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Heavy metals from heavy land use? Spatio-temporal patterns of urban runoff metal loads

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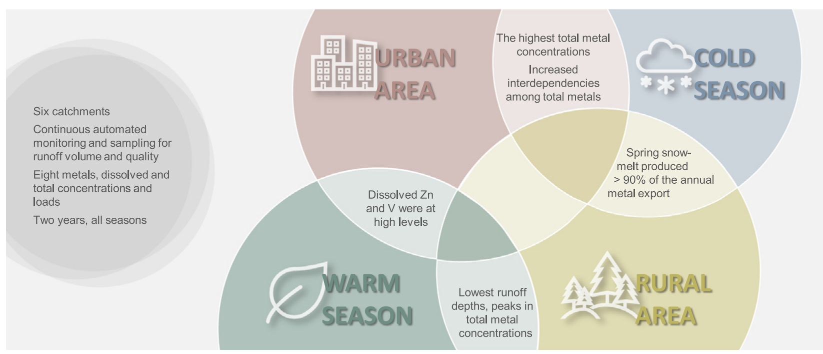
HIGHLIGHTS

- Impact of urban land use on metal export was studied by monitoring six catchments.
- Continuous monitoring, automatic sampling and statistical modelling were performed.
- Urban intensity increased seasonality in concentrations, especially for Zn and Cu.
- Highest total metal load occurred in winter; seasonality in dissolved metals was modest.

GRAPHICAL ABSTRACT



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ABSTRACT

Urban hydrology is characterized by increased runoff and various pollutant sources. We studied the spatio-temporal patterns of stormwater metal (Al, V, Cr, Mn, Fe, Cu, Zn, and Pb) concentrations and loads in five urbanized and one rural catchment in Southern Finland. The two-year continuous monitoring revealed a non-linear seasonal relationship between catchment urban intensity and metal export. For runoff, seasonal variation decreased with increasing imperviousness. The most urbanized catchments experienced greatest temporal variation in metal concentrations: the annual Cu and Zn loads in most of the studied urbanized catchments were up to 86 times higher compared to the rural site, whereas Fe loads in the urbanized catchments were only circa 29% of the rural load. Total metal levels were highest in the winter, whereas the winter peak of dissolved metal concentrations was less pronounced. The collection of catchment characteristics explained well the total metal concentrations, whereas for the dissolved concentrations the explanatory power was weaker. Our catchment-scale analysis revealed a mosaic of mainly diffuse pollutant sources and calls for catchment-scale management designs. As urban metal export occurred across seasons, solutions that operate also in cold conditions are needed.

1. Introduction

Urbanization significantly modifies hydrological characteristics of an area; it increases runoff depths and peak flows, elevates pollutant levels, and introduces new pollutants (Sillanpää and Koivusalo, 2015; Ferreira et al., 2018; Müller et al., 2020). Increasing imperviousness together with

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intensive land use are focal determinants of runoff pollution in cities (Goonetilleke et al., 2005; Grimm et al., 2008). Urban runoff is unanimously a significant pollutant pathway, as it is usually conveyed untreated to nearby aquatic systems (Fletcher et al., 2013; Cettner et al., 2014). Metals in particular have a complicated role in urban areas as they are simultaneously essential trace elements for living organisms, and damaging to biota in excessive concentrations and via bioaccumulation (Fu and Wang, 2011; Nystrand and Österholm, 2013). Further, the organisms' resistance to chemical transformation (Davis and Birch, 2010) poses a challenge to management practices, as some metals (e.g., Cu, Pb, and Zn) have been included into the European Water Framework Directive (Directive 2000/60/EC).

Metals leach from urban catchment either in dissolved form, when they are highly mobile and bioavailable, and in particulate form, having the potential of transforming into dissolved form. Their export is strongly associated with rainfall and melting, as baseflow from highly urbanized catchment is usually small. Metal exchange from soil surface to overland flow is controlled by environmental conditions, such as temperature, pH, and oxygen (McKenzie and Young, 2013; Zhang et al., 2020), and especially Cd, Cu, and Pb are of concern due to their high persistensy in the environment (Joshi and Balasubramanian, 2010). Following the "exchange layer" theory (Zhang et al., 2020), the thin layer of water closest to the soil or building material surface transfers the dissolved metals from the surface to runoff, which then quickly conveys the pollutants away from the catchment. Mobilization of particulate-bound metals is linked to crustal leaching, corrosion, the presence of organic material, and the erosive power of rainwater when hitting for example building surfaces (Blecken et al., 2012; Joshi and Balasubramanian, 2010). Overall, fragmentation of land use, water retention times, and the level of metals accumulated in the soil are known to control metal export from the catchment (Graney and Eriksen, 2004; Miranda et al., 2022).

An increasing body of literature reports contradicting views on the urban water problems, thus rendering local runoff management challenging (Rodak et al., 2019). The current diversity of sampling designs with limited spatial or temporal coverage undermines the potential of understanding the problem holistically. Thus, to achieve a more comprehensive understanding of the urban pollution (including metals) problem, continuous, all-season catchment-scale research on urban pollutant export is needed (Müller et al., 2020). Firstly, urban runoff metal studies traditionally focus on a specific surface, such as roads (Hallberg et al., 2007; Helmreich et al., 2010) while experimental studies at the catchment scale that include an array of surface types are scarce (Bressy et al., 2012; Valtanen et al., 2015). Road-scale studies emphasize traffic as the main pollutant source, especially due to abrasion and exhaust (Liu et al., 2018; Du et al., 2019). Metal build-up on roads is known to be higher than on roofs (Egodawatta et al., 2009). However, as roads cover only a small portion of the catchment area, the catchment water quality assessment cannot solely be based on road studies. Secondly, stormwater studies often rely on discrete temporal monitoring, such as grab sampling or sampling only during rainfall events (cf. Kayhanian et al., 2008), with a limited number of samples (Thompson et al., 2021). Thirdly, metals should be studied for their dissolved and total fractions, as the metals relevant at road environments often occur in the dissolved phase exposing the receiving ecosystems to a considerable pollution risk (Huber et al., 2016). Finally, the urban-derived metal problem is difficult to evaluate due to the lack of long-term data on the baseline concentrations.

This spatial complexity is further complicated by seasonality and related activities in cold climate areas. Similar to snow ploughing and application of anti-skid substances, traffic emissions and other combustion processes are highest during the cold season, both of which increase the transport of road-derived materials in winter-time runoff (Marsalek et al., 2003; Reinosdotter and Viklander, 2007). Hitherto, only a few studies have reported urban water quality in these settings (Valtanen et al., 2014; Sillanpää and Koivusalo, 2015).

Catchment metal build-up derives from both lithospheric and anthropogenic sources (Egodawatta et al., 2009). The primary objective of this research was to challenge the assumption that the key land use classes are the key determinant for the catchment metal export (c.f. Miranda et al., 2022). We explore the non-linear relationship between catchment characteristics and water quality to better understand how different types of catchments produce metal export, and how seasonally sensitive the export is. This study is based on a novel time series data from six Finnish catchments with different degrees of land use intensities and an extensive data set of concentrations of several metals and their fractions, runoff volume, precipitation, and temperature. At these sites runoff was continuously monitored, and composite samples were collected for aluminum (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), and lead (Pb). Nickel (Ni), arsenic (As), cadmium (Cd), and tin (Sn) were also monitored, but were excluded from the analysis as their concentrations were mainly below the detection limit. We hypothesize that urban land use intensity increases temporal and seasonal variation of hydrological processes and thus metal export, and that dissolved metals are more strongly controlled by land use intensity compared to the total fractions of the same metals.

2. Material and methods

2.1. Study catchments

The study was conducted at six catchments in southern Finland (Fig. 1, Table 1). Three catchments were located in the city of Helsinki (60° 2′ N 25° 0′ E; population 628,000), residing by the Baltic Sea, and three in an inland city of Lahti (60°59′ N, 25°39′ E; population 103,000), which is ca. 100 km north from Helsinki.

The study area is characterized by a cold continental climate (Peel et al., 2007) with four distinct seasons: a long winter with snow accumulating from December to February, followed by an intermittent snowmelt season (March–May), warm summer (June–August) and cool fall (September–November). In terms of mean annual temperature, the studied years 2013–2015 in both Helsinki (7.0–7.8 °C) and Lahti (5.5–6.0 °C) were warmer than the climatological reference period 1981–2010 (5.9 °C in Helsinki and 4.5 °C in Lahti). In Helsinki, the annual precipitation (594–645 mm) was close to the climatological mean for 1981—2010 (655 mm), whereas in Lahti, year 2014 (523 mm) was drier than the long-term average (636 mm) (Supplementary Table S1; Pirinen et al., 2012).

The study catchments were selected according to their imperviousness (Fig. 1) and labelled according to the city (L for Lahti, H for Helsinki) and to their percentage of the catchment imperviousness. All catchments represent typical housing areas without industrial activities or large commercial properties such as shopping malls (detailed descriptions for the Helsinki and Lahti catchments can be found in Krebs et al., 2014; Valtanen et al., 2014; and Taka et al., 2017). The five urban catchments are compared to a fully rural L0% catchment for a reference baseline for metal concentrations and loads. The catchments were delineated with geospatial analytical tools in QGIS and GRASS GIS (see Warsta et al., 2017) and the delineations are based on a digital elevation model (spatial resolution 2 m, elevational resolution 0.1 m; NLS, 2014) and sewer network data.

2.2. Runoff and water quality data

Stormwater monitoring stations, located at the stormwater sewer outlet of each catchment, collected runoff data and water samples continuously for 22 months (from September 2013 to June 2015). Each station was equipped with an ultrasonic flow meter (Nivus) which monitored the flow rate (l/s) with 1-minute resolution (part of H36% data was measured with 5-min resolution). Occasional gaps in the Helsinki data were simulated with SWMM model (Rossman, 2015), and the simulated runoff was assessed against observed runoff (see Warsta et al., 2017; Niemi et al., 2017). Runoff data gaps in L0% were excluded from the analysis. Total runoff depths (mm) were calculated from cumulative flow data measurements and catchment area. Due to occasional gaps and other challenges in the

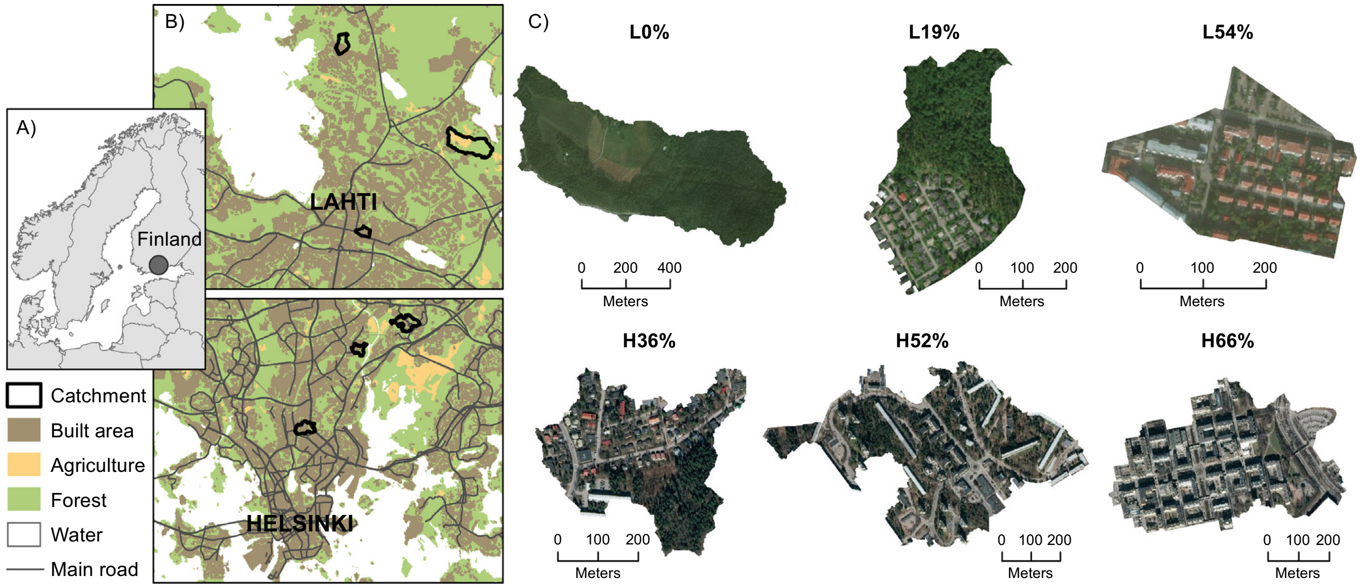

Fig. 1. Location of the studied cities – both locating within the dark dot – in southern Finland A), and the detailed aerial images of the catchments C) (ESRI, 2019). The catchments are labelled according to the city (L for Lahti, H for Helsinki) and to their percentage of the catchment imperviousness. City labels in B) indicate the location of city center (SYKE, 2015).

observed runoff data in Helsinki catchments, temporally continuous runoff was simulated at 4-minute intervals using the SWMM model (for the simulation process, see Taka et al., 2017).

An automatic water sampler (Aquacell) collected flow-proportional subsamples (á 200 ml) based on the accumulated runoff volume and merged them into a composite sample stored in fridge. One composite sample represented one and two-week periods in Helsinki and Lahti respectively. Water samples were analyzed for soluble (hereafter dissolved; only in Helsinki sites) and total concentrations of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Sn and Pb. For the analysis of dissolved metal concentration analyses, the samples were filtered through a 0.45 μm membrane filter (ISO 17294-2) and preserved in HNO3 (67% suprapure). For total metal concentrations, unfiltered samples were preserved in HNO3 (67% suprapure). The samples were stored in the dark and below +4 °C, and analyzed using plasma mass spectroscopy (ICP-MS) complying with 3015A (EPA, 2019) and ISO 17294-2 (ISO, 2003) (see Taka et al., 2016). Only elements with ≥95% of values above limit of detection (LOD) were used in the analysis; thus, Ni (LOD 60.6 ppb), As (LOD 2.57 ppb), Cd (LOD 0.30 ppb), and Sn (LOD 0.23 ppb) were excluded. For concentrations below the limit of detection (LOD), a common substitution method [LOD/√2] was assigned, as it produces the smallest errors compared to traditional methods of [LOD] and [LOD/2] (Ganser and Hewett, 2010; Hornung and Reed, 1990).

Table 1
Characteristics of land cover and anthropogenic activity in the study catchments in the cities of Lahti (Krebs et al., 2014) and Helsinki. The catchments are labelled according to the city (L for Lahti, H for Helsinki) and to their percentage of the catchment imperviousness.

	Unit	Catchments in city of Lahti			Catchments in city of Helsinki		
		L0%	L19%	L54%	H36%	H52%	H66%
Area	ha	51	13	7	14	34	25
Catchment description		Natural and thinned forest, uncultivated field	Residential; single-family housing	High-density residential and commercial area, apartment buildings	Single-family housing, continuous forest	Residential suburb, fragmented green area	Densely built commercial and housing area; continuous concrete floor for pedestrians
Total impervious area	%	0	19	54	36	52	66
Number of composite water samples		27	35	41	66	67	51
Catchment mean slope	%	11.1	10.8	6.5	5.3	7.4	6.0
Roofs	%	0.4	10.8	19.2	12.4	12.9	19.5
Asphalt	%	0	6.9	25.4	14.5	26.4	20.1
Stone paver, rock outcrops	%	0	0.9	7.5	1.9	7.8	0.3
Sand, gravel	%	1.4	0.3	16.4	4.1	5.2	7.5
Vegetation	%	93.7	81.0	31.4	65.4	47.4	26.7
Open water bodies	%	0	0	0	0	0.3	0
Stormwater pipeline density	km/km^2	0	11	29	10.2	7.8	11.8
Dominant soil type		Sand and gravel till, clay and silt deposits	Sand and gravel till, clay and silt deposits	Land fill	Rocky ground	Rocky ground	Land fill
Traffic		No data	100% mix-used streets and walkways	30% of streets for commutation, 70% mix-used streets and walkways	4,000 vehicles/day	12,000 vehicles/day	62,400 vehicles/day

2.3. Data analysis

The data were aggregated to winter (December–February), spring (March–May), summer (June–August) and autumn (September–November) periods. "Warm period" refers to summer and autumn seasons, when precipitation mainly occurs as rain, while "cold period" refers to winter and spring seasons, when precipitation is mostly snow or rain-on-snow. In the studied catchments, snow usually melts by early April. In some years, freezing temperatures occur already in autumn at the end of October.

Correlations among all water quality data were tested using pairwise correlations (Pearson correlation coefficients for log-transformed data). The differences in weekly metal concentrations and the corresponding loads between the catchments and the seasons were tested for significance using Wilcoxon signed-rank test. Hierarchical clustering analysis (HCA) was used to examine the similarity in metal concentrations in the temporal (i.e., weekly and seasonal) data. HCA produces hierarchical clusters of metals by using weekly concentrations, first combining metals with the highest correlation into clusters, whereby the metals with the greatest distance are the least similar. The clusters that join closely have a stronger correlation with each other. This clustering was performed with a multiscale bootstrap approach (999 runs) and the results were reported as approximately unbiased (au) p values (Suzuki and Shimodaira, 2019). The number of clusters was defined by the data. For a cluster with au p value >95, the hypothesis that "the cluster does not exist" is rejected with 0.05 level of significance. All data processing and analyses were performed using R version 3.4.3 (R Core Team, 2020).

Nonmetric multidimensional scaling (nMDS; as implemented in R-package *vegan*) (Oksanen et al., 2019) was used to identify the main directions of variation. First, the metals were scaled using *metaMDS* function, which uses several random starts to find the stable scaling of the data. The explanatory catchment variables were then fit into this scaled ordination to examine their effects on the metal concentrations. The significance for each variable's linear fit was tested using a permutation approach with 999 repeats. Each metal is analyzed separately in the model. The adequacy of nMDS representation is assessed with stress values, where <0.05 indicates an excellent representation without any misinterpretation; values <0.1 gives a good ordination without any real prospect of misleading interpretation, and <0.2 produces a potentially useful two-dimensional picture (Clarke and Warwick, 2001). nMDS was conducted for dissolved and total concentration data separately. Finally, redundancy analysis (RDA, performed in R using *vegan* package) was carried out to illustrate the main trends in the variables controlling the water quality. Both nMDS and RDA are widely used in community ecology to evaluate the explanatory power of environmental variables in the community composition.

3. Results

3.1. Runoff

Both the volume and the quality of urban runoff showed strong spatio-temporal variation. Runoff generation highlighted the differences between the catchments: during the 22-month study period, total runoff depths were 223 mm (H36%), 326 mm (L19%), 355 mm (H52%), 392 mm (L54%), and 579 mm (H66%). Despite a 5-month gap in L0% data, the catchment produced 329 mm of runoff, indicating a high runoff generation potential comparable to urban study catchments.

Seasonal variation in urban catchment runoff peaks was modest (Supplementary Fig. S1), indicating that urban runoff patterns strongly resemble seasonality in precipitation. This effect was best reflected by the ratio of runoff to precipitation at the study catchments in Lahti (Supplementary Fig. S2), which represented opposite ends of land use intensity (from 0% to 54% imperviousness) but shared similar weather conditions. The largest seasonal variation in runoff was observed at the rural L0% catchment, where unlike in the urban catchments the runoff depths were considerably higher in the spring than in the summer growing season. In Helsinki, the runoff depths increased with catchment imperviousness (Fig. S1).

3.2. Metal concentration patterns

In terms of total metal concentrations (Fig. 2), Cu and Zn had a strong positive relationship with urban land use ($p \leq 0.05$), whereas Al, Fe, Cr, and Mn concentrations decreased with increasing catchment imperviousness. However, these trends were partly masked by the residential catchment L54% in terms of its highest concentrations and their widest range; in fact, L54% had the highest median concentrations for all total metals except Cu (highest medians in H52% and H66%). Additionally, the sparsely built H36% stood out with high total Pb concentrations, even though all other metals occurred with moderate concentrations.

Compared to total metals, concentrations of dissolved Cu and Zn, but also V and Cr were positively and significantly ($p \leq 0.05$) related to catchment imperviousness (Fig. 3). In contrast Al, Fe, and Pb concentrations were lowest in the most urbanized H66% catchment, whereas the highest median concentrations of dissolved Al, Mn – and unexpectedly for Pb – were detected in H36% with a large, forested area. When examining all metals simultaneously, the best explanatory variables for both dissolved and total concentrations were catchment imperviousness ($R^2 = 0.24$ and 0.12, respectively) and vegetation coverage ($R^2 = 0.24$ and 0.11), whereas pipeline density and precipitation were insignificant environmental variables (Supplementary Fig. S5). The environmental explanatory variables, such as land use and weather (see Supplement Fig. S5), performed better in explaining total concentrations than dissolved concentrations. However, the first axis in RDA explained 76% of the variance in dissolved metals and 75% in the total metal concentrations. RDA highlights the primary importance of land use in explaining the metal levels in water, while the seasonality was the second primary factor (Supplementary Fig. S6).

3.3. Seasonal variation in metal concentrations

The highest total metal concentrations in the urban Helsinki catchments were usually observed during winter (Fig. 4). In contrast, L54% had the highest concentrations usually in spring. In some cases, such as Cu at the H52% and H66% (Fig. S4), and Zn and Pb at the L54%, total metal concentrations were constantly high, showing little-to-no seasonality. The explanatory power of seasons was relatively similar for both dissolved and total concentrations ($R^2 = 0.012$ and 0.015, respectively; Supplementary Fig. S5).

Pairwise correlations among all studied total metals increased with imperviousness in the cold season, but this pattern was absent in the warm season (Fig. S3). In L0%, correlations among the studied metals were similar in both seasons. The seasonal concentrations in H36% remained at a moderate level, except for Pb, for which the concentrations were similar to L54% (Fig. 4). However, the seasonality of Pb concentrations between these catchments was completely different. The L54% catchment also differed from other catchments, with consistently higher Zn concentrations throughout the year and extremely high Cd concentrations in summer.

The sites with low median metal concentrations were also characterized by moderate seasonal variation. Overall, seasonal variation in metal concentrations was pronounced in the most urban catchments, especially in L54%. The seasonal differences in metal concentrations were statistically significant ($p \leq 0.05$) for all Helsinki catchments and metals, and in L54% for all metals except for Zn. At L19%, statistically significant seasonal variation was observed for Al, Fe, and Cr. While significant seasonal variations were observed for total metal (Al, Pb, Zn, Cu, Mn) concentrations (Figs. 4, S4), seasonality in dissolved concentrations was far less pronounced (Fig. 5). Similarly, the wintertime peaks detected for total concentrations of V, Cr, and Fe were not observed for dissolved concentrations. In L0%, the high concentrations for some metals in autumn (Al, V, Cr, Fe, and Pb) and summer (Mn) were the main sign of seasonality.

The clustering analysis further revealed metals with potentially similar sources and pathways. The differences between the cold and warm season suggested that, for some catchments and metals, the sources and pollutant transport mechanisms were season dependent (Fig. 6). In the warm season, in L19% only three metals (Fe, Al, Mn) formed a

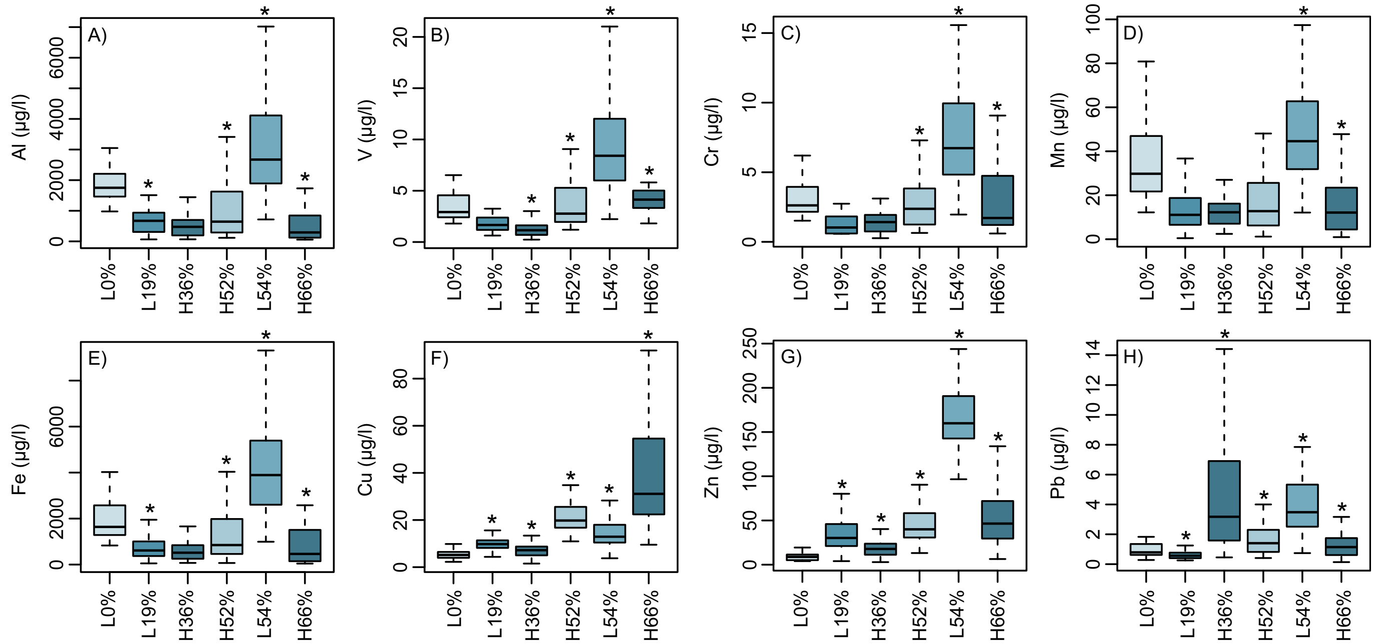

Fig. 2. The median concentrations (µg/l) of the total metals (Al, V, Cr, Mn, Fe, Cu, Zn, Pb) at the study catchments. Boxplots present the median, first and third quartiles, and whiskers indicate the maximum 1.5 × IQR (interquartile range). The analysis is based on weekly and biweekly composite samples. Asterisks in the catchment box plot indicate a statistically significant difference to the catchment with a lower imperviousness ($p \leq 0.05$). For example, asterisk at H66% indicates a statistically significant difference to L54%. For the purpose of clarity, outliers are not shown. Note differences in the magnitude of values on the y-axis.

statistically significant cluster, whereas in H36% and H66% all the metals (except for V in H66%) formed significant clusters. The results highlighted the catchment-specific temporal behavior of metal concentrations without clear patterns across the catchments. In Helsinki, all sites across the seasons formed a statistically significant Cu-Zn cluster (except for H52% in the warm season), which was not present at the Lahti sites (except for L54% in the cold season); in Lahti, Zn stood out from other metals across the catchments and seasons.

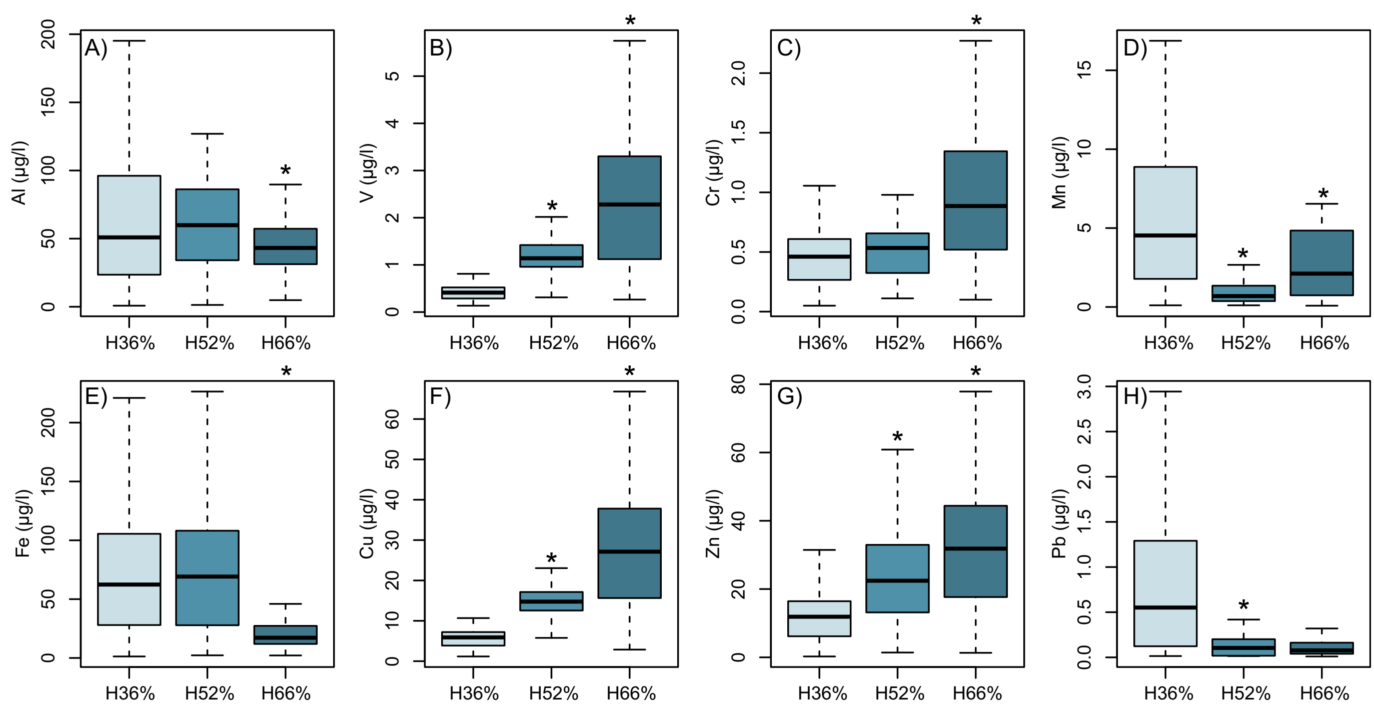

Fig. 3. Dissolved metal concentrations in three catchments in Helsinki. Boxplots present the median, first and third quartiles, and whiskers indicate the maximum 1.5 × IQR (interquartile range). The analysis is based on weekly and biweekly composite samples. Asterisks in the catchment box plot indicate statistically significant difference to the catchment with less imperviousness ($p \leq 0.05$). For example, asterisk on H66% indicates statistically significant difference to L54%. For purposes of clarity, outliers are not shown. Note differences in the magnitude of values on the y-axis.

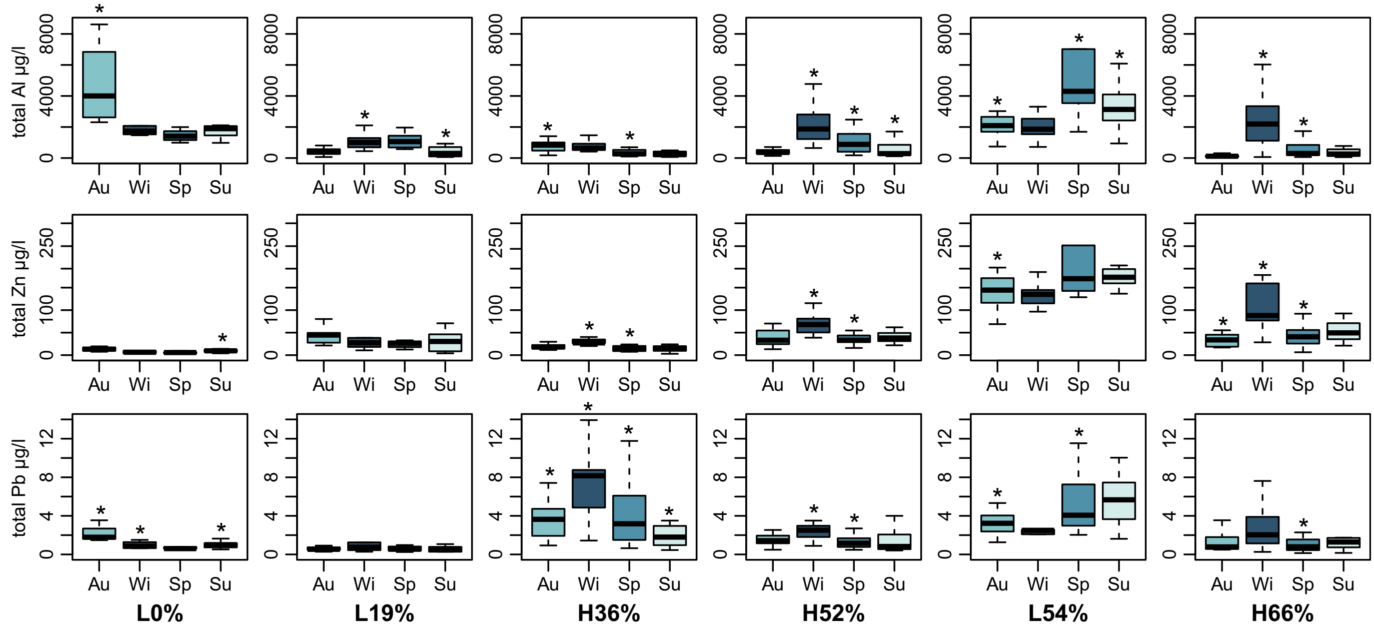

Fig. 4. Seasonal total metal concentrations (µg/l) of total Al, Zn, and Pb. See Supplement Fig. S4 for all studied metals. Boxplots present the median, first and third quartiles, and whiskers indicate the maximum 1.5 × IQR (interquartile range). The analysis is based on weekly and biweekly composite samples. Asterisks in the catchment box plot indicate a statistically significant difference to the preceding season ($p \leq 0.05$). For example, the asterisk on winter indicates statistically significant difference between autumn and winter. For purposes of clarity, outliers are not shown. Au = autumn (Sep—Nov), Wi = winter (Dec—Feb), Sp = spring (Mar—May), Su = summer (Jun—Aug).

3.4. Total metal loads across the urban gradient

Spatial variation for metal loads was similar across all the studied metals, except for Cu and Pb. The highest annual total metal loads were observed at the most urbanized catchments L54% and H66% (Fig. 7), where the loads for Zn, and Cu were up to 76 and 86 times higher than in the rural catchment. However, the relationship between loads and catchment imperviousness was not linear. For most metals, the highest loads occurred in L54% due to high concentrations, although H66% produced the largest annual runoff volumes among all the catchments. For Cu, the highest concentrations were observed in H52% and H66% (Figs. 2 and 3), giving rise to the largest annual loads at these catchments. Despite yielding otherwise-negligible loads compared to other catchments, H36% produced Pb loads comparable with more densely built catchments.

Based on partial data from rural L0% catchment, two six-month periods (June—November 2014 and March—August 2015) were used

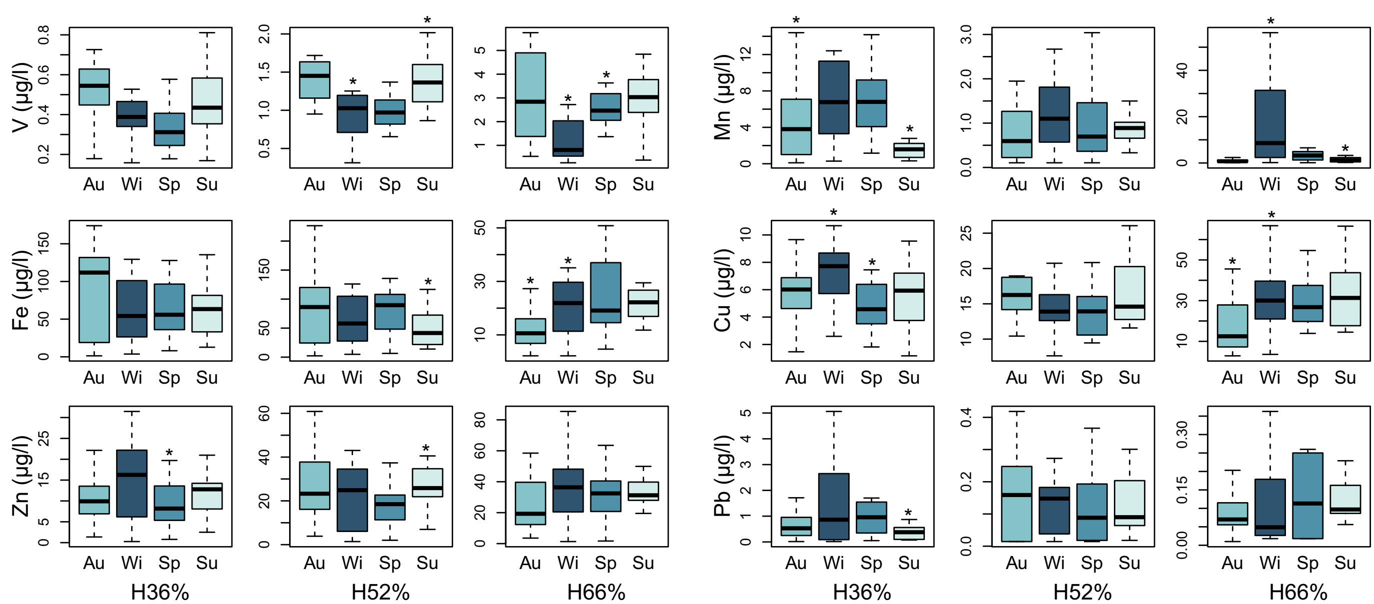

Fig. 5. Seasonal dissolved metal concentrations (µg/l) of V, Mn, Fe, Cu, Zn, and Pb at the study catchments in Helsinki: H36%, H52%, and H66%. Boxplots present the median, first and third quartiles, and whiskers indicate the maximum 1.5 × IQR (interquartile range). Analysis based on weekly and biweekly composite samples. Asterisks in the catchment box plot indicate statistically significant difference to the preceding season ($p \leq 0.05$). For example, the asterisk on winter indicates statistically significant difference between autumn and winter. For purposes of clarity, outliers are not shown. Dissolved metal concentrations were not available for the catchments located in Lahti. Au = autumn (Sep—Nov), Wi = winter (Dec—Feb), Sp = spring (Mar—May), Su = summer (Jun—Aug).

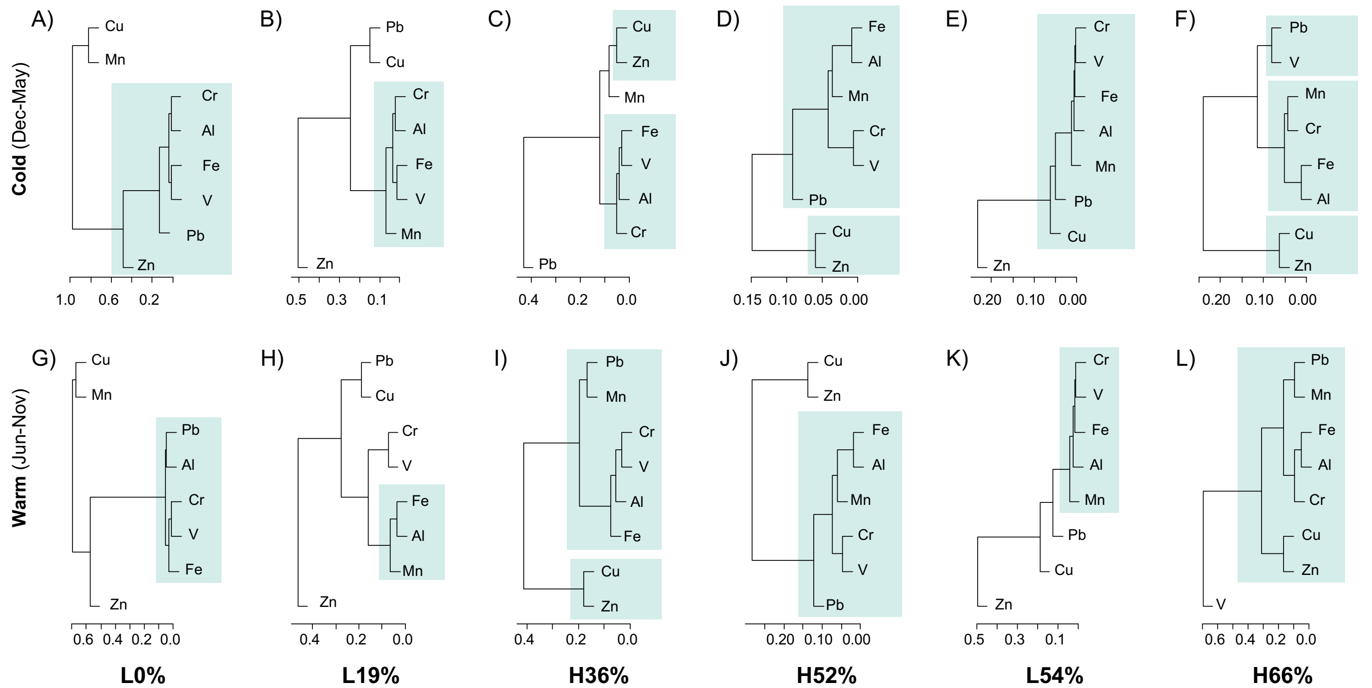

Fig. 6. Hierarchical cluster dendrograms of total metal concentrations for both cold (subfigures A—F) and warm (G—L) seasons for each catchment L0% - H66%. Analysis based on weekly and biweekly composite samples. Each horizontal distance indicates the degree of correlation between the metals and clusters, i.e. the sooner one cluster joins another metal, the stronger is their correlation. The colored rectangle encloses a group strongly supported by the data (approximately unbiased $p \geq 95$).

to estimate metal loads (Table S3). The difference to urban catchments was strong for Zn, Cu, and Pb, whereas for other metals the loads were comparable to the low-density residential areas L19% and H36%. The loads from the L0% catchment were particularly large in the period March—August 2015, likely due the late spring snowmelt that produced over 90% of the metal loads for the entire period. In urban catchments, however, the contribution of spring loads was considerably smaller (7–41% and 2–71% depending on the year) and depended on both the catchment and the metal. Additionally, the Fe loads were over three times the loads of the most urbanized H66% (Supplement Table S3).

In the Helsinki catchments, a substantial part of metal exports in the cold period were produced already during the mid-winter months (Jan—Mar) (Supplement Figs. S7–S8), whereas in the Lahti catchments (situated ca. 100 km inland), the cold period metal loads were delayed towards spring months. In general, the two years of active monitoring yielded varying seasonal pollution patterns in the urbanized catchments and, hence, no season overpowered others in metal export.

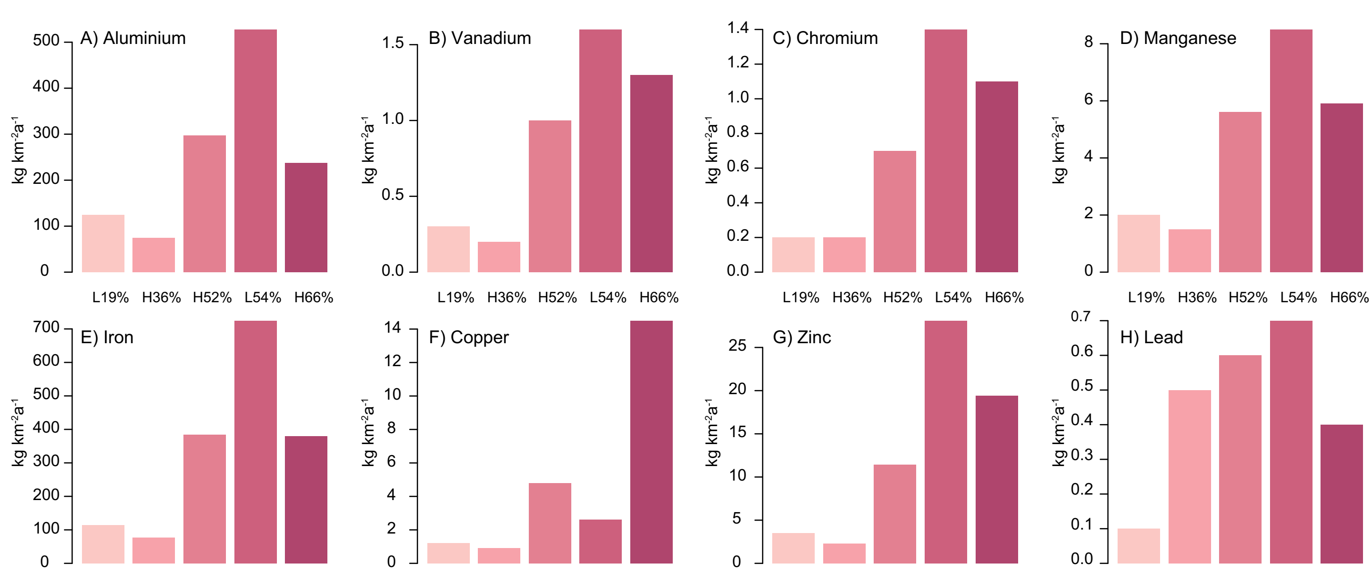

Fig. 7. Average annual total metal loads at each catchment. The annual loads for the rural L0% catchment were not determined due to gaps in the flow data. Note the different y-axis scale for each metal (A–H).

4. Discussion

Our results emphasize the complexity of the relationships of metals with catchment characteristics and seasonality. The imperviousness in Helsinki catchments increased runoff depth but decreased its seasonal variation. The shift of annual runoff towards a more temporally homogeneous distribution is known to result from increased runoff generation during the growing season in cold climatic conditions. However, only a few studies have documented long-term runoff generation patterns across the urban-rural gradient (Valtanen et al., 2014; Sillanpää and Koivusalo, 2015). The importance of identifying and including dissolved fraction in stormwater strategies was highlighted by the large dissolved fraction of metals and the somewhat spatially and temporally arbitrary concentrations observed (Huber et al., 2016). During peak flows, highest loads of dissolved metals originated from urban and traffic areas, and especially Cu, Zn, and Pb have been observed at levels above the freshwater criteria (McKenzie and Young, 2013). This paper illustrates how the dissolved phase of a metal export is also seasonally sensitive.

This new understanding — based on continuous monitoring — challenges traditional assumptions, according to which (1) water pollutant levels increase with increasing urban intensity; (2) traffic is the main source of urban water metal pollution; and (3) in cold climate regions, metal export is dominated by the spring melting season.

4.1. Concentrations cannot be predicted by land use intensity

The continuous monitoring at the six catchments demonstrated that the relationship between urban land use intensity and elevated metal concentrations is not straight forward; interestingly, the more urbanized catchments experienced a larger range with higher concentrations only for some metals. Of these, Cu and Zn concentrations in particular (both dissolved and total) increased with growing land use efficiency, with their concentrations at times above water quality guidelines (Alm et al., 2010; Table S4). In urban runoff, Cu and Zn are reported to originate from building materials, corrosion of metal structures, and heavy duty traffic (Davis and Birch, 2010; Liu et al., 2018) with manyfold higher loads from aged surfaces (Charters et al., 2021). Heavy metal export from roofs especially contains a significant dissolved phase (Charters et al., 2021), while the particles may remain on the surfaces and mobilize only during larger rain events (Egodawatta et al., 2009).

The L54% catchment with the highest average metal concentrations highlights how the metal export from a catchment is not a linear function of the catchment land use intensity. In contrast, total Al, Fe, Cr, and Mn concentrations were commonly the highest in non-urban sites (except for L54%), indicating lithogenic and erosion-related sources to be important for these metals (Batlle-Aguilar et al., 2014; Troch et al., 2015). The importance of these sources is, however, diminished by impervious pavements, indicating these substances may not be of primary concern in urban areas compared to other metals with a clear link to urban land uses. Al, Fe, Cr, and Mn are easily oxidized from granite bedrock, which is dominant in our catchments (Heal et al., 2002; Miller et al., 2003). The reason for the high loads of these metals in L54% remains obscure but may relate to soil properties, as the majority of the export occurred in spring and summer. Despite these high concentrations in non-urban sites, L54% produced the largest loads of all total metals (except for Cu).

The concentrations of metals in urban runoff should be considered in association with the health and ecological risks they pose. The need for hazard indices and concentration thresholds has been discussed extensively (c.f. Crabtree et al., 2009; Ma et al., 2016) and few studies have examined the usefulness of biomarkers (Yanagihara et al., 2018). Even though metals in urban runoff are one of the main concerns due to their bioavailability and thus toxicity at levels common in stormwater (Ma et al., 2016), their dissolved fractions have been inadequately examined (Flanagan et al., 2019). In our study the different behavior between dissolved and total concentrations merits recognition: Pb and Cr were mainly particle-bound, while Zn and Cu were mainly in dissolved fraction. Worryingly, median total Zn concentrations in the most urbanized sites (L54%, H52%, H66%) were constantly above the values set in water quality criteria (Alm et al., 2010), and median Cu concentrations were above the proposed guidelines in H52% and H66%.

4.2. Seasonality highlights the eccentricity of metals

This study reveals significant temporal variation of metal sources. While dissolved concentrations indicated no clear dependency on seasons, the highest total metal concentrations in urban areas were observed in winter (in L54%), even though high temperatures increase metal release from, for example, building materials (Müller et al., 2019). Roofs seem to be the key source for Cu in Helsinki catchments, as the levels were high across seasons and elevated with warmer seasons. The correlations among metals were stronger in the cold season (compared to warm) only in the most urbanized catchments, potentially due to heating and deicing practices as intensive use of chloride is known to increase mobilization of dissolved metals (Reinosdotter and Viklander, 2007; Novotny et al., 2009; Flanagan et al., 2019).

Significant seasonal variation in some dissolved (V, Cu) and total metal (Al, Zn) concentrations were evident (Fig. 5), suggesting that temporal variation should be included into monitoring and management practices. Further, the common assumption that, in cold climate regions, spring is associated with significant pollutant levels (Westerlund et al., 2003; Helmreich et al., 2010) does not always seem to apply to urban catchments. Concentrations of dissolved metals were especially high in winter, indicating that metal mobilization and export occurs throughout the year. This is supported by Sillanpää and Koivusalo (2015), who observed urban development to fragment the cold season runoff into numerous shorter events, which was particularly pronounced in our coastal Helsinki catchments (Fig. S1). Earlier studies report pollutant loads in the cold season to be strongly controlled by runoff, with land cover having a minor impact, whereas in the warm season the relationship is reversed (Valtanen et al., 2015; Taka et al., 2017). However, the differences of urban runoff among catchments decrease in winter (Sillanpää and Koivusalo, 2015).

The observed seasonality in metal loads illustrates how neglecting winter months can give incomplete information about pollutant export. In Helsinki, metal loads were usually the smallest in spring and highest in summer or winter, depending on the metal. This high winter-time export is alarming when considering the predicted increase in wintertime precipitation and rainfall replacing snowfall (Luomaranta et al., 2019), thus increasing surface runoff, and the importance of snow cover in controlling local albedo and runoff generation (Järvi et al., 2017). Predicted climate change will change seasonality especially in cold-climate regions (EEA, 2017), changing leaching rates and pathways of metals. This, combined with traditional sewer infrastructure, calls for significant onsite treatment solutions.

The differences in measurement designs likely contribute to the differences in concentrations, thus our results may differ from previous studies that focused on specific surfaces or were performed using grab sampling (Table S4). Our study design focused on the whole catchment and was based on sampling design that considered runoff and long-term temporal variations. Besides metal concentration per se, the fractionation of metals should also be considered in management (Maniquiz-Redillas and Kim, 2014; Lange et al., 2020).

4.3. The urban mosaic of metal sources

The identified metal-specific spatio-temporal variation of water quality highlights how it is controlled by a plethora of catchment characteristics and dynamic activities. For instance, metals leaching from pavements are controlled by static variables, such as the material, but also by more dynamic factors, for example, by speed limit and traffic density (De Silva et al., 2016). Winter-time loads are also affected e.g. by heating, vehicle cold start, studded tires, and de-icing practices. In relation to land cover and land use data, stormwater studies would benefit from human activity profiles of, for example, traffic characteristics and irrigation (Järvi et al., 2017).

The understanding of the interplay between natural and anthropogenic sources is incoherent; dissolved metals have been linked to land use and total metals to soil (Taka et al., 2016), but dissolved metals have also been linked to soil erosion (Batlle-Aguilar et al., 2014; Troch et al., 2015). Although soil weathering is an important internal source of Zn, Cu, and Pb in boreal forests (Starr et al., 2003), the concentrations of these metals increased with urban land use intensity.

As the cause-effect relationships between catchment land use and water quality are difficult to define (Goonetilleke et al., 2005; Wijesiri et al., 2021), studies on urban runoff metals should focus on catchment scale phenomena. This assessment of the contribution of sources and pathways on metal export (c.f. Tuomela et al., 2019) should be complemented with a micro-scale sampling to identify the mainly diffuse sources for management (Davis and Birch, 2010; Supplementary Table S4). For example, the unexpectedly high Pb levels and their independence from other metals in H36% showcases the catchment-specific sources. The observed Pb load likely originated from old building structures, such as roofs and paints (Davis and Birch, 2010; De Silva et al., 2016), and the winter-time elevated levels are likely linked to rain-on-snow events, daytime roof heating, and short-term melting (Semadeni-Davies et al., 2001; Oberts, 2003). This cold season challenges the performance of green infrastructure solutions to remove metals from stormwater. Green infrastructure, such as rain gardens and wetlands contain numerous biological and chemical processes, such as absorption, dispersion, and accumulation, to remove heavy metals from water. However, these processes are very sensitive to environmental conditions including climate, water pH and conductivity, vegetation and fauna, soil structure and depth. Moreover, the knowledge of dissolved metal removal is insufficient (Sharma et al., 2021; Sharma and Malaviya, 2021).

An empirical study such as ours is not without its limitations. The study design and the selection of catchments showcase specific urban areas with their pollutant sources and pathways. For example, the H36% high Pb levels, or L54% extremely high concentrations of several metals cannot be generalized to all urban areas. Further, the sudden gaps in the data, caused by freezing devices, electricity breaks, or other circumstances hinder our time-series assessment of the metal export. Furthermore, the explanatory environmental variables used in this study may not be ideal for stormwater quality modelling, which calls for a wider set of suitable environmental data that better describe the land use and anthropogenic activities. Finally, a longer monitoring time would likely help with distinguishing the factors that cause potential differences in water quality between the years.

5. Conclusions

Continuous, long-term monitoring of runoff from six catchments revealed seasonality of eight metals and their complex relationships with land use intensity in urbanized milieus. Zn, Cu, and Cr were present predominantly in runoff originating from intensively developed areas, whereas other metals, such as Al, Fe, and Mn, were more prevalent in less urbanized areas. In contrast to most studies operating at road-scale and emphasizing traffic-derived pollutants, we targeted metal pollution at the catchment scale. Our key conclusions are:

- Urban land use intensity increased metal concentrations and their temporal variability for most of the studied metals. Metal export at the urban catchments was evident across the seasons, and the highest total metal concentrations were observed in the winter season. In rural catchment, the growing season increased metal export. Dissolved metal concentrations' seasonal variation, in contrast, decreased with increasing imperviousness.
- A non-linear relationship between urban land-use intensity and metals (in terms of concentrations and loads in runoff) was identified with our novel time series data.
- Only some of the observed concentrations were above the water quality criteria, mainly for Zn and Cu. We thus suggest that the impacts of urbanization on water quality are to be based on key metals, such as Cu, Zn, V, and Cr.
- Strong positive relationships among the studied metals, such as Al-Fe-Mn and Cu-Zn, and their similar seasonal distribution indicate temporally constant, shared sources and pathways.

Based on our long-term monitoring and statistical analyses, heavy land use causes high heavy metal concentrations but only for some metals and the relationship with catchment land use intensity is not linear. These metals should be included into local monitoring programmes. Seasonal variation and the significant fraction of the dissolved phase should be acknowledged.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT authorship contribution statement

Maija Taka: Formal analysis, Investigation, Visualization, Writing - original draft. **Nora Sillanpää**: Conceptualization, Formal analysis, Visualization, Writing - original draft. **Tero Niemi**: Resources, Formal analysis, Writing - original draft. **Lassi Warsta**: Resources, Formal analysis, Writing - original draft. **Teemu Kokkonen**: Project administration, Funding acquisition, Writing - original draft. **Heikki Setälä**: Conceptualization, Project administration, Funding acquisition, Writing - original draft.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152855.

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