



A study of the distribution and composition of pollutants in snow collected from streets and a treatment system for recycling snow in winter cities

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ABSTRACT

In winter, cold cities have a severe shortage of water resources. Snow is a potential water resource, and the effective classification and recycling of snow is, therefore, significant for addressing the sustainable utilization of urban water resources in cities during the winter months. In this study, the water quality and pollutant composition of snow collected along a transect across a typical street were analyzed to develop an on-site treatment technique based on the classification of snow water. The levels of suspended substances, COD, salt, ammonia, and oil in snow from urban streets were relatively high. The salinity, conductivity, and chloride levels were also high due to the application of a snow-melting agent. Twenty-nine major pollutants were identified, and the oily substances were dominated by hexadecane accompanied by toxic substances such as BTEX and naphthalene. Snow can adsorb and receive pollutants from the streets, while becoming a carrier for pollutants. The underground space below city streets is proposed for establishing a snow-melting system. The snow meltwater may be directly discharged into double subsurface tanks if the concentration of suspended substances is less than 200 mg/L. A V-type filtering tank may be used if the concentration of suspended substances is greater than 200 mg/L. This method, which integrates city planning and municipal technology, accomplishes both the recycling and utilization of snow water, as well as the on-site treatment of pollutants.

Keywords: Winter cities; Street section; Snow; Pollutants; Recycling and utilization pattern

1. Introduction

There has been considerable global interest in rain-water management in recent years. However, there is

little research on snow management, especially in China where there is a severe shortage of water resources and a lack of emphasis on the use of water recycling and management. China is widely covered by abundant water resources, and approximately 56%

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of the area of China is covered with snow for more than 30 d on average. The northeastern and western areas are two extremely cold areas [1].

Harbin, which is a typical central city in north-east China, faces a heavy burden of snow removal from the roads to prevent urban disasters in winter. Other winter cities in the world have developed several technologies for snow melting and removal. For example, heat from sea water [2,3] and geothermal energy are used to melt snow on pedestrian streets and parking lots [4,5]. Other technologies for snow melting and removal include cable heat storage, solar heating, ground source heat power, mechanical operations, and chemical methods [6–10]. Unfortunately, many cities in China including Harbin still use traditional ways of removing snow. Mechanical operations are used to transport snow to the suburbs, leading to severe environmental pollution and high costs. These mechanical methods are used because of economic issues and a lack of feasible alternative technologies, such as the use of expensive environmental friendly snow-melting agents and issues associated with heating frozen road surfaces, as well as a lack of ecological awareness regarding the pollution mitigation problems caused by transporting the snow [11–13]. The snow, which contains fewer pollutants during the initial period after falling on the urban streets, is polluted again during the removal and piling process. In particular, $PM_{2.5}$ levels are increased, and the snow has the capacity to adsorb particulate pollutants. Snow, which represents a precious water resource, is been treated properly. Snow on urban streets, as a carrier of pollutants, can easily cause secondary pollution, which is unfavorable for transportation and travel. Snow classification and selection as well as the optimization of treatment processes can be conducted based on fundamental research that includes the analysis of the composition, distribution, and adsorption of pollutants in snow and the water quality of melted snow. Previous work has been performed on the use of recycled snow water [14].

In this paper, the pollutant composition of snow obtained from streets, the distribution characteristics of the pollutants in the city of Harbin, and the quality of the sampled snow were analyzed to propose a classification system for snow collection based on the characteristics of snow water. The underground space below the street is used to establish a snow-melting system. Additionally, the implementation of an extensive processing technique and the facility configuration are presented.

2. Characteristic analysis and classified methods of snow quality in winter

2.1. Experimental materials and methods

Snow collection areas and sampling sources. Snow was collected from a cross-section of West Dazhi Street, which is typical urban street in Harbin. This area is significantly disturbed by humans and vehicles. West Dazhi Street, which runs from east to west, is the one of the most important arterial roads and is located within 60 m of the boundary line of roads. This region is characterized by a central historical area surrounded by museums, squares, commercial buildings, cultural and official facilities, and high-rise buildings. The sampling site was located at the intersection of West Dazhi Street, Quxian Street, and Hujun Street, where the vehicle flow is heavy and provides an additional source of pollution.

Samples were collected between eight to ten hours after a winter snowfall. Snow was also collected during the snowfall events. The sampling sites are marked on an imagery from Google Earth (Map data: Google, CNES/Astrium) as shown in Fig. 1.

Analytical methods for determining the water quality of the snow. COD was determined using potassium dichromate. Total organic carbon (TOC), TC, TN, and inorganic compound (IC) were measured

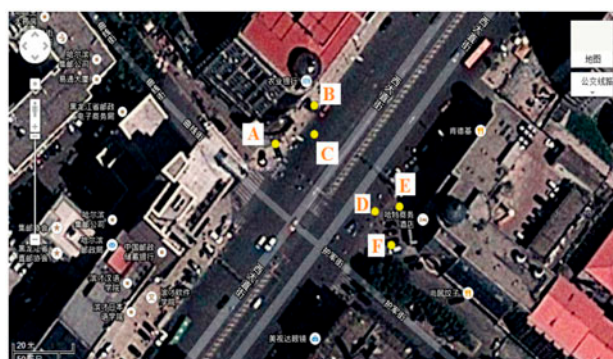


Fig. 1. Distribution of the sampling sites at the street section.

Notes: (A): snow on the sidewalk of the Agricultural Bank of China on West Dazhi Street, with snow on the sidewalk. (B): snow on the sidewalk of the Agricultural Bank of China on West Dazhi Street, snow under the trees on the sides of the motorway and the collected snow. (C) and (D): motorway of the Harbin Institute of Technology on West Dazhi Street, which was a snow-covered motorway. (E): side road of the Harbin Institute of Technology on West Dazhi Street, with snow under the tree behind the bus route. (F): snow on the side road of Harbin Institute of Technology on West Dazhi Street.

using a total organic carbon analyzer (Shimadzu TOC-5000A). Nitrate, chloride, and ammonia nitrogen were analyzed using an ion chromatograph (HIC-20A super) equipped with a conductivity detector and an IC-SA2 analytical column. The amount of oil was determined using three-dimensional fluorescence spectroscopy (Aqua-log) according to the standard method SY/T0530-93.

Gas chromatography (GC, Agilent Technologies 7890A) coupled with mass spectrometry (MS, Agilent Technologies 7890A) was also used to determine the composition of the organic compounds. The operational conditions of the GC/MS system were as follows. The injector temperature was maintained at 250°C. Temperature programming was used to vary the column temperature. The chromatographic column temperature and the initial column temperature were maintained at 35°C for 3 min. The temperature was then gradually increased to 280°C at a rate of 10°C/min and held for 5 min; the ion source temperature of the MS was 240°C. High-purity nitrogen was used as the buffer gas. Diluted samples were prepared using methyl tert-butyl ether (MTBE).

3. Results and discussion

3.1. Quality analysis of snow water obtained from the street cross-section

The analysis of the snow water quality is helpful for understanding the quality of snow for water reuse. The accumulation of pollutants in snow on the street favors the classification of snow water for selecting reasonable methods and basic parameters for the treatment of the snow water. For the street cross-section, where the motorway is the central area and the sidewalks are at the periphery, the suspended substances (SS), pH, salinity, chloride ions, and conductivity were analyzed at points A–F.

As shown in Fig. 2, the pH at different sites along the street cross-section was generally less than 7.0, likely due to the accumulation of acidic substances or the addition of a snow-melting agent from the air. The salinity at the motorway and sidewalk sampling sites was higher, particularly in samples collected from the motorway, which reached 19‰. The same effect was observed with respect to chloride ion concentrations. The presence of the snow-melting agent led to a

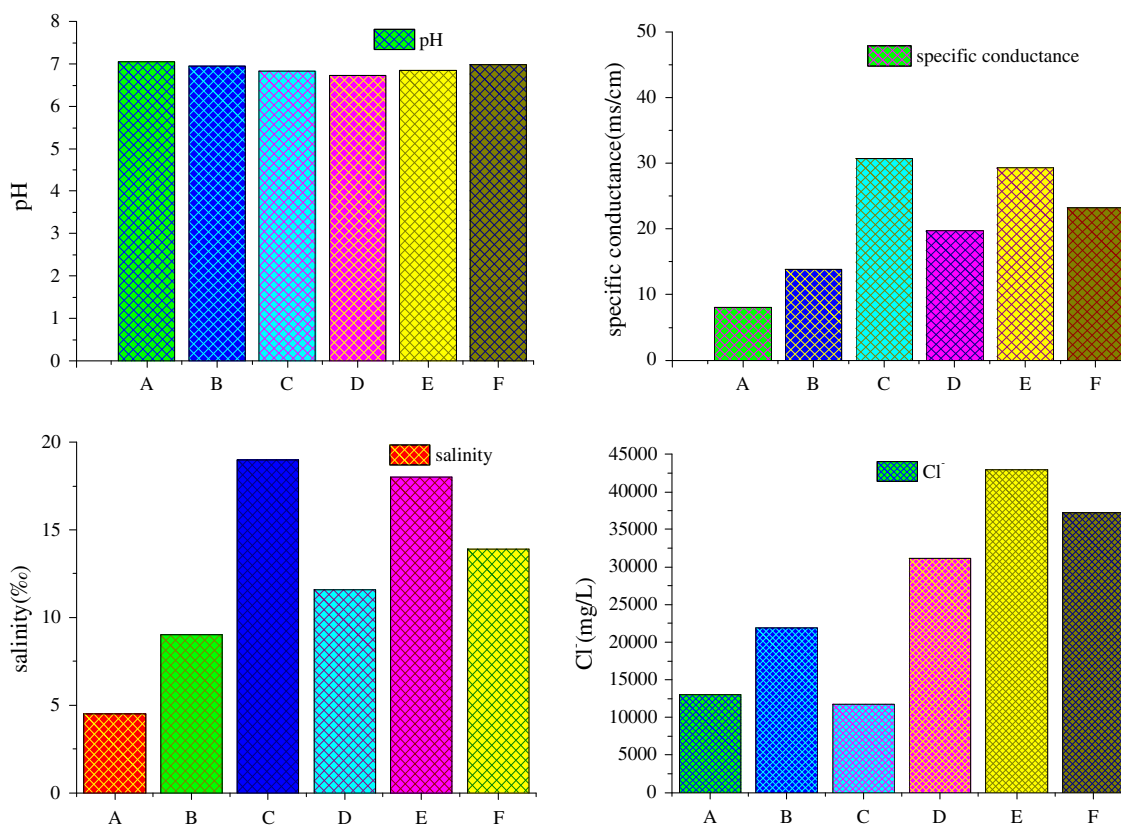


Fig. 2. Concentration variation of pH, conductivity, salinity, and chloride ions contained in snow water.

higher salinity. The snow-melting agent on both sides of the roadway is spread outward towards the edge of the roadway. In addition, the artificial removal of snow by the melting agent affects the balance of the salinity distribution.

As shown in Fig. 3, the SS content is higher in the snow and in the snow piled on the roadway. The SS contained in the snow on the roadway reached 874 mg/L. The relative TOC, IC, and COD contents were 5.2, 429.25, and 146 mg/L, respectively. The COD of the melting snow exceeded 100 mg/L on average, and the total nitrogen content was greater than 40 mg/L. A small amount of nitrate was found in the snow water collected from the sidewalk, totaling approximately 20 mg/L. Ammonia nitrogen contained in the snow proper was derived from airborne dust and dirt from the street. The pollutant indices and COD of the snow water were generally higher than the pollutant indices of municipal sewage. The concentrations of ICs were higher than the TOC contents.

The snow water contained a high content of oil, and reaching 22 mg/L at point F. The amount of oil was greater than 10 mg/L at every sampling point.

Oily substances result from the incomplete combustion of fuel in cars and buses. This oil is dispersed onto the ground or into the air, forming particulates that increase the amount of oil in the snow water. Snow has a strong adsorption capacity, which effects air purification and pollutant concentrations. The snow itself, meanwhile, becomes the carrier of the pollutant, which requires a specific type of treatment when the pollution reaches a high level. The concentration of suspended substances contained in the snow water on the street exceeded 500 mg/L on average, which is higher than that of domestic sewage. Thus, the snow water requires further treatment.

3.2. Composition and distribution of the main organic substances contained in snow water from the street cross-section

In this study, the pollutants contained in snow water at points A–F were dynamically analyzed using three-dimensional fluorescence spectroscopy. As shown in Fig. 4, three-dimensional fluorescence spectroscopy can provide fluorescence intensity information while the excitation wavelength (λ_{ex}) and

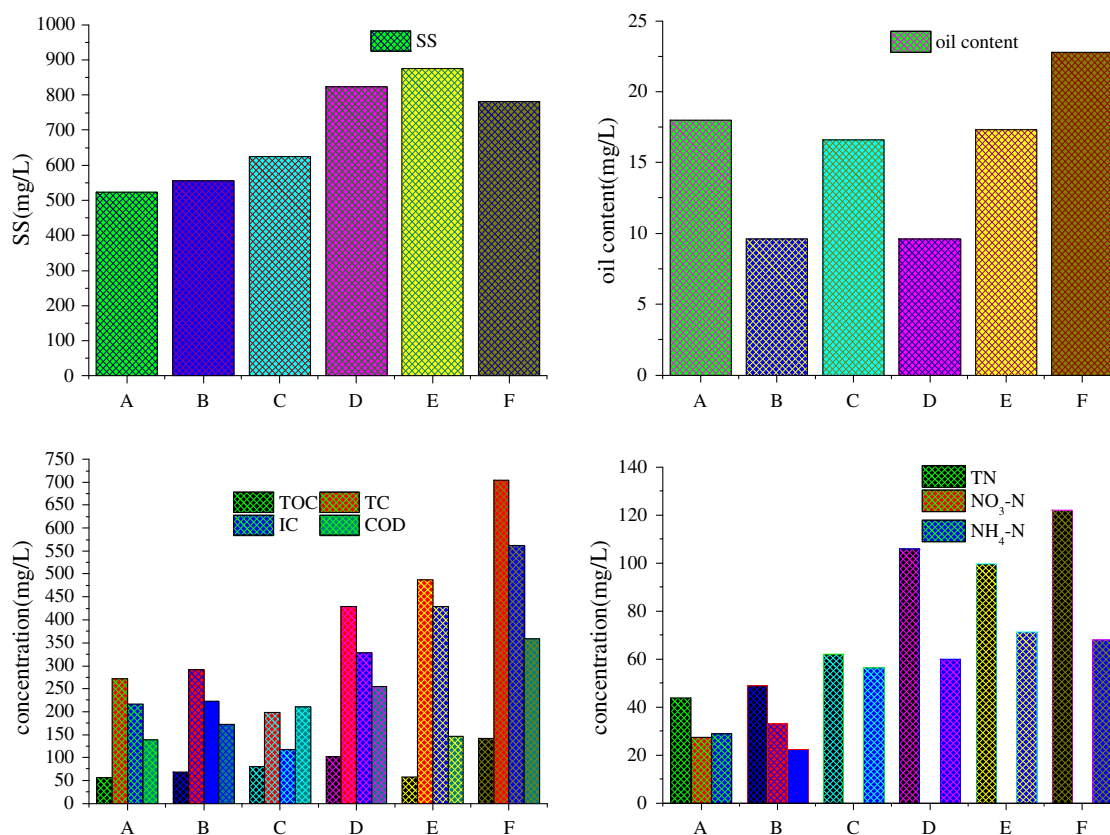


Fig. 3. Concentration variation of SS, oil, TOC, and ammonia.

emission wavelength (λ_{em}) vary simultaneously. The excitation and emission wavelengths can reveal the classification of the organic pollutants and the amount of pollutant, which can be used to determine the water quality. Four three-dimensional fluorescence peaks were detected in the snow water, and these peaks were mainly distributed within the range λ_{ex} (220–280 nm) and λ_{em} (350–400 nm). The pollutants belonged to a class of common organic compounds such as proteins, humic acids, and vegetable oils, as indicated by comparison with the three-dimensional fluorescence peaks obtained for known dissolved organic substances, thus demonstrating the variability of the snow water. The composition distribution of the organic substances in snow water was considerably different for each sampling site. The pollutants in snow water from the roadway were more abundant and diverse than the snow water from the pedestrian street, mainly because the pollutants were derived from the street, vehicles, and other pedestrians.

The composition of the organic substances in snow water from different sampling sites was analyzed by GC/MS. Fig. 5 shows that the main pollutants had similar peak characteristics but differed in their quantities and types, because the sampling sites and pollution sources were relatively close in proximity.

As shown in Table 1, the GC/MS data obtained for six samples were compared, leading to the conclusion that there were more than 50 types of major pollutants. Twenty-nine pollutants could be detected directly. The predominant pollutants in snow water from the four sampling sites included petroleum-based substances dominated by hexadecane, decane, octadecane, eicosane, heneicosane, and other long-chain petroleum hydrocarbons. The characteristic toxic pollutants consisted of benzene, butylated hydroxytoluene, benzoic acid, phthalic acid, and naphthalene. Other toxic pollutants included acids, dibutyl phthalate, cyclohexanone, cyclic octaatomic sulfur, wood alcohol, and other substances. The different pollutants showed a varied spatial distribution, possibly caused by human behavior and disturbances resulting from vehicles. Considering the environmental characteristics of the city, these organic substances were likely derived from the exhaust and incomplete combustion of oil from vehicles, dust from tire wear, and external contaminants. In addition, some of the substances and contaminants in the air were adsorbed on the snow during the sedimentation process. Initial research indicated that toxic pollutants were present at high levels in the snow water, which favors their purification from air. However, the air represents a new source as a pollutant carrier. The proposal of snow classification methods and on-site treatment is, therefore, useful for

future city development by avoiding the need for secondary mitigation of these pollutants.

4. Research on the recycling and utilization of snow from streets

Urban snowfall is divided into two categories based on the characteristics of the snow water. One type is snow containing motor gas and impurities from motor vehicles in areas having concentrated population. The other type of urban snowfall is purified snow from pedestrian streets, squares, and green spaces. Suspended matter and COD contained in melting snow water serve as classification indicators for comparison with the suspended matter and COD contained in municipal sewage. The concentration of the suspended substances in municipal sewage is approximately 200 mg/L, whereas a lower level of COD was found in snow water. Therefore, these data suggest that the concentration of COD contained in snow water should be set at 100 mg/L based on the COD contained in the lightly polluted snow. The concentration of suspended substances is 200 mg/L. V-type filtration using a subsurface double tank could be applied for snow having a higher concentration of suspended substances. Clean snow water with a lower amount of suspended substances can be treated directly using subsurface double tanks.

The distribution of facilities should consider the road system, squares, green spaces, and other underground spaces for the installation of multi-connected areas forming a snow collection and treatment network according to the treatment classification. Considering the cost issues, the snow-melting system should reflect the principle of sharing and compatibility. A simple design can be used to process snow having different quality standards, such as snow with higher levels of suspended substances and clean snow water with light pollution. Each facility should properly encompass the surrounding areas, within a radius of 100–300 m, such that the pipelines are more economical and feasible. The snow-removal operation is, therefore, convenient for realizing continuous and multi-level treatment.

As shown in Fig. 6, an integrated snow-melting system using double subsurface tanks was designed in this study. A source of waste heat is utilized, and the open space is used to realize an ecological, economical, and cross-seasonal continuous operation for the snow-melting system.

The design of the snow melting system should allow for low-temperature operation in the winter and address antifreeze issues. A double-tank subsurface snow-melting system consists of snow-melting wells

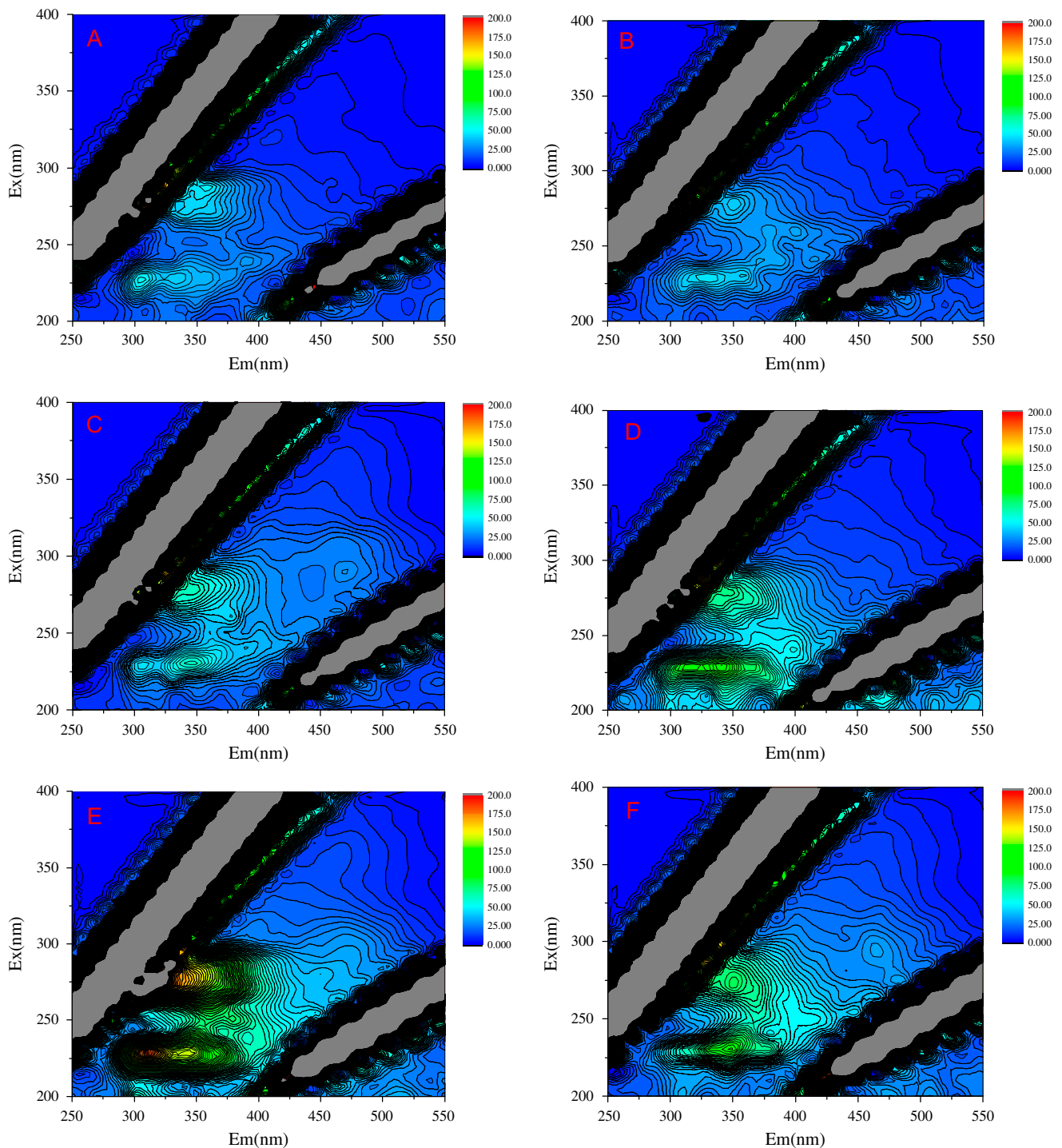


Fig. 4. Three-dimensional fluorescence spectroscopy analysis of snow water at point A–F.

and two subsurface tanks. The three-dimensional design of the facilities allows the operational temperature of the treatment units to be maintained between 4 and 6°C. The first tank serves as the filter and pre-treatment units for snow melting, whereas the second

tank is used for storage and further treatment of the snow meltwater. The snow-melting wells include a heat preservation door, collection wells, collection grids, heating assemblies, and sedimentation improvement devices. A heat preservation door and cover

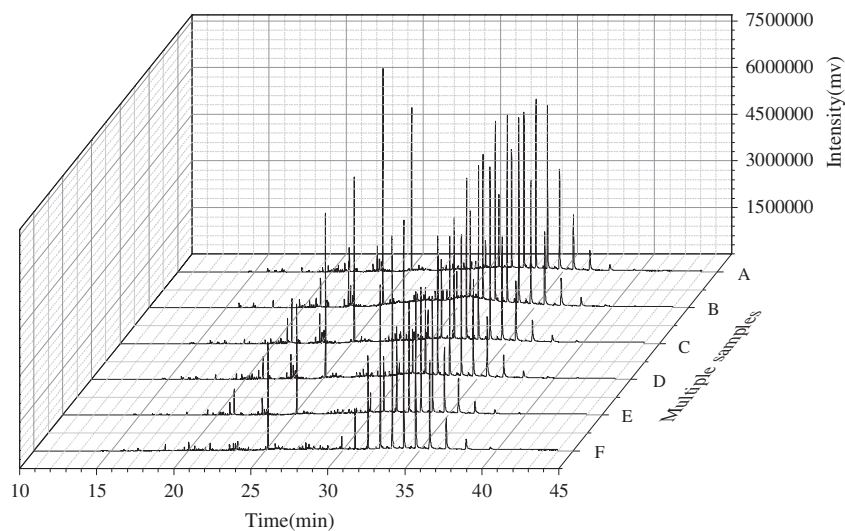


Fig. 5. GC-MS illustrative plates of snow water at point A–F.

Table 1

Composition and distribution of the main pollutants of GC-MS contained in snow water

No.	Hit name	Mol weight (amu)	A	B	C	D	E	F
1	Cyclohexene, 3,5,5-trimethyl-	124.125	+	+	–	+	+	+
2	4,4-Dimethyl-3-oxopentanenitrile	125.084	+	+	+	–	+	+
3	Hexadecane	226.266	+	+	+	+	+	+
4	Undecane, 2-methyl-	170.203	–	+	+	+	+	+
5	Decane, 3,8-dimethyl-	170.203	–	+	–	–	+	+
6	Benzene, 1,3-bis(1,1-dimethylethyl)-	190.172	+	+	–	+	+	+
7	Propanoic acid, 2-methyl-	216.173	+	–	–	+	–	+
8	Butanoic acid, butyl ester	144.115	+	+	+	+	+	–
9	Octadecane, 1-iodo-	380.194	+	+	–	+	+	+
10	Butylated hydroxytoluene	220.183	+	+	+	+	–	+
11	Benzoic acid, 4-ethoxy-, ethyl ester	194.094	+	+	+	+	+	+
12	Eicosane	282.329	+	+	+	+	+	+
13	Allyldimethyl(prop-1-ynyl)silane	138.086	+	+	+	–	+	+
14	Dibutyl phthalate	278.152	–	–	+	+	+	+
15	Cyclohexanone, 3-butyl-	154.136	+	–	+	+	+	+
16	Heneicosane	296.344	+	+	+	+	+	+
17	Octadecanoic acid, methyl ester	298.287	+	+	+	+	–	+
18	Hexadecane, 2,6,10,14-tetramethyl-	282.329	+	–	+	+	+	+
19	Octadecane	254.297	+	+	+	+	+	+
20	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	278.152	+	–	–	+	+	+
21	Heptadecane	240.282	+	+	+	+	+	+
22	Dibutyl phthalate	278.152	+	–	+	+	+	+
23	N-(4-Methoxyphenyl)-2-hydroxyimino-acetamide	194.069	+	+	–	+	+	+
24	3-Decen-5-one, 2-methyl-	168.151	+	+	+	+	–	–
25	Cyclic octaatomic sulfur	255.777	+	+	–	–	+	+
26	Benzene, (3-methyl-1-methylenebutyl)-	160.125	–	+	+	+	–	+
27	Naphthalene, 1,2,3,4-tetrahydro-2,6-dimethyl-	160.125	+	–	+	+	–	+
28	Spiro(tetrahydrofuryl)2.1'(decalin), 5',5',8'a-trimethyl-	236.214	–	+	–	+	+	+
29	2-Methyl-1-octadecene	266.297	+	+	+	+	+	+

Notes: (+) Existence of the organic substance; (–) no.

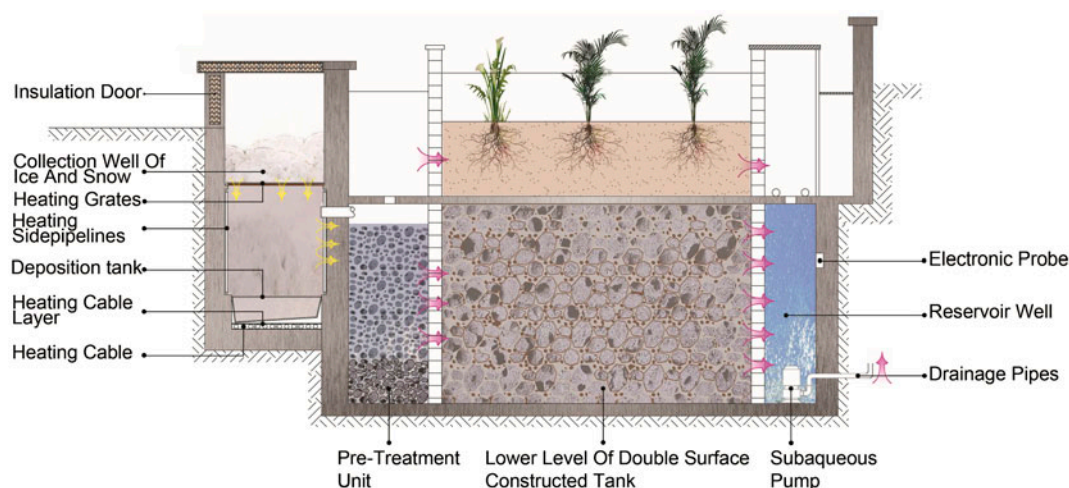


Fig. 6. Illustration of integrated snow-melting system of double subsurface constructed tanks.

isolate the snow-melting wells from the outdoor environment to improve the working efficiency of the heating assemblies inside the well and reduce heat loss. Snow-melting wells utilize a low-temperature heat pump with a network of underground pipelines to melt snow. Sand is regularly removed from the bottom using a pump or an artificial mechanical lifting device to reduce the amount of sand and improve efficiency. A monitoring probe is placed inside the well to monitor the water level and guarantee the effective ordering of the filling and melting process. Electronic devices would indicate to a worker that the well should be refilled once it is nearly empty.

This subsurface double-tank system imitates the principle of a double subsurface artificial wetland system using a horizontal flow system. Such wetlands are used to dispose of wastewater under low-temperature conditions in northern cities. Withered vegetation, surface snow, frozen water, vegetation cover, autoclaved aerated concrete, and a lower tank covered by an air layer are used to form a thermal barrier. The lower tank is located below the frost line or has heat insulation. Advantageous oligotrophic bacteria are added and stabilized in the filler of the lower tanks through enhanced biological technology with the aim of having the system continuously purify water in a low-temperature and hypoxic environment. In winter, the system incorporates the snow water collected from vehicle roads, pedestrian streets, and green spaces. The snow should be collected immediately after the snowfall event and should be dumped directly into the disposal wells located in the green belt on both sides of the road. Heat tubes are placed at the bottom of the well circumferentially to melt the snow. The upper layer of snow melts naturally, forming an

insulating layer that ensures the complete melting of the lower layer. The melting snow water enters the conditioning tank in the weir pool after the pre-treatment step and is admitted into the lower subsurface tanks using a natural gradient or an elevator pump. After infiltration, the filter and oligotrophic cold-tolerant bacteria will spread and form a biofilm to increase the filtering effect.

5. Conclusion

- (1) The salinity was higher at the sampling points within the motor vehicle roadways and pedestrian streets. In particular, the salinity and conductivity on the motor vehicle roadways reached approximately 19%. The pH was generally less than 7.0, and use of a salt-containing snow-melting agent led to an increase in salinity. The snow-melting agent is spread outward into the pedestrian areas by rolling vehicles. In addition, snow removal by humans causes an imbalance in the salinity distribution.
- (2) The snow water on pedestrian streets contains less nitrate ammonium than snow in the roadways. The total amount of ammoniacal nitrogen was approximate 20 mg/L. Except for the COD, the pollutant indicators contained in snow water were generally higher than in municipal sewage.
- (3) More than 50 main types of pollutants were detected in snow water from the street cross-section, and 29 of these pollutants were directly identified. The petroleum-based

substances from six snow water samples were dominated by cetane, which includes hexadecane, decane, octadecane, eicosane, heneicosane, and other long-chain petroleum hydrocarbons. Other characteristic toxic pollutants included benzene, butylated hydroxytoluene, benzoic acid, phthalic acid, and naphthalene. Considering the environmental characteristics of the city, these organic substances were likely derived from the exhaust and incomplete combustion of oil from vehicles, dust from tire wear, and the transport of external contaminants. Snow also adsorbed certain pollutants from the air during the snowfall events.

- (4) According to the characteristics of snow water from the street, a recycling and utilization system is proposed based on an integrated snow-melting system using double subsurface tanks. This system provides a new pattern for the utilization, removal, and recycling of snow from streets in winter cities in north China.

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