Noranda)	rural	5.4	2.44	4.01		0.92
Barrie and Vet (1984)	snowpack	Val-d'Or region, western Quebec	rural		1.86–7.15 (2.11)	0.67–5.03 (1.27)	0.60 (0.60)	
Jonasson (1973)	snowpack	eastern Ontario	rural	10	8			
			Remote					
this study	snowpack	>200 km from Rouyn-Noranda, Quebec	remote	2.6	0.76	1.2		0.11
Kliza et al. (2000)	snowpack	>200 km from Rouyn-Noranda, Quebec	remote	2.8	2.13	1.80		0.05
	snowpack	Kola Peninsula, Russia	remote	3.52	0.75	0.34	0.22	0.04
Barrie and Vet (1984)	snowpack	northern Quebec	remote		0.8–12.4	0.2–1.5	0.9–25	
Jickells et al. (1992)	fresh fallen snow	Scottish Highlands	remote	0.3–63 (4.2)		0.4–5 (0.7)		
Gorzelska (1989)	fresh fallen snow	20 km from Inuvik, Nunavut	remote	0.8	0.63	0.26	0.18	0.012
Gorlach and Boutron (1992)	recent snow	Antarctic	extreme remote	0.0042	0.0054	0.01		0.00031
Suttie and Wolf (1992)	recent snow	Antarctic	extreme remote	0.0004	0.004	0.01		0.00008
Davidson et al. (1981)	recent snow	Greenland	extreme remote	0.21	0.14	0.04	0.05	0.011
Boutron et al. (1993)	fresh snow	Dye 3, Greenland	extreme remote	0.016–0.300	0.013–2.7	0.013–2.65		0.0002–0.0145
Wolff and Peel (1985)	fresh snow	Dye 3, Greenland	extreme remote	0.008–0.048	0.005–0.09	0.002–0.015		0.0002–0.0013

DL = detection limit
[1] Parts per billion (ppb) are the units equivalent to μg/L of thawed snow.

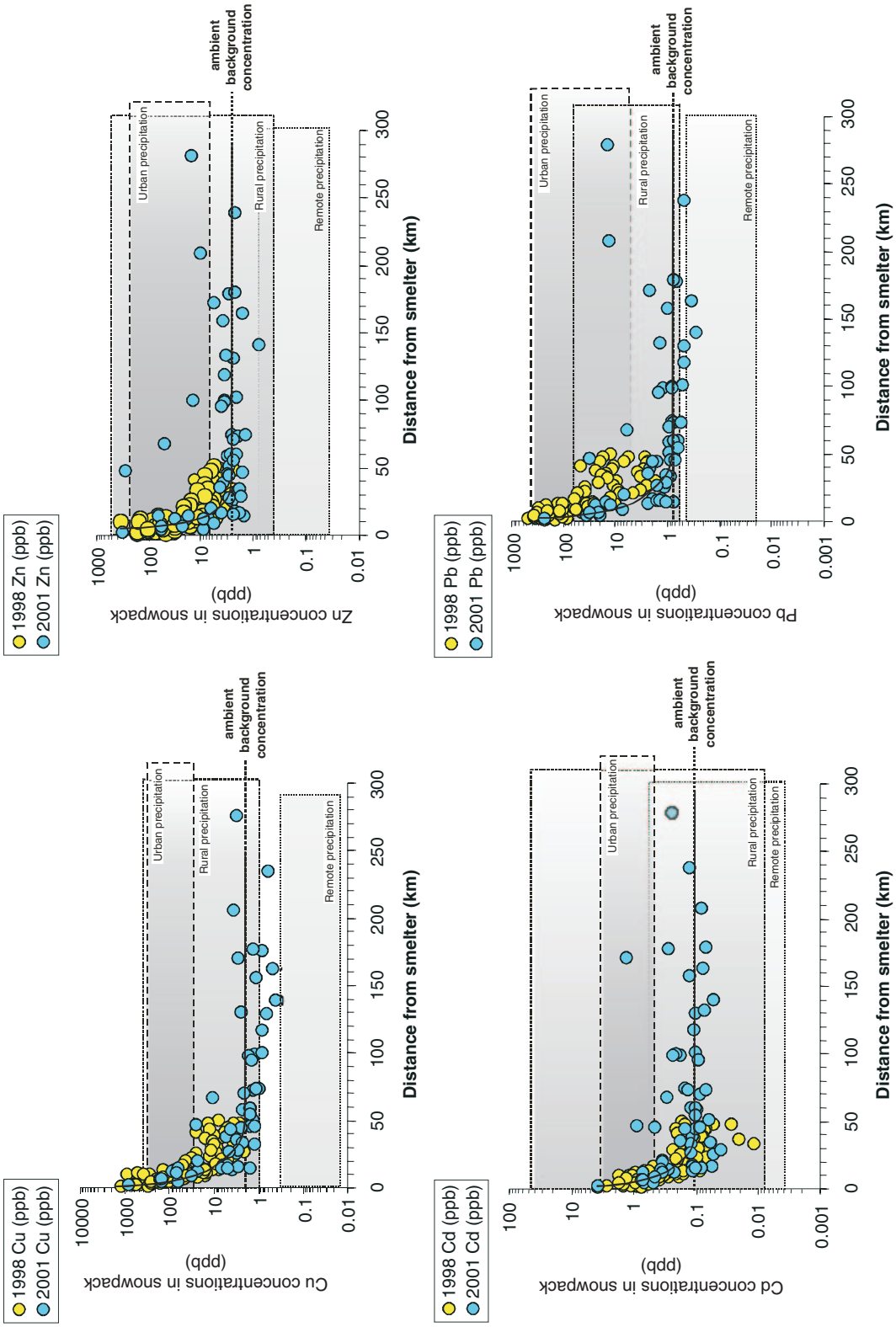


Figure 6. *Concentrations (ppb or µg/L) of Cu, Pb, Zn, and Cd plotted against distance from the smelter (km). Ranges of remote, urban, and rural concentrations in wet deposition based on a world-wide survey by Galloway et al. (1982) are superimposed.*

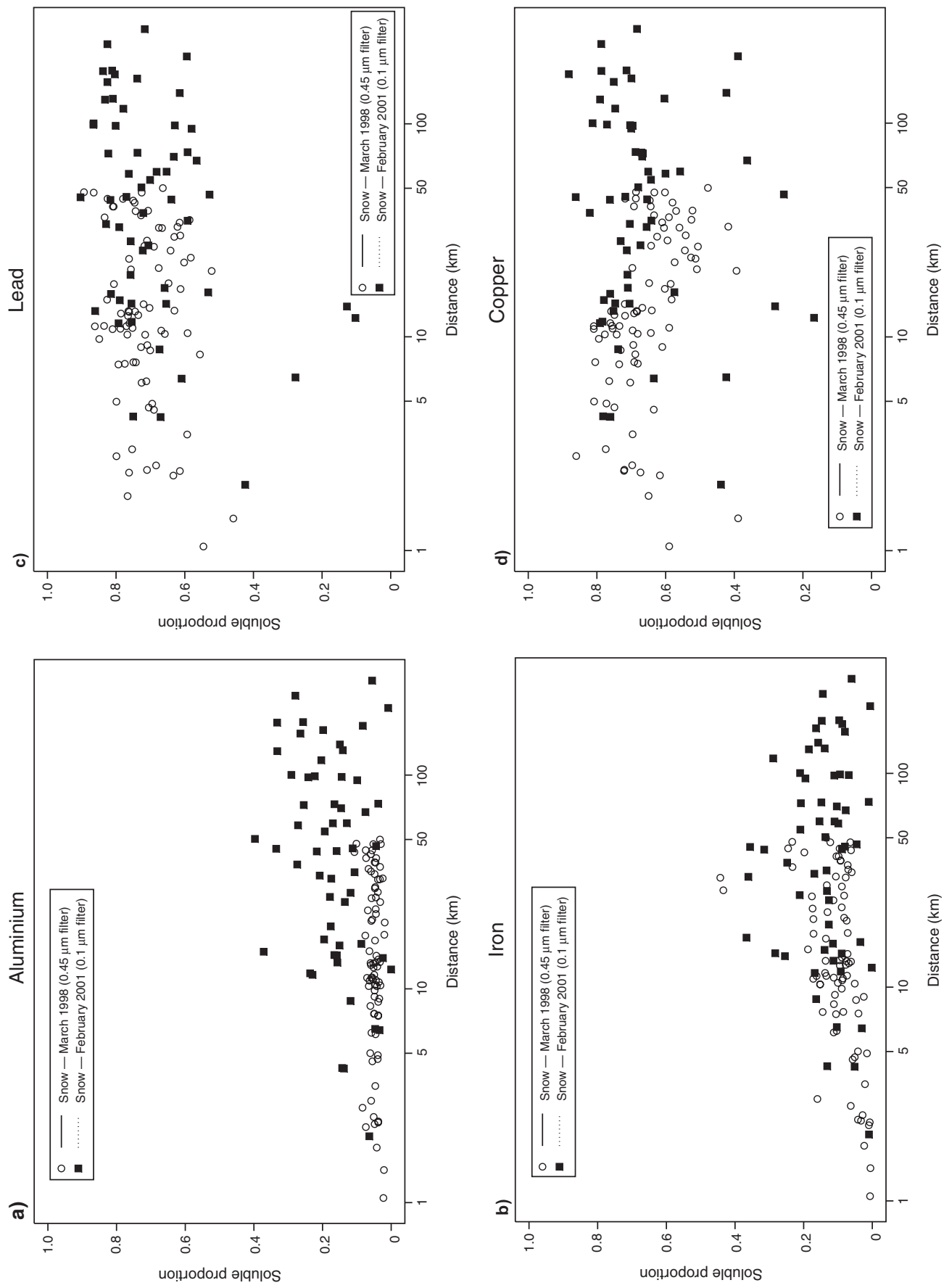


Figure 7. *Plots showing changes in element solubility with increasing distance from smelter by sample year. 'Solubility' for an element in a snow sample is defined here as the proportion of total element mass that passes through a filter, i.e. (Dissolved/ (dissolved+particulate)).*

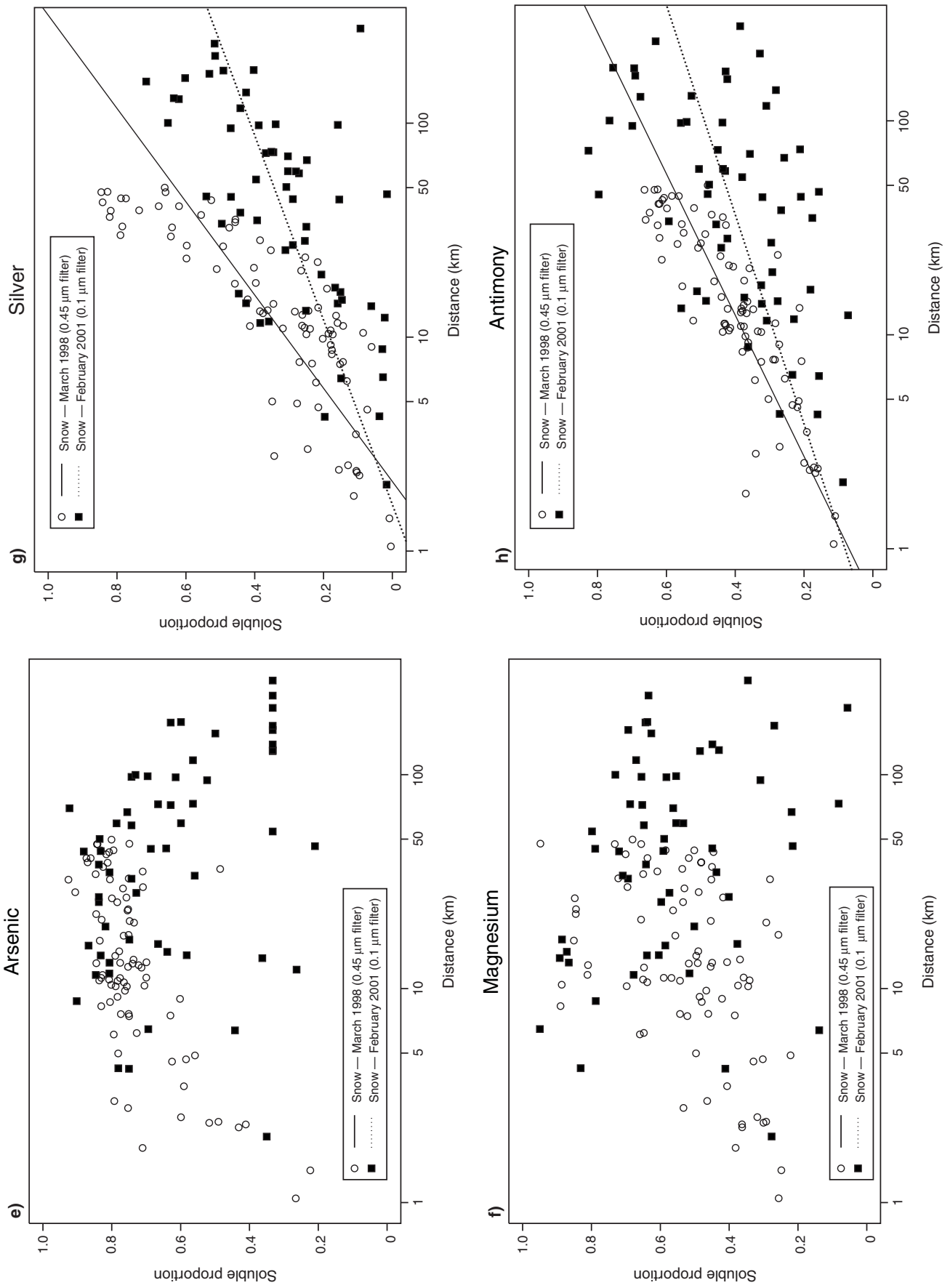


Figure 7. (Cont.)

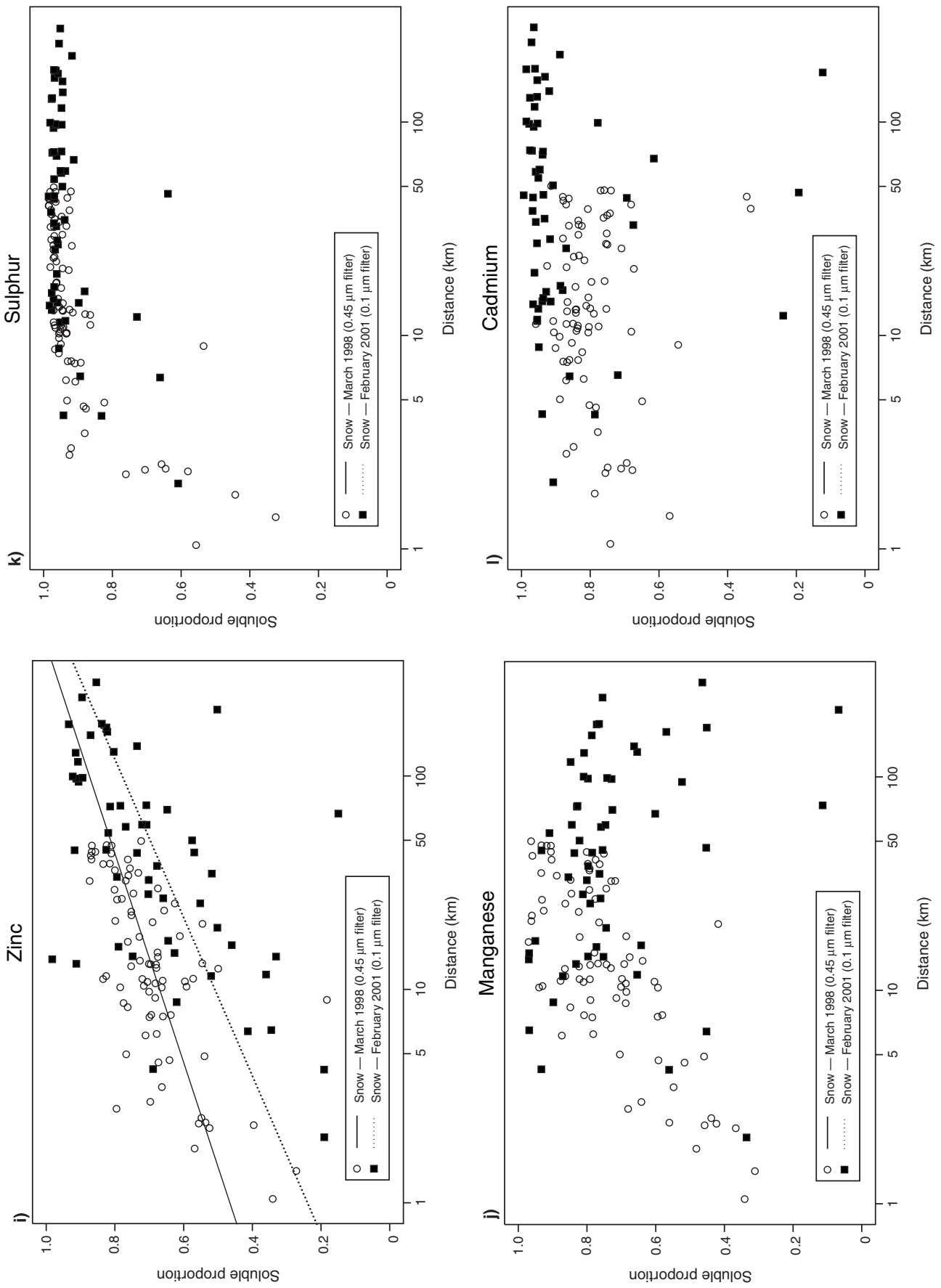


Figure 7. (Cont.)

Table 9. Median values of the soluble:total ratio for 1998 and 2001, in order of increasing value, based on 1998 values. Values approaching 1 indicate very high solubility; values approaching 0 indicate very low solubility.

Element	1998	2001
Al	0.05	0.14
Fe	0.01	0.17
Ag	0.23	0.39
Ni	0.35	0.30
Sb	0.32	0.32
Mg	0.41	0.51
Cu	0.42	0.70
Zn	0.40	0.68
Pb	0.78	0.66
As	0.73	0.63
Mn	0.72	0.73
Cd	0.88	0.95
S	0.95	0.94

CONCLUSIONS

In general, the 2001 snow data confirm the conclusions drawn from the data collected in 1998 as discussed by Telmer et al. (2004).

1. Metals emitted from the smelter show a large, approximately circular, footprint in snow around the Horne smelter at Rouyn-Noranda. After subtracting the effects of ambient background levels of element deposition from the atmosphere, the influence of the smelter can be recognized reliably only to about 50 km from Rouyn-Noranda. This is not the maximum distance travelled by smelter emissions; rather, it is the distance at which the influence of the smelter emissions, after deposition, can be distinguished reliably from other sources of material in the atmosphere. As shown by Bonham-Carter et al. (2005) from a comparison of loading rates between snow, peat, and soil, the amount of metal in the geochemical anomaly around the smelter is insufficient to account for the known emission tonnages. This suggests that some smelter emissions travel well beyond the obvious smelter footprint, but become so dilute that the influence of the smelter cannot be seen on the ground beyond 50 km.

2. Levels of metals in snow around the Rouyn-Noranda smelter as compared to published studies from other parts of the world suggest that metals concentrations are higher than a range of values typical for snow in an urban environment only out to a maximum distance of 15 and 20 km from the smelter.

3. Estimates of solubility show different behaviour between elements. Some elements such as S and Cd are highly soluble and their impact on the environment may be greater than less soluble elements such as Fe and Al. Of the toxic metals being emitted by the smelter, about 90% of Cd in snow is soluble, 65 to 75% of Pb and As are soluble, and Cu is more variable, with annual medians ranging from 42% to 70% soluble.

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