Effect of Long-Term Application of Biosolids for Land Reclamation on Surface Water Chemistry

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ABSTRACT

Biosolids are known to have a potential to restore degraded land, but the long-term impacts of this practice on the environment, including water quality, still need to be evaluated. The surface water chemistry (NO_3^-, NH_4^+, and total P, Cd, Cu, and Hg) was monitored for 31 yr from 1972 to 2002 in a 6000-ha watershed at Fulton County, Illinois, where the Metropolitan Water Reclamation District of Greater Chicago was restoring the productivity of strip-mined land using biosolids. The mean cumulative loading rates during the past 31 yr were 875 dry Mg ha^{-1} for 1120-ha fields in the biosolids-amended watershed and 4.3 dry Mg ha^{-1} for the 670-ha fields in the control watershed. Biosolids were injected into mine spoil fields as liquid fertilizer from 1972 to 1985, and incorporated as dewatered cake from 1980 to 1996 and air-dried solids from 1987 to 2002. The mean annual loadings of nutrients and trace elements from biosolids in 1 ha were 735 kg N, 530 kg P, 4.5 kg Cd, 30.7 kg Cu, and 0.11 kg Hg in the fields of the biosolids-amended watershed, and negligible in the fields of the control watershed. Sampling of surface water was conducted monthly in the 1970s, and three times per year in the 1980s and 1990s. The water samples were collected from 12 reservoirs and 2 creeks receiving drainage from the fields in the control watershed, and 8 reservoirs and 4 creeks associated with the fields in the biosolids-amended watershed for the analysis of NO_3^-–N (including NO_2^-–N), NH_4^+–N, and total P, Cd, Cu, and Hg. Compared to the control (0.18 mg L^{-1}), surface water NO_3^-–N in the biosolids-amended watershed (2.23 mg L^{-1}) was consistently higher; however, it was still below the Illinois limit of 10 mg L^{-1} for public and food-processing water supplies. Biosolids applications had a significant effect on mean concentrations of ammonium N (0.11 mg L^{-1} for control and 0.24 mg L^{-1} for biosolids) and total P (0.10 mg L^{-1} for control and 0.16 mg L^{-1} for biosolids) in surface water. Application of biosolids did not increase the concentrations of Cd and Hg in surface water. The elevation of Cu in surface water with biosolids application only occurred in some years of the first decade, when land-applied sludges contained high concentrations of trace metals, including Cu. In fact, following the promulgation of 40 CFR Part 503, the concentrations of all three metals fell below the method detection level (MDL) in surface water for nearly all samplings. Nitrate in the surface water tends to be higher in spring, and ammonium, total P, and total Hg in summer and fall. Mean nitrate, ammonium, and total phosphorus concentrations were found to be greater in creeks than reservoirs. The results indicate that application of biosolids for land reclamation at high loading rates from 1972 to 2002, with adequate runoff and soil erosion control, had only a minor impact on surface water quality.

S TRIP MINING has caused large areas of land degradation in Illinois, due to the removal of topsoil. Recla-mation of strip-mined sites is important for maintaining agriculture and grassland ecosystems in the Midwestern United States. Disturbed land resulting from both surface and underground mining can result in major water quality problems as well as being unsightly and unproductive (Sopper, 1992). Lands degraded by strip mining are hard to regenerate as they lack organic matter, nutrients, and microorganisms (Shankar et al., 1993; Kundu and Ghose, 1994). Furthermore, the soil compaction can prevent root growth and revegetation on the strip-mine land. For an effective restoration of such degraded land, additions of organic matter and nutrients are needed (Shankar et al., 1993).

Biosolids from wastewater treatment plants have been recognized as beneficial nutrient sources for plant growth and crop production (Lue-Hing et al., 1974). Application of biosolids could also improve the microbial community (Denis and Fresquez, 1989) and soil physical properties (Metzger and Yaron, 1987; Gschwind and Pietz, 1992). The application of biosolids to degraded soils has long been considered an economical alternative to inorganic fertilizer (Fresquez et al., 1990). Meyer et al. (2001) reported that biosolids application on a severely burned and previously forested site near Denver increased plant cover. In Canada, agro-industrial wastewater and municipal sewage were used to restore Frank Lake, a 1246-ha northern prairie marsh in southern Alberta, Canada (White and Bayley, 2001). In a review, Sopper (1992) emphasized that stabilized municipal sludge, if applied properly, could be a better alternative to conventional techniques in reclamation of mined land. Like any other nutrient source, biosolids contain N, P, and trace elements. In reclamation settings, biosolids are often applied at greater than agronomic rates to build up soil organic matter and improve soil tilth. Nutrients, which may thereby be applied in excess, cannot be fully absorbed by plants, and may tend to move from reclaimed land in either snowmelt, rainfall, or irrigation to lakes and streams (Nicholaichuk and Read, 1978), resulting in water pollution. Hence, it is necessary to evaluate the impacts on water quality from the land application of biosolids for soil reclamation as with other nutrient recycling practices.

It is reasonable to assume the application of biosolids to strip-mined land can have both positive and negative impacts on surface water chemistry. A fraction of the biosolids chemical constituents can move to surface water along with the runoff and through ground water, resulting in an elevation of NO_3^-, NH_4^+, phosphorus, and trace element concentrations. This is particularly true for P, as the current N-based approach to biosolids management does result in increase of soil P to values well

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Abbreviations: MDL, method detection level.

above those needed for optimum crop yields and leading to an increased risk of P loss to water sources (Shober and Sims, 2003). On the other hand, the buildup of soil organic matter and inorganic constituents of biosolids may chelate and bind the metals and reduce their mobility. Although it has become commonly accepted that nutrient addition to ecosystems leads to pollution of the water, Cessna et al. (2001) did not believe that the increase in N and P, due to fertilizer application, was always substantial because of the possibly insignificant movement of these nutrients to water sources and the dilution of drainage water in rivers. Aluminum and Fe salts in biosolids may mitigate the environmental risk to water quality associated with land application of P in biosolids (Shober and Sims, 2003).

We hypothesize that proper application of biosolids will not cause a significant adverse impact on surface water quality. While the impacts of application of nutrients from animal wastes and chemical fertilizer on chemistry of surface water are well studied, less information is available on the watershed scale for biosolids, an aged stabilized nutrient source from municipal wastewater treatment, that meets the federal criteria for land application. Because of the time-dependent transformations of nutrients from biosolids application (Keller et al., 2002), there is clearly a need to conduct such large-scale studies for a long-term duration. The objective of the study was to assess the impact of biosolids applications to strip-mined land on surface water NO_3^-, NH_4^+, and total P, Cd, Cu, and Hg at the time scale of decades.

MATERIALS AND METHODS

The Site

The study site is located on 6000 ha of predominantly strip-mined land in Fulton County in western Illinois, approximately 300 km southwest of Chicago. The site has a continental climate with annual mean temperature of 10.4°C, and annual precipitation of 1013 mm. The 30-yr mean monthly precipitation in mm is 34.8 (January), 48.3 (February), 77.7 (March), 101.9 (April), 121.7 (May), 109.7 (June), 112.8 (July), 92.5 (August), 90.2 (September), 77.0 (October), 84.3 (November), and 61.5 (December). The 30-yr mean monthly snowfall in mm is 27.9 (November), 129.5 (December), 193.0 (January), 99.1 (February), 30.5 (March), and 10.2 (April). Seventy-eight percent of the land at the study site had previously been strip-mined, and was in need of reclamation at the time it was purchased by the Metropolitan Water Reclamation District of Greater Chicago (District). The nonmined soils of the site consist of Aquic Argiudolls, Typic Endoaquolls, Typic Argiudolls, Udollic Endoaqualfs, Typic Hapludalfs, and Mollic Hapludalfs (Granato et al., 2004). The surface (0–15 cm) of the strip-mined soil had the following characteristics before reclamation: pH = 7.4, organic carbon = 6.1 g kg^{-1}, cation exchange capacity = 14.3 cmol kg^{-1}, 0.1 M HCl–extractable metals concentrations (mg kg^{-1}) = 0.20 for Cd and 4.79 for Cu, bulk density = 1.61 g cm^{-3}, and loam, silty clay loam, and clay loam texture. For the nonmined areas, the surface (0–15 cm) had the following characteristics before reclamation: pH = 6.5, organic carbon = 16.4 g kg^{-1}, cation exchange capacity = 19.5 cmol kg^{-1}, 0.1 M HCl–extractable metals concentrations (mg kg^{-1}) = 0.08 for Cd and 2.62 for Cu, bulk density = 1.29 g cm^{-3}, and loam and silt loam texture (Peterson et al., 1979). The District has been applying biosolids at the site since 1972 to increase organic matter and soil fertility in the strip-mined soils to reclaim and restore the land to full agricultural productivity.

Treatments and Operations

In the 6000 ha of land comprising calcareous strip-mined soil, nonmined land, acidic coal refuse material, mine lakes (reservoirs), and wooded areas, approximately 1790 ha of calcareous strip-mined soil and nonmined land were developed into approximately 80 fields for biosolids application and crop production. Most of the fields in the north, central, and east quadrants (Fig. 1) of the study site received biosolids at cumulative rates of 388 to 1816 dry Mg ha^{-1} for 5 to 22 yr in rotation from 1972 to 2002. The mean loading rate based on the total area of the fields (1120 ha) in these three quadrants (4500 ha) was 875 dry Mg ha^{-1} cumulatively or 28.2 dry Mg ha^{-1} annually during the past 31 yr. However, most of the fields in the west quadrant received only supernatant from 1977 to 1979, and occasionally in the 1980s, with cumulative biosolids application rates of 2.5 to 46.5 dry Mg ha^{-1}. The mean loading rate based on the total area of the fields (670 ha) in this quadrant (1500 ha) was 4.3 dry Mg ha^{-1} cumulatively and 0.13 dry Mg ha^{-1} annually. Subsequently, we considered the north, central, and east quadrants as the biosolids-amended watershed, and the west quadrant as the control watershed (Fig. 1).

Although initially all biosolids were applied by means of spray application, only a very small portion of the biosolids were applied by this method. Biosolids were injected as liquid fertilizer from 1972 to 1985, and incorporated as dewatered cake from holding basins from 1980 to 1996, and air-dried solids from 1987 to 2002. The biosolids were produced from wastewater treatment at the Stickney and Calumet water reclamation plants in Chicago and were anaerobically digested. During the 1970s, the digested liquid biosolids were pumped to barges for transportation down the Illinois River to Fulton County. The barges were docked at Liverpool, Illinois, and the liquid biosolids were pumped through a 17-km pipeline to three holding basins at the land reclamation site. Since the mid-1980s, the biosolids have been transported to Fulton County in an air-dried state by trucks or barges. Biosolids applications were made in the summer and fall from June through September, normally.

Each agricultural field receiving biosolids, in the biosolids-amended watershed, was bermed so that the runoff could be contained and directed to a field retention basin through a pipe. Each basin was designed to capture the runoff from a 100-yr, 24-h storm event for the Fulton County region. Runoff water was released to reservoirs and creeks through a pipe only after it met the applicable State of Illinois effluent standards, which are ≤99 mg L^{-1} for total suspended solids, ≤33 mg L^{-1} for biochemical oxygen demand, pH in the range of 6.0 to 10.0, and ≤500 counts/100 mL for fecal coliform. Time period of release after a rainfall event could vary from 1 d to a month, depending on the amount of water in the basin vs. its holding capacity. Solids that accumulated from sediments in retention basins were distributed back onto the protected fields once every 5 yr; however, this practice continued only until 1980. No field retention basin was constructed for fields in the control watershed, though some of these fields have berms.

Over the 31 yr, fields in the biosolids-amended watershed were, on average, cropped for 19 yr. Cropping patterns are various rotations of corn, wheat, sorghum, soybean, grass, and fallow. Soybean was planted mainly during the most recent decade. Some fertilizer application on biosolids-amended fields occurred during periods of leasing by the farmers. Fields in the control watershed were used mainly for hay, but half of these fields were cropped with corn or soybean during the
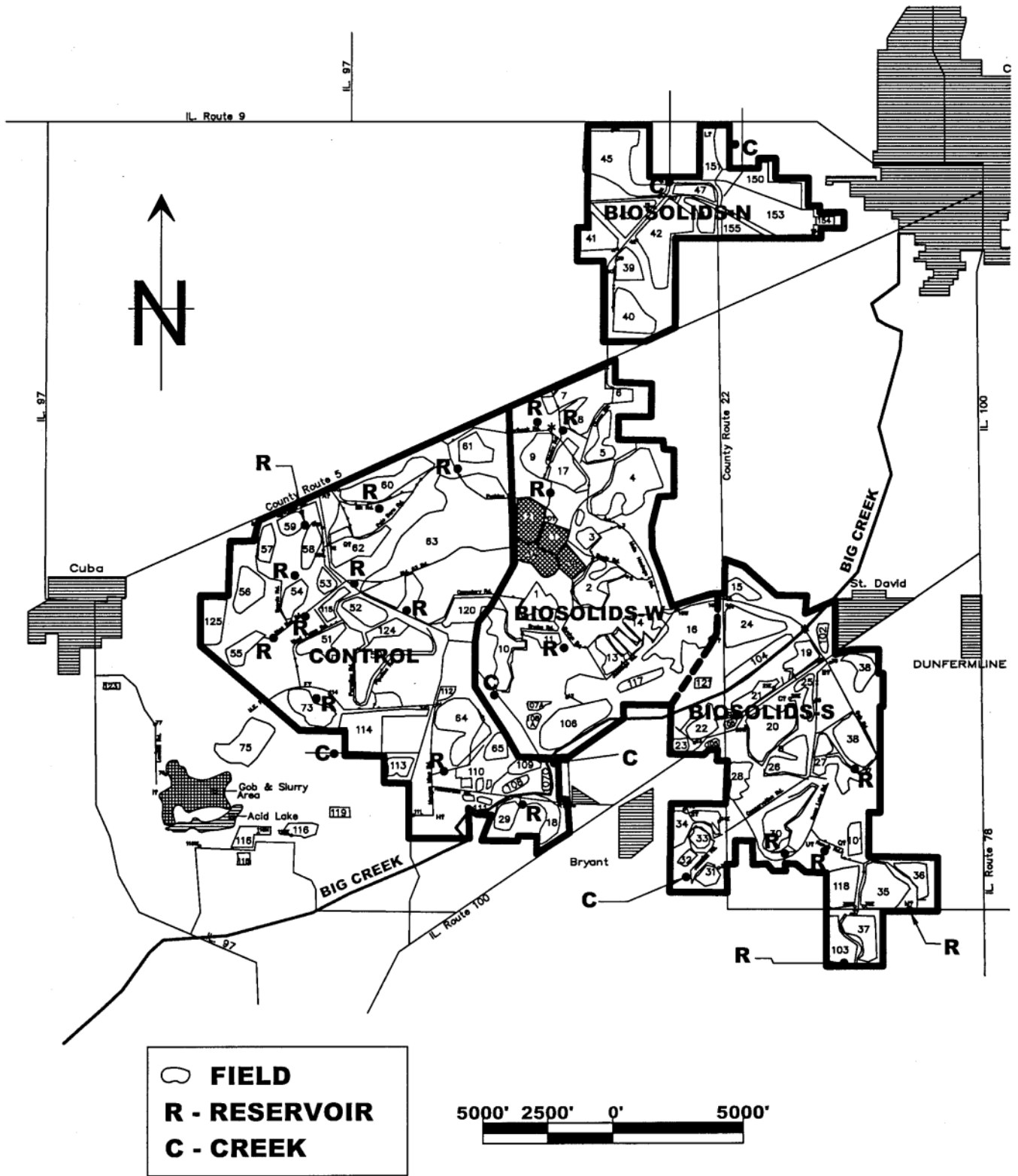
Fig. 1. Layout of fields and sampling sites at Fulton County land reclamation site, Canton, IL.

most recent decade. Fields in the control watershed that were cropped during the most recent decade received agronomic rates of N, P, and K fertilizer for the cropped years. The amount of fertilizers applied by the farmers on the leased fields was never determined. The fertilizer application time was either spring or fall. For the most recent three years,

corn yields ranged from 5.2 to 13.2 Mg ha^{-1} in the biosolids-amended fields and 3.7 to 8.7 Mg ha^{-1} in the control fields.

Sampling and Analysis

Sampling of surface water was performed monthly from 1972 to 1981, and at intervals of three times per year from

1982 to 2002. From 1982 through 2002, two of these three samples were collected following significant rainfall events between the months of April and November, and the third annual sample was taken during a drier period in summer. The wet weather samples were invariably taken during the spring or fall, while the dry weather samples were taken during the summer. As biosolids were applied from June to September, the spring samples were taken before the biosolids application and fall sample at the end of biosolids application. Sampling was not done in winter. The sampling period was determined by the Illinois Environmental Protection Agency (IEPA). Fifteen sampling sites (12 reservoirs and 3 creeks) are located in the control watershed (Fig. 1); however, one creek was excluded from the data set, as the creek receives effluent from the Canton water treatment plant. Fourteen sites (8 reservoirs and 6 creeks) are located in the biosolids-amended watershed; however, two creeks are excluded from the data set as they passed by a landfill site. There are over 480 ha of reservoirs and creeks in the 6000-ha site. Most of the reservoirs were man-made through the strip-mining process. The width of reservoirs was up to 30 m, and that of creeks up to 3 m. Some creeks were seasonal, depending on runoff.

Water samples were shipped in coolers packed with ice to the District's laboratory in Chicago for next-day chemical analysis. Samples were not filtered before analysis. The NO_3^-–N plus NO_2^-–N and NH_4^+–N were analyzed by colorimetry in an autoanalyzer (Technicon [Tarrytown, NY] from 1971 to 1999 and Lachat [Milwaukee, WI] from 2000 to 2002). For the determination of total P, water samples were digested in the presence of sulfuric acid, K_2SO_4, and $HgSO_4$ (USEPA, 1983), and P was determined by colorimetry using an autoanalyzer (Technicon from 1971 to 1999 and Lachat from 2000 to 2002). For the determination of total Cd and Cu, the water samples were digested in the presence of nitric acid (Greenberg et al., 1992), and the metals were determined using atomic absorption spectrophotometry from 1971 to 1998 and inductively coupled plasma spectroscopy (ICP–AES) from 1999 to 2002. For the determination of total Hg, the water samples acidified with H_2SO_4 and HNO_3 were digested in the presence of $KMnO_4$ and $K_2S_2O_8$ (Greenberg et al., 1992), and the Hg in the digestion was analyzed by atomic emission spectrophotometry from 1971 to 1997 and by atomic absorption spectrophotometry from 1998 to 2002. The selection of the above metals for monitoring in the surface water was based on the requirements of the Illinois Environmental Protection Agency who issued the permit for the land application of biosolids at Fulton County.

The annual samples of biosolids were analyzed for pH, total nitrogen, ammonia, and total P, Cd, Cu, and Hg. The pH was measured in 1:2 water. The total N was determined using Kjeldahl digestion, followed by colorimetry. The total P was determined in the above Kjeldahl digestion using the molybdate blue method. For the determination of total Cd and Cu, the biosolids samples were digested in the presence of nitric acid. For the determination of total Hg, the biosolids samples were liquidized in water and digested in the same way as for water samples. Then, the Cd, Cu, and Hg in the digestion were measured using the same approaches as for those in the digestion of water samples.

The 31-yr data were sorted by four factors: treatment (two levels: control and biosolids), water body (two levels: reservoir and creek), sampling season (three levels: wet-spring, dry-summer, and wet-fall), and years (31 levels: 1972–2002). The analysis of data from this study can be achieved by traditional ANOVA under the assumption of normality of population distribution and the assumption of equal variance across each level of a factor. When analysis involves multiple factors, the normality and equal variance assumptions must be met for all

possible levels due to interactions (Walpole and Myers, 1989). The normality assumption was verified by Kolmogorov and Smirnov method, and found to be met in this study. We then applied the F test on the equality of variance when a factor had two levels and Bartlett's test on equality of variance when a factor had more than two levels. These tests indicated equal variance assumptions were not met for all factors (levels of some factors did not have equal variance). If the error distributions across all levels satisfy normality, but the variances are heterogeneous, the traditional ANOVA approach might lead to an erroneous conclusion, and the analysis of these data must be performed by either ANOVA under unequal error variance known as exact ANOVA or multiple comparison which involves only two levels at a time (Weerahandi, 1995). Significance of treatment, water body, and season effects were therefore computed using the Multiple Comparison Procedure (MCP). Due to a preponderance of data below the method detection levels, the standard error of trace metals, especially Cd and Cu, was zero for many years and therefore it was not possible to analyze the effect of year. The data of various years were therefore pooled in conducting multiple comparison for the other three factors (treatment, water body, and sampling season).

The 31-yr data sets were plotted to show monthly dynamics (mean of all sampling sites) of surface water chemistry parameters. A linear trendline that describes a long-term trend was inserted if the correlation coefficient of the regression of constituent concentration against time (year) was significant ($P < 0.05$). Yearly mean values for NO_3^-–N, NH_4^+–N, and total P, Cd, Cu, and Hg were calculated and tested for the significance of difference between the biosolids-amended and control watersheds. We compared the means of water chemistry of three major periods (1972–1984, 1985–1993, and 1994–2002). During the first major period, nearly all fields in the biosolids watershed received biosolids. From 1985 through 1993, biosolids application was almost ceased in two-thirds of fields (mainly located in the north and the east quadrants of the reclamation site). A federal regulation (40 CFR Part 503) was promulgated in 1993, and from 1994 onward exceptional quality biosolids (metal levels meet pollutant concentration limits of Table 3 of Section 503.13) was applied. Simple correlation analysis was conducted to test if there were correlations between each of the water chemistry parameters and the annual biosolids/element loading rate. All statistical tests were performed using the SAS fixed model (Littell et al., 1996).

RESULTS

Loading Rate and Chemical Composition of Biosolids

The mean annual loading rates of biosolids for the fields in the biosolids-amended watershed increased from 1972 to 1980, and decreased from 1980 to 1986. The mean annual loading rates increased again for most years from 1986 to 1995, and decreased again from 1995 to a stable level close to 20 Mg ha^{-1} (Fig. 2). The mean cumulative loading rate for 31 yr was 875 Mg ha^{-1}. The mean annual loading for the three major periods was 35.6 from 1972 to 1984, 22.9 from 1985 to 1993, and 22.8 from 1994 to 2002. Annual loading of biosolids in fields of the control watershed was negligible for nearly all 31 yr.

Biosolids applied as liquid fertilizer during the early periods tended to contain more N, P, and trace metals (Cd, Cu, and Hg) as compared to those in dewatered cake and dried biosolids applied during later stages
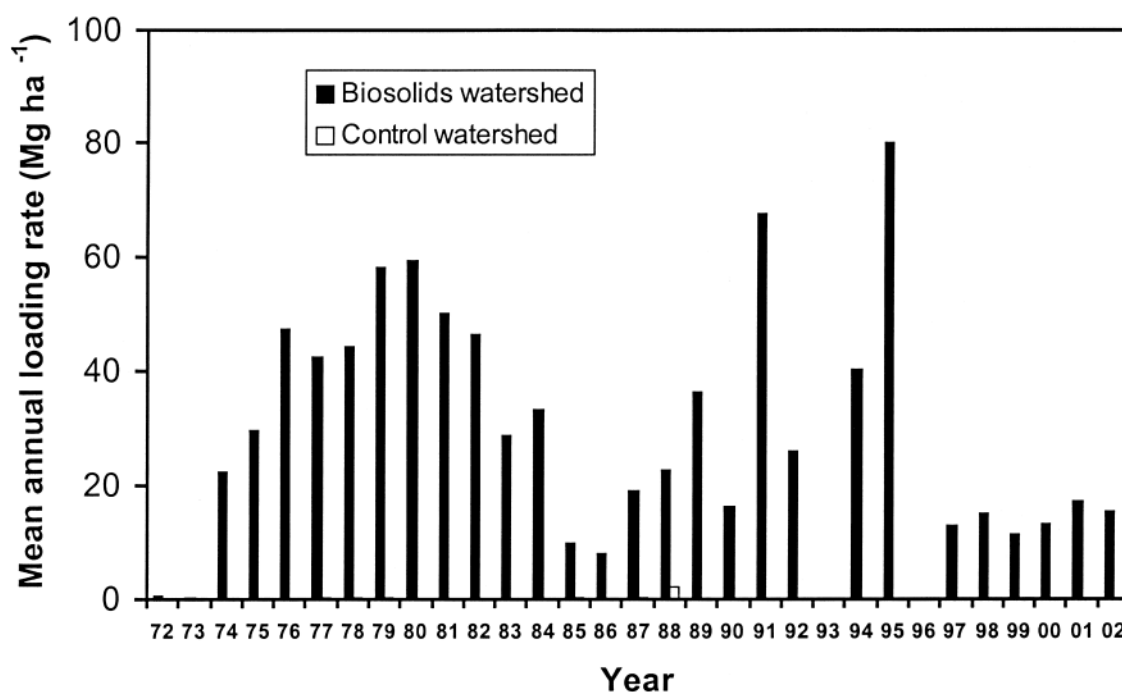
Fig. 2. Mean annual loading rates (dry weight) of biosolids applied to fields in the biosolids-amended and control watersheds from 1972 to 2002.

Table 1. Mean (dry weight basis) pH, total N, NH₃–N, and total P, Cd, Cu, and Hg in liquid, dewatered cake, and dried biosolids applied to strip-mine land from 1972 to 2002, and mean ± SE for each type of biosolids over application years.

Year	pH	Total N	NH$_3$–N	Total P	Total Cd	Total Cu	Total Hg
			g kg^{-1}			mg kg^{-1}	
1972	ND†	ND	ND	ND	ND	ND	ND
1973	ND	ND	ND	ND	ND	ND	ND
1974	ND	51.0	29.1	26.2	292.7	1659	4.88
1975	ND	56.6	24.8	38.1	304.3	1849	7.02
1976	ND	47.6	21.1	21.1	298.6	1879	4.70
1977	ND	48.0	21.3	10.4	322.6	1786	5.65
1978	ND	49.0	22.0	29.8	277.9	1718	8.78
1979	ND	40.4	16.8	30.4	283.2	1773	4.08
1980‡	ND	24.6	7.7	24.6	195.2	1179	4.38
1981‡	ND	32.4	10.9	28.1	223.3	1561	5.33
1982‡	ND	24.5	8.6	17.9	155.0	1053	4.18
1983‡	ND	47.6	19.2	29.1	165.7	1372	4.49
1984‡	6.8	28.6	8.4	18.0	116.8	937	4.07
1985‡	6.4	20.4	4.9	20.0	180.5	1072	3.71
1986‡	6.9	4.9	0.5	6.1	66.0	466	1.20
1987‡	7.2	6.6	1.1	6.4	71.7	518	1.55
1988‡	7.2	5.4	0.7	5.6	58.0	427	2.65
1989‡	7.3	7.8	2.1	14.7	142.5	1007	3.10
1990‡	7.1	7.1	1.3	8.6	127.7	933	4.90
1991‡	6.9	16.4	3.8	18.2	125.5	946	5.65
1992‡	7.2	22.4	5.6	20.6	140.5	1440	2.60
1993	ND	ND	ND	ND	ND	ND	ND
1994§	6.5	2.5	0.2	2.9	22.0	147	0.40
1995§	7.0	2.9	2.5	3.0	34.0	271	0.39
1996	ND	ND	ND	ND	ND	ND	ND
1997	7.0	17.3	3.2	18.7	11.5	363	0.76
1998	7.4	21.6	5.6	21.5	13.1	355	0.92
1999	7.1	21.9	4.8	16.8	7.9	467	0.97
2000	6.6	13.3	1.4	16.3	12.3	265	0.76
2001	7.0	18.7	4.0	22.0	7.0	363	0.53
2002	6.8	24.1	4.1	25.2	6.6	396	0.40
Liquid (1974–1985)	ND	46.7 ± 1.6	19.3 ± 1.5	26.5 ± 1.9	264 ± 15.4	1706 ± 49	5.64 ± 0.43
Dewatered cake (1980–1996)	7.1 ± 0.1	8.2 ± 1.7	1.7 ± 0.5	12.0 ± 2.2	102 ± 16.2	687 ± 113	3.00 ± 0.66
Dried biosolids (1987–2002)	7.0 ± 0.1	15.4 ± 1.9	3.0 ± 0.5	16.4 ± 1.8	49.7 ± 13.0	599 ± 101	1.41 ± 0.24

† Not determined.
‡ Dewatered cake and dried biosolids containing clay inadvertently scraped from the earthen surfaces of either holding basins or unpaved lagoons/drying cells.
§ Pre-Part 503 biosolids being mixed with sand to meet pollutant concentration limits as allowed.

(Table 1). The ammonia N in liquid biosolids was six and eleven times higher than that in dried solids and dewatered cake, respectively. The trace metals in biosolids clearly declined from the 1970s to the 1990s (Table 1) because of the District's enforcement of local industrial waste ordinances resulting from federal pretreatment
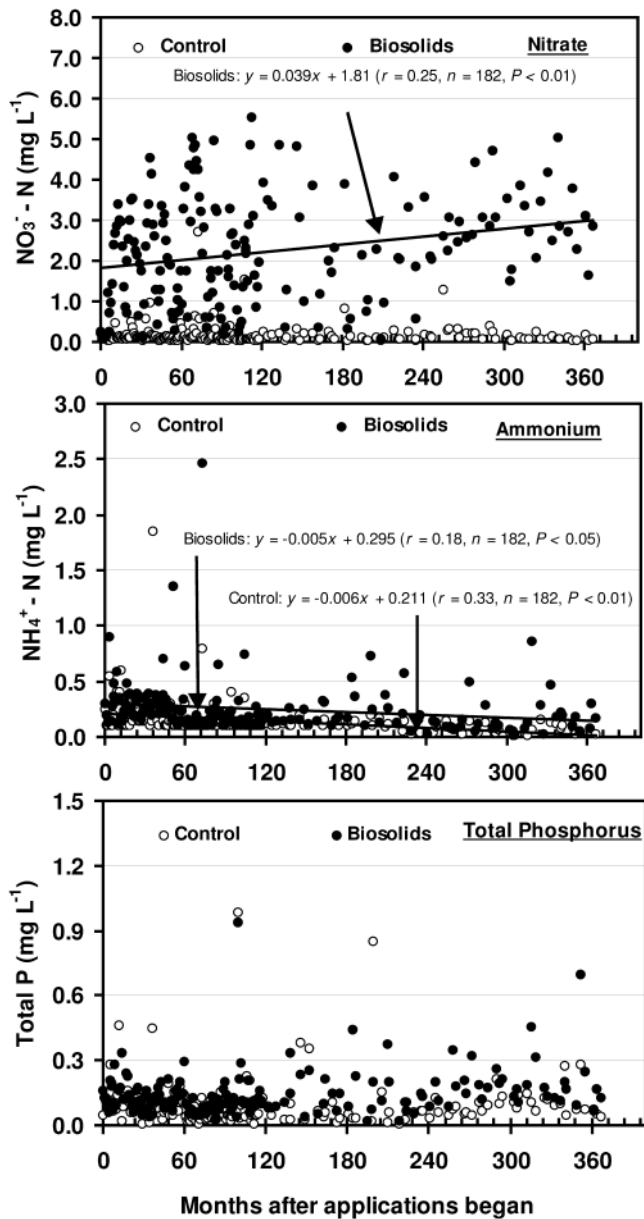
Fig. 3. Concentrations of nitrate, ammonium, and total phosphorus in surface water (mean of reservoirs and creeks) in biosolids-amended and control watersheds from 1972 to 2002. A trendline was drawn when constituent concentrations were significantly correlated to time in either control or biosolids-amended watersheds.

regulations. The dewatered cake and dried biosolids were generally neutral in pH.

Nitrogen and Phosphorus

The monthly mean concentration of nitrate in surface water across water bodies appeared to be unchanged in the control watershed during the study period but increased over time in the biosolids-amended watershed (Fig. 3). In both reservoir and creek and at all seasons, NO_3^-–N in surface water was significantly higher in the biosolids-amended watershed than the control watershed (Table 2). The yearly mean NO_3^-–N concentration in surface water ranged from 0.06 to 0.64 mg L^{-1} in the

Table 2. Comparisons in concentrations of N, total phosphorus, and trace metals in surface water between control and biosolids-amended watersheds for each sampling season and water body (μ_1, control mean; μ_2, biosolids mean, from 1972–2002).

Season	Water body	Treatment means		H_0: $\mu_1 = \mu_2$ significant probability†
		Control	Biosolids	
		mg L^{-1}		
			NH_4^+–N	
Unknown‡	reservoir	0.18	0.29	0.00
Unknown	creek	0.23	0.29	0.18
Unknown	combined	0.21	0.29	0.00
Dry-summer	reservoir	0.08	0.17	0.00
Dry-summer	creek	0.08	0.29	0.00
Dry-summer	combined	0.08	0.21	0.00
Wet-fall	reservoir	0.12	0.22	0.00
Wet-fall	creek	0.08	0.27	0.02
Wet-fall	combined	0.11	0.23	0.00
Wet-spring	reservoir	0.10	0.14	0.00
Wet-spring	creek	0.11	0.10	0.69
Wet-spring	combined	0.10	0.12	0.01
Combined	reservoir	0.11	0.24	0.00
Combined	creek	0.14	0.25	0.00
Combined	combined	0.11	0.24	0.00
			Total P	
Unknown	reservoir	0.08	0.14	0.01
Unknown	creek	0.14	0.18	0.29
Unknown	combined	0.11	0.15	0.05
Dry-summer	reservoir	0.07	0.17	0.00
Dry-summer	creek	0.13	0.21	0.11
Dry-summer	combined	0.08	0.18	0.00
Wet-fall	reservoir	0.12	0.15	0.07
Wet-fall	creek	0.12	0.23	0.00
Wet-fall	combined	0.12	0.18	0.00
Wet-spring	reservoir	0.08	0.11	0.00
Wet-spring	creek	0.19	0.11	0.14
Wet-spring	combined	0.09	0.11	0.11
Combined	reservoir	0.09	0.14	0.00
Combined	creek	0.14	0.18	0.09
Combined	combined	0.10	0.16	0.00
			NO_3^-–N	
Unknown	reservoir	0.27	1.29	0.00
Unknown	creek	0.16	4.17	0.00
Unknown	combined	0.22	2.10	0.00
Dry-summer	reservoir	0.06	1.47	0.00
Dry-summer	creek	0.32	3.35	0.00
Dry-summer	combined	0.09	2.07	0.00
Wet-fall	reservoir	0.10	1.94	0.00
Wet-fall	creek	0.27	1.96	0.00
Wet-fall	combined	0.13	1.95	0.00
Wet-spring	reservoir	0.12	2.06	0.00
Wet-spring	creek	1.34	5.06	0.00
Wet-spring	combined	0.29	3.06	0.00
Combined	reservoir	0.11	1.54	0.00
Combined	creek	0.44	3.80	0.00
Combined	combined	0.18	2.23	0.00
			Total Cd	
Unknown	reservoir	0.012	0.013	0.16
Unknown	creek	0.012	0.012	0.60
Unknown	combined	0.012	0.012	0.49
Dry-summer	reservoir	0.013	0.013	0.95
Dry-summer	creek	0.014	0.013	0.51
Dry-summer	combined	0.013	0.013	0.87
Wet-fall	reservoir	0.013	0.013	0.40
Wet-fall	creek	0.013	0.013	0.82
Wet-fall	combined	0.013	0.013	0.52
Wet-spring	reservoir	0.013	0.013	0.91
Wet-spring	creek	0.013	0.013	0.95
Wet-spring	combined	0.013	0.013	0.88
Combined	reservoir	0.013	0.013	0.28
Combined	creek	0.013	0.013	0.53
Combined	combined	0.013	0.013	0.19
			Total Cu	
Unknown	reservoir	0.023	0.023	0.90
Unknown	creek	0.017	0.023	0.09
Unknown	combined	0.020	0.023	0.26

Table 2. Continued.

Season	Water body	Treatment means		H_0: $\mu_1 = \mu_2$ significant probability†
		Control	Biosolids	
Dry-summer	reservoir	0.015	0.018	*0.02*
Dry-summer	creek	0.015	0.016	0.68
Dry-summer	combined	0.015	0.017	*0.02*
Wet-fall	reservoir	0.016	0.017	0.36
Wet-fall	creek	0.015	0.016	0.64
Wet-fall	combined	0.016	0.017	0.34
Wet-spring	reservoir	0.015	0.018	*0.03*
Wet-spring	creek	0.014	0.015	0.62
Wet-spring	combined	0.015	0.017	*0.04*
Combined	reservoir	0.016	0.020	*0.00*
Combined	creek	0.016	0.019	*0.05*
Combined	combined	0.016	0.020	*0.00*
		——— $\mu g\ L^{-1}$ ———		
		Total Hg		
Unknown	reservoir	0.20	0.17	0.38
Unknown	creek	0.18	0.17	0.37
Unknown	combined	0.19	0.17	0.26
Dry-summer	reservoir	0.20	0.15	*0.01*
Dry-summer	creek	0.18	0.18	0.88
Dry-summer	combined	0.20	0.16	*0.02*
Wet-fall	reservoir	0.17	0.19	0.54
Wet-fall	creek	0.18	0.18	0.95
Wet-fall	combined	0.18	0.19	0.51
Wet-spring	reservoir	0.15	0.15	0.71
Wet-spring	creek	0.15	0.16	0.61
Wet-spring	combined	0.15	0.15	0.98
Combined	reservoir	0.18	0.17	0.29
Combined	creek	0.18	0.17	0.64
Combined	combined	0.18	0.17	0.24

† Italic type indicates a significant difference at the 0.05 probability level.
‡ All months except wet-spring (April), dry-summer (July), and wet-fall (October) during the first 10 yr (1972–1981).

control watershed and 0.86 to 3.6 mg L^{-1} in the biosolids-amended watershed over the period that biosolids were applied (Table 3). The mean NO_3^-–N concentration over 31 yr in surface water in the biosolids-amended watershed was significantly higher than that in the control watershed (Table 3). When data from the three major periods were compared, the NO_3^-–N was lower in 1994–2002 than 1972–1994 in the control watershed, and higher in 1994–2002 than 1972–1984 and 1985–1993 in the biosolids-amended watershed (Table 3). Despite the yearly mean NO_3^-–N concentration in the biosolids-amended watershed being higher than that in the control watershed for most years, there were no months in which NO_3^-–N in surface water receiving drainage from the biosolids-amended watershed exceeded 10 mg L^{-1} (Fig. 3). The rate at which NO_3^-–N increased in surface water of the biosolids-amended watershed was as low as 0.4 mg L^{-1} per decade, based on the trend line in Fig. 3. Irrespective of water body and treatment, NO_3^-–N was always highest in wet-spring (Table 4). Creek water had a greater NO_3^-–N concentration than reservoir water, independent of sampling season and treatment (Table 5).

The monthly mean concentration of NH_4^+–N in surface water across water bodies tended to decline with time in both watersheds (Fig. 3). In nearly all water bodies and sampling seasons, NH_4^+–N concentration in surface water was greater in the biosolids-amended watershed than the control watershed (Table 2). There were fewer years, as compared to NO_3^-–N, in which mean surface water NH_4^+–N concentration in the bio-

solids-amended watershed was significantly higher than that in the control watershed (Table 3). There was a significant difference between the mean surface water NH_4^+–N concentration over 31 yr in the biosolids-amended watershed and in the control watershed (Table 3). Ammonium N in surface water was considerably lower than the Illinois limit of 6.95 mg L^{-1}, the acute limit for general use water with mean water pH = 8.1 (Illinois Pollution Control Board, 2003). For the entire study period across water bodies and treatments, NH_4^+–N was higher in the wet-fall and dry-summer than in the wet-spring (Table 4). The mean NH_4^+–N concentrations across water bodies were the same in both the wet-spring and wet-fall in the control watershed, and in both the dry-summer and wet-fall in the biosolids-amended watershed (Table 4). As compared to reservoirs, creek water contained higher NH_4^+–N in the dry-summer and lower NH_4^+–N in the wet-spring and wet-fall (Table 5).

The monthly mean concentration of total phosphorus in surface water across water bodies was nearly unchanged in both the control and biosolids-amended watersheds (Fig. 3). For three of the first thirteen years of the project, annual mean total P concentrations in surface water were significantly higher in the biosolids-amended watershed than in the control watershed (Table 3). From 1985 to 1993, there were five years in which yearly mean total P concentrations in surface water was higher in the biosolids-amended than the control watershed, and one year it was significantly lower in the biosolids-amended than control watershed. For the most recent nine years, we observed five years (1994, 1995, 1998, 2001, and 2002) in which annual mean total P concentrations in surface water were significantly higher in the biosolids watershed than in the control watershed (Table 3). The mean total P concentration over 31 yr in the biosolids-amended watershed was greater than that in the control watershed (Table 3). For the entire study period across water bodies and treatments, the total P concentration was higher in the dry-summer and wet-fall than the wet-spring (Table 4). Total P tended to be more concentrated in creeks than reservoirs, and this occurred for the biosolids-amended watershed in wet-fall and the control watershed in wet-spring (Table 5).

Statistical tests did not indicate a significant correlation between concentrations of nitrate, ammonium, and total P in surface water and annual biosolids loading rate in the biosolids-amended watershed or between each nutrient and its annual loading rate.

Trace Elements

Concentrations of total Cd in surface water over the 31-yr study period were mostly below the method detection levels (MDLs) (Table 3), which were close to the Illinois limit of 0.01 mg L^{-1} for public supply and food processing water (Illinois Pollution Control Board, 2003).

The monthly mean copper concentrations in surface water across water bodies declined with time in both control and biosolids-amended watersheds (Fig. 4). Annual mean Cu concentrations in surface water in the first year were very high relative to the rest of the study

Table 3. Yearly mean of concentrations of N, total P, and trace metals in surface water in control (C) and biosolids-amended (B) watersheds.†

Year	NO₃⁻–N C	NO₃⁻–N B	MDL§	NH₄⁺–N C	NH₄⁺–N B	MDL	Total P C	Total P B	MDL	Total Cd C	Total Cd B	MDL	Total Cu C	Total Cu B	MDL	Total Hg C	Total Hg B	MDL
								mg L⁻¹									μg L⁻¹	
1971‡	0.38	0.20	0.02	0.38	0.40	0.1	0.19	0.25	0.01	0.015	0.018	0.01	*0.014*	*0.027*	0.01	0.20	0.15	0.1
1972	*0.11*	*0.86*	0.02	0.27	0.36	0.1	0.16	0.14	0.01	0.012	0.014	0.01	0.068	0.088	0.01	0.30	0.28	0.1
1973	0.13	2.30	0.02	0.20	0.28	0.1	0.14	0.17	0.01	0.011	0.011	0.01	0.020	0.023	0.01	0.15	0.14	0.1
1974	*0.19*	*1.79*	0.02	*0.20*	*0.29*	0.1	0.07	0.10	0.01	0.010	0.010	0.01	0.010	0.014	0.01	0.13	0.18	0.1
1975	*0.19*	*2.47*	0.02	0.33	0.33	0.1	0.11	0.12	0.01	0.010	0.010	0.01	0.011	0.011	0.01	0.26	0.19	0.1
1976	*0.08*	*1.56*	0.02	*0.15*	*0.29*	0.1	0.12	0.13	0.01	0.011	0.011	0.01	*0.011*	*0.018*	0.01	*0.10*	*0.12*	0.1
1977	*0.19*	*2.87*	0.02	*0.12*	*0.20*	0.1	*0.05*	*0.10*	0.01	0.010	0.010	0.01	*0.011*	*0.021*	0.01	0.11	0.11	0.1
1978	0.36	2.46	0.02	0.17	0.34	0.1	0.07	0.24	0.01	0.010	0.010	0.01	*0.010*	*0.011*	0.01	*0.16*	*0.13*	0.1
1979	*0.21*	*1.80*	0.02	*0.14*	*0.23*	0.1	*0.06*	*0.11*	0.01	0.011	0.010	0.01	0.010	0.015	0.01	0.24	0.23	0.1
1980	*0.14*	*1.61*	0.02	0.13	0.21	0.1	0.12	0.18	0.01	0.018	0.018	0.0175	*0.018*	*0.020*	0.0175	0.21	0.19	0.1
1981	0.25	2.54	0.02	*0.10*	*0.15*	0.1	*0.08*	*0.11*	0.01	0.020	0.020	0.02	0.021	0.021	0.02	0.28	0.22	0.1
1982	*0.19*	*3.60*	0.02	*0.11*	*0.16*	0.1	0.07	0.08	0.01	0.020	0.020	0.02	0.020	0.021	0.02	0.40	0.23	0.1
1983	*0.11*	*2.16*	0.02	0.10	0.19	0.1	0.05	0.20	0.01	0.020	0.020	0.02	0.028	0.039	0.02	0.19	0.25	0.1
1984	*0.20*	*2.96*	0.02	0.13	0.17	0.1	0.25	0.18	0.01	0.020	0.020	0.02	0.020	0.020	0.02	0.13	0.16	0.1
1985	*0.11*	*1.80*	0.02	*0.13*	*0.26*	0.1	0.05	0.12	0.01	0.020	0.021	0.02	0.020	0.028	0.02	0.18	0.14	0.1
1986	0.15	1.93	0.02	*0.10*	*0.14*	0.1	0.05	0.12	0.01	0.020	0.020	0.02	0.020	0.020	0.02	0.16	0.13	0.1
1987	0.33	1.61	0.02	0.12	0.36	0.1	0.04	0.25	0.01	0.020	0.020	0.02	0.021	0.021	0.02	0.15	0.14	0.1
1988	*0.06*	*1.35*	0.02	0.13	0.36	0.1	*0.30*	*0.09*	0.01	0.020	0.020	0.02	0.020	0.020	0.02	0.16	0.13	0.1
1989	0.08	1.14	0.02	0.13	0.25	0.1	*0.07*	*0.23*	0.01	0.020	0.020	0.02	0.020	0.020	0.02	0.10	0.11	0.1
1990	0.15	2.73	0.02	0.10	0.31	0.01	0.05	0.06	0.01	0.020	0.020	0.02	0.020	0.021	0.02	0.17	0.17	0.1
1991	*0.12*	*1.91*	0.02	0.04	0.13	0.01	*0.06*	*0.11*	0.01	0.013	0.014	0.013	0.014	0.013	0.013	0.23	0.23	0.23
1992	0.15	2.56	0.02	0.06	0.10	0.01	*0.08*	*0.13*	0.01	0.011	0.010	0.01	0.010	0.011	0.01	0.30	0.30	0.3
1993	0.64	2.64	0.02	0.10	0.08	0.01	*0.07*	*0.20*	0.01	0.010	0.010	0.01	0.010	0.010	0.01	0.28	0.29	0.3
1994	0.21	2.66	0.02	0.07	0.25	0.01	*0.06*	*0.22*	0.01	0.010	0.010	0.01	0.010	0.010	0.01	0.30	0.29	0.3
1995	0.17	3.38	0.02	0.07	0.15	0.01	*0.09*	*0.16*	0.01	0.010	0.010	0.01	0.029	0.028	0.01	0.29	0.30	0.3
1996	0.23	3.46	0.02	*0.06*	*0.11*	0.01	0.15	0.22	0.01	0.010	0.011	0.01	0.018	0.019	0.02	0.10	0.11	0.1
1997	0.09	2.28	0.02	*0.02*	*0.05*	0.01	0.11	0.13	0.01	0.010	0.010	0.01	0.016	0.014	0.02	*0.14*	*0.11*	0.1
1998	0.09	3.31	0.03	0.04	0.36	0.01	*0.11*	*0.32*	0.03	0.005	0.005	0.005	0.006	0.006	0.005	0.05	0.05	0.04
1999	0.14	3.25	0.02	0.11	0.26	0.02	0.11	0.14	0.01	0.004	0.003	0.004	*0.008*	*0.007*	0.008	0.07	0.06	0.04
2000	0.08	3.44	0.01	*0.10*	*0.20*	0.02	0.14	0.16	0.01	0.003	0.003	0.003	*0.007*	*0.015*	0.005	0.10	0.10	0.1
2001	*0.07*	*2.90*	0.015	0.05	0.11	0.009	*0.14*	*0.34*	0.08	0.007	0.006	0.007	0.007	0.006	0.005	0.04	0.04	0.04
2002	*0.09*	*2.52*	0.01	0.05	0.18	0.02	*0.06*	*0.12*	0.04	0.004	0.004	0.004	0.007	0.007	0.007	0.05	0.05	0.04
Means																		
1972–1984	*0.19a¶*	*2.15b*	0.02	*0.15a*	*0.26a*	0.10	*0.10a*	*0.14b*	0.01	*0.014b*	*0.013b*	0.014	*0.018a*	*0.022a*	0.014	0.20a	0.18a	0.10
1985–1993	*0.20ab*	*1.98b*	0.02	*0.10b*	*0.22ab*	0.06	*0.09a*	*0.15b*	0.01	*0.017a*	*0.017a*	0.017	*0.017a*	*0.018b*	0.017	0.19a	0.19a	0.16
1994–2002	*0.13b*	*3.03a*	0.02	*0.06c*	*0.18b*	0.01	*0.11a*	*0.20a*	0.02	*0.007c*	*0.007c*	0.007	*0.012b*	*0.013c*	0.010	0.13b	0.12b	0.12
Overall	*0.18*	*2.23*	0.02	*0.11*	*0.24*	0.06	*0.10*	*0.16*	0.01	0.013	0.013	0.013	*0.016*	*0.020*	0.014	0.18	0.17	0.12

† Italic type indicates a significant difference at the 0.05 probability level between biosolids-amended and control watersheds in a given year.
‡ Year before application started.
§ Method detection level.
¶ Values followed by the same letters within three periods are not significantly different at the 0.05 probability level.

period in both the biosolids-amended watershed and the control watershed (Table 3). For the first nine years, during which Cu concentration was above the MDL, the mean surface water Cu concentration in the biosolids-amended watershed was significantly greater than that in the control watershed in 1976, 1977, 1978, and 1980 (Table 3). The effect of sampling season on Cu concentration in surface water was not significant for all water bodies and treatments (Table 4). There is almost no effect of water body on the Cu concentration in surface water (Table 5).

The dynamics of monthly mean mercury concentration in surface water across water bodies over 31 yr in the biosolids-amended watershed were similar to that in the control watershed (Fig. 4). Lower Hg concentration in surface water was observed in the biosolids-amended watershed than the control watershed for reservoirs sampled in dry-summer (Table 2). The annual mean Hg concentration in surface water from the biosolids-amended watershed was significantly greater for one year (1976), but significantly lower for two years (1978 and 1997) than that in the control watershed (Table 3). The mean Hg concentrations in surface water for the 31-yr period were 0.17 μg L⁻¹ for the biosolids-amended watershed and 0.18 μg L⁻¹ for the control watershed. For the reservoir in the control watershed, mercury concentration was higher in dry-summer and wet-fall than wet-spring (Table 4). There is no significant difference in Hg concentration between creeks and reservoirs (Table 5).

Statistical tests also did not indicate a significant correlation between concentrations of trace metals in surface water and annual biosolids loading rate in the biosolids-amended watershed or between each metal and its annual loading rate.

DISCUSSION

Higher NO₃⁻–N, NH₄⁺–N, and total P concentrations in surface water in the biosolids-amended watershed as compared with the control watershed throughout the study were most likely due to the input of N and P from the biosolids.

With the mean annual N input to the biosolids watershed as high as 735 kg ha⁻¹ on the 1120 ha of application fields, the elevation of the surface water NO₃⁻ and NH₄⁺ seems to be unavoidable, as N sources can move to surface water through runoff. A study using ¹⁵N showed that nitrate, generated from commercial land application of

Table 4. Multiple comparisons† of concentrations of N, total P, and trace metals in surface water between sampling seasons for each water body and treatment (μ_1, dry-summer mean; μ_2, wet-fall mean; and μ_3, wet-spring mean, from 1972–2002).‡

Water body	Treatment	Season means			Pairwise comparisons		
		μ_1 (summer)	μ_2 (fall)	μ_3 (spring)	H_0: $\mu_1 = \mu_2$, significant probability	H_0: $\mu_1 = \mu_3$, significant probability	H_0: $\mu_2 = \mu_3$, significant probability
		— mg L^{-1} —					
					NH$_4^+$–N		
Reservoir	control	0.08	0.11	0.10	*0.00*	*0.01*	0.06
Reservoir	biosolids	0.17	0.22	0.14	0.13	0.16	*0.00*
Reservoir	combined	0.12	0.16	0.11	*0.01*	0.84	*0.00*
Creek	control	0.08	0.08	0.11	0.94	0.18	0.16
Creek	biosolids	0.29	0.27	0.10	0.86	*0.00*	*0.04*
Creek	combined	0.22	0.20	0.10	0.85	*0.01*	0.07
Combined	control	0.08	0.11	0.10	*0.00*	*0.00*	0.27
Combined	biosolids	0.21	0.23	0.12	0.50	*0.00*	*0.00*
Combined	combined	0.14	0.17	0.11	0.14	*0.04*	*0.00*
					Total P		
Reservoir	control	0.07	0.12	0.08	*0.00*	0.76	*0.01*
Reservoir	biosolids	0.17	0.15	0.11	0.44	*0.02*	*0.00*
Reservoir	combined	0.11	0.13	0.09	0.17	*0.05*	*0.00*
Creek	control	0.13	0.12	0.19	0.86	0.29	0.19
Creek	biosolids	0.21	0.23	0.11	0.59	*0.03*	*0.00*
Creek	combined	0.18	0.19	0.14	0.68	0.23	*0.05*
Combined	control	0.08	0.12	0.09	*0.01*	0.32	0.08
Combined	biosolids	0.18	0.18	0.11	0.83	*0.00*	*0.00*
Combined	combined	0.13	0.15	0.10	0.18	*0.03*	*0.00*
					NO$_3^-$–N		
Reservoir	control	0.06	0.10	0.12	*0.00*	*0.00*	0.18
Reservoir	biosolids	1.47	1.94	2.06	0.26	0.09	0.76
Reservoir	combined	0.63	0.85	0.90	0.21	0.07	0.77
Creek	control	0.31	0.27	1.33	0.64	*0.00*	*0.00*
Creek	biosolids	3.35	1.96	5.06	*0.01*	*0.01*	*0.00*
Creek	combined	2.30	1.36	3.82	*0.01*	*0.00*	*0.00*
Combined	control	0.09	0.12	0.29	0.10	*0.00*	*0.00*
Combined	biosolids	2.07	1.95	3.06	0.71	*0.00*	*0.00*
Combined	combined	1.00	0.96	1.57	0.81	*0.00*	*0.00*
					Total Cd		
Reservoir	control	0.013	0.014	0.013	0.54	0.69	0.30
Reservoir	biosolids	0.013	0.013	0.013	0.63	0.75	0.87
Reservoir	combined	0.013	0.013	0.013	0.80	0.61	0.43
Creek	control	0.014	0.013	0.013	0.46	0.53	0.93
Creek	biosolids	0.013	0.013	0.013	0.91	0.91	0.83
Creek	combined	0.013	0.013	0.013	0.78	0.68	0.89
Combined	control	0.013	0.013	0.013	0.83	0.52	0.37
Combined	biosolids	0.013	0.013	0.013	0.85	0.85	1.00
Combined	combined	0.013	0.013	0.013	1.00	0.56	0.55
					Total Cu		
Reservoir	control	0.015	0.016	0.015	0.11	0.78	0.32
Reservoir	biosolids	0.018	0.017	0.018	0.85	0.87	0.73
Reservoir	combined	0.016	0.017	0.016	0.59	0.72	0.83
Creek	control	0.015	0.015	0.014	0.89	0.45	0.57
Creek	biosolids	0.016	0.016	0.015	1.00	0.40	0.45
Creek	combined	0.016	0.016	0.015	1.00	0.28	0.33
Combined	control	0.015	0.016	0.015	0.12	0.87	0.26
Combined	biosolids	0.017	0.017	0.017	0.84	0.94	0.89
Combined	combined	0.016	0.016	0.016	0.59	1.00	0.60
		— µg L^{-1} —					
					Total Hg		
Reservoir	control	0.20	0.17	0.15	0.16	*0.01*	*0.05*
Reservoir	biosolids	0.15	0.19	0.15	0.18	0.77	0.15
Reservoir	combined	0.18	0.18	0.15	0.99	*0.01*	*0.03*
Creek	control	0.18	0.18	0.15	0.95	0.19	0.24
Creek	biosolids	0.18	0.18	0.16	0.74	0.43	0.22
Creek	combined	0.18	0.18	0.16	0.76	0.18	0.09
Combined	control	0.20	0.18	0.15	0.18	*0.01*	*0.03*
Combined	biosolids	0.16	0.19	0.15	0.17	0.46	0.08
Combined	combined	0.18	0.18	0.15	0.94	*0.01*	*0.01*

† Data of unknown seasons, that is, all months except wet-spring (April), dry-summer (July), and wet-fall (October) during the first 10 yr (1972–1981), are not included.

‡ Italic type indicates a significant difference at the 0.05 probability level.

swine waste within a North Carolina Coastal Plain catchment, could move to surface water by ground water passing beneath the spray fields and adjacent riparian buffers (Karr et al., 2001). The soil compaction brought about by strip-mining in our study area may have promoted the runoff and movement of NO$_3^-$–N to stream

Table 5. Comparisons in concentrations of N, total P, and trace metals in surface water between reservoir and creek for each sampling season and treatment (μ_1, reservoir mean; μ_2, creek mean, from 1972–2002).†

| Season | Treatment | Water body means | | H_0: $\mu_1 = \mu_2$ significant probability |
		Reservoirs	Creek	
		— mg L^{-1} —		
		NH$_4^+$–N		
Unknown‡	control	0.18	0.23	0.23
Unknown	biosolids	0.29	0.29	0.95
Unknown	combined	0.28	0.27	0.86
Dry-summer	control	0.08	0.08	0.72
Dry-summer	biosolids	0.17	0.29	0.08
Dry-summer	combined	0.12	0.22	*0.03*
Wet-fall	control	0.12	0.08	*0.00*
Wet-fall	biosolids	0.22	0.27	0.51
Wet-fall	combined	0.16	0.20	0.39
Wet-spring	control	0.10	0.11	0.64
Wet-spring	biosolids	0.14	0.10	*0.00*
Wet-spring	combined	0.11	0.10	0.32
Combined	control	0.11	0.14	*0.01*
Combined	biosolids	0.24	0.25	0.55
Combined	combined	0.18	0.22	*0.04*
		Total P		
Unknown	control	0.08	0.14	*0.01*
Unknown	biosolids	0.14	0.18	0.35
Unknown	combined	0.14	0.17	0.28
Dry-summer	control	0.07	0.13	0.08
Dry-summer	biosolids	0.17	0.21	0.41
Dry-summer	combined	0.11	0.18	*0.02*
Wet-fall	control	0.12	0.12	0.88
Wet-fall	biosolids	0.15	0.23	*0.01*
Wet-fall	combined	0.13	0.19	*0.01*
Wet-spring	control	0.08	0.19	*0.02*
Wet-spring	biosolids	0.11	0.11	0.91
Wet-spring	combined	0.09	0.14	*0.02*
Combined	control	0.09	0.14	*0.00*
Combined	biosolids	0.14	0.18	0.07
Combined	combined	0.12	0.17	*0.00*
		NO$_3^-$–N		
Unknown	control	0.27	0.16	0.14
Unknown	biosolids	1.29	4.17	*0.00*
Unknown	combined	1.16	3.04	*0.00*
Dry-summer	control	0.06	0.32	*0.00*
Dry-summer	biosolids	1.47	3.35	*0.00*
Dry-summer	combined	0.63	2.30	*0.00*
Wet-fall	control	0.10	0.27	*0.01*
Wet-fall	biosolids	1.94	1.96	0.98
Wet-fall	combined	0.85	1.36	*0.04*
Wet-spring	control	0.12	1.34	*0.00*
Wet-spring	biosolids	2.06	5.06	*0.00*
Wet-spring	combined	0.90	3.82	*0.00*
Combined	control	0.11	0.44	*0.00*
Combined	biosolids	1.54	3.80	*0.00*
Combined	combined	0.91	2.74	*0.00*
		Total Cd		
Unknown	control	0.012	0.012	0.38
Unknown	biosolids	0.013	0.012	0.28
Unknown	combined	0.012	0.012	0.51
Dry-summer	control	0.013	0.014	0.48
Dry-summer	biosolids	0.013	0.013	0.92
Dry-summer	combined	0.013	0.013	0.74
Wet-fall	control	0.013	0.013	0.62
Wet-fall	biosolids	0.013	0.013	0.75
Wet-fall	combined	0.013	0.013	0.86
Wet-spring	control	0.013	0.013	0.95
Wet-spring	biosolids	0.013	0.013	0.93
Wet-spring	combined	0.013	0.013	0.89
Combined	control	0.013	0.013	0.78
Combined	biosolids	0.013	0.013	0.71
Combined	combined	0.013	0.013	0.54
		Total Cu		
Unknown	control	0.023	0.017	0.14
Unknown	biosolids	0.023	0.023	0.88
Unknown	combined	0.023	0.021	0.57

Table 5. Continued.

| Season | Treatment | Water body means | | H_0: $\mu_1 = \mu_2$ significant probability |
		Reservoirs	Creek	
Dry-summer	control	0.015	0.015	0.56
Dry-summer	biosolids	0.018	0.016	0.20
Dry-summer	combined	0.016	0.016	0.73
Wet-fall	control	0.016	0.015	0.61
Wet-fall	biosolids	0.017	0.016	0.42
Wet-fall	combined	0.016	0.016	0.43
Wet-spring	control	0.015	0.014	0.58
Wet-spring	biosolids	0.018	0.015	*0.04*
Wet-spring	combined	0.016	0.015	0.09
Combined	control	0.016	0.016	0.80
Combined	biosolids	0.020	0.019	0.45
Combined	combined	0.018	0.018	0.75
		— μg L^{-1} —		
		Total Hg		
Unknown	control	0.20	0.18	0.58
Unknown	biosolids	0.17	0.17	0.63
Unknown	combined	0.18	0.17	0.63
Dry-summer	control	0.20	0.18	0.39
Dry-summer	biosolids	0.15	0.18	0.18
Dry-summer	combined	0.18	0.18	0.80
Wet-fall	control	0.17	0.18	0.75
Wet-fall	biosolids	0.19	0.18	0.79
Wet-fall	combined	0.18	0.18	0.93
Wet-spring	control	0.15	0.15	0.83
Wet-spring	biosolids	0.15	0.16	0.49
Wet-spring	combined	0.15	0.16	0.67
Combined	control	0.18	0.18	0.73
Combined	biosolids	0.17	0.17	0.90
Combined	combined	0.17	0.17	0.81

† Italic type indicates a significant difference at the 0.05 probability level.
‡ All months except wet-spring (April), dry-summer (July), and wet-fall (October) during the first 10 yr (1972–1981).

water as observed by others (Coupe and Macy, 1993; Croke et al., 2000). Nitrate may cause human and animal health problems when concentrations exceed 10 mg L^{-1} as N. In no months did the NO$_3^-$–N concentration in surface water in the biosolids-amended watershed exceed \10 mg L^{-1}, implying that at this site the application of biosolids for land reclamation will not have any significant effect on human health or the environment with respect to NO$_3^-$–N.

The NH$_4^+$–N in surface water in the biosolids-amended watershed was also far below a concentration that could adversely affect aquatic organisms.

The elevation of total P concentration in surface water associated with the biosolids applications for 13 of 31 yr of the project is modest considering that the mean annual P input from biosolids was as high as 530 kg ha^{-1} on the 1120 ha of application fields in the biosolids-amended watershed, and that mean surface soil total P (0.7%) in the fields within the biosolids-amended watershed was already 13 times higher than that in the fields within the control watershed in 2001. This elevation in surface water P concentrations might not have occurred if the annual loading of biosolids had not exceeded the agronomic rate at the early stage of the project. Furthermore, the 31-yr mean surface water total P concentration of 0.16 mg L^{-1} for the biosolids-amended watersheds at Fulton County was even close to the low end of the range of 0.06 to 0.4 mg L^{-1} for drainage from agricultural sites in the Western Lake Michigan watershed in Wisconsin and upper Michigan from 1992–
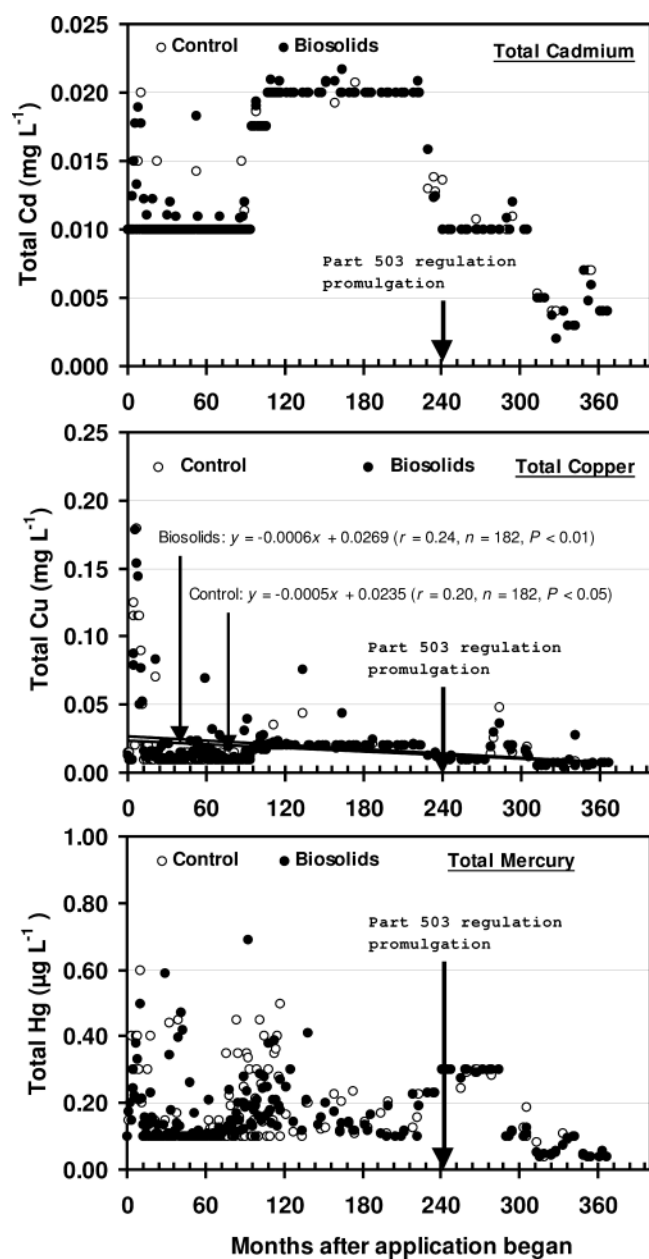
Fig. 4. Concentrations of trace metals in surface water (mean of reservoirs and creeks) in biosolids-amended and control watersheds from 1972 to 2002. A trendline was drawn when element concentrations were significantly correlated to time in either control or biosolids-amended watersheds.

1995 (http://water.usgs.gov/pubs/circ/circ1156/circ1156.4B.html; verified 23 Aug. 2005).

Two years after the project began, the Cd concentration went below the MDL until 2002 in both the biosolids-amended and control watersheds, suggesting biosolids application did not increase the Cd concentration in surface water. Although results showed higher Cu in surface water in the biosolids-amended watershed, this mainly occurred within the first 10 yr of the project, when the land-applied sludge carried a substantially high amount of Cu. From 1981, most measurements of Cu concentration were below the MDL, suggesting no

discernable impact on Cu concentration in surface water could be expected in the use of biosolids.

Mercury concentrations in surface water were significantly higher for only one year, but significantly lower for two years in the biosolids-amended watershed than in the control. The low mobility of mercury to water bodies has been confirmed by results of Granato et al. (1995).

The Cd, Cu, and Hg concentrations in surface water of both the control and biosolids-amended watersheds became higher during the middle of the 31-yr land reclamation project. This trend occurred from 1980 to 1990 for Cd and Cu, and from 1991 to 1995 for Hg. Such elevations might be due to the greater value of the MDL, which is probably the result of changes in instrument sensitivity. These areas are downwind of coal-fired power plants. Aerial plumes from these plants could also contribute to these increases. For the trace metals we monitored, their concentrations were either below the MDL or not significantly different in two watersheds, while the application of biosolids during the 31 yr increased the concentrations of these trace elements in soil in the biosolids-amended watershed (data not shown). Granato et al. (1995, 2004) indicated that at the same Fulton County site, from 80 to 100% of the Cd, Cu, and Hg applied to soils in sewage sludge/biosolids since 1972 still resided in the plow layer or top 15 to 23 cm of soil. Sloan et al. (2001) also observed the accumulation of biosolids mercury in soil in a Minnesota agricultural watershed amended with biosolids for two decades.

Normally, at this site, spring and fall are relatively wet seasons, and summer a relatively dry season due to the difference in temperature that affects the evaporation. High P concentrations in wet-fall could be due to high runoff in the fall, which transported the particulate form of P into water bodies. Since water was not filtered before analysis, some of the P should be in the particulate form. Summer is the season for biosolids application, and this may explain why the high P concentration in surface water also occurred in summer in the biosolids watershed. Nitrate concentrations in water did not follow this pattern, implying the movement of NO_3^- may be controlled by other factors. Biosolids were typically applied either in summer or early fall and only an annual cover crop was planted. For fall applications the cover crop did not establish as well as crops following summer applications and did not produce as much biomass, possibly making it less effective in reducing NO_3^- concentrations in soil and/or mitigating erosion. The soil soluble N can move to water bodies along with water from rains at the onset of spring. Farmers apply nitrogen fertilizer in spring, generally before the first water sampling of a year. In summer and fall, less NO_3^- in soil is available for moving to water bodies because of use by crops in fields. This is probably why the NO_3^- concentration in surface waters in the biosolids-amended watershed was always higher in spring than summer and fall. We could not determine a plausible reason for higher mercury concentration in surface water in the dry-summer and wet-fall than in the wet-spring in the control watershed.

Relatively greater concentrations of NO_3^-, NH_4^+, and total P were observed in creeks than in reservoirs, irrespective of watershed and sampling season. In the Fulton County reclamation site, reservoirs are far larger than the creeks, and hence there is a smaller volume of water generally present in the creek than the reservoir. The difference in concentration of nutrients between the two water bodies could therefore be explained by the different dilution in the reservoir as compared with the creek. Concentrations of Cd, Cu, and Hg were apparently not affected by water body, further confirming the insignificant amount of these metals moving into water bodies from the application fields.

The statistical analysis revealed no correlation between each water chemistry parameter and annual biosolids/element loading rate. Since the biosolids are applied starting in June and the summer is usually a dry period, the first two surface water samplings, spring and mid-summer, would not seem to be of any value in correlation determinations. However, there were also no correlations between wet-fall water chemistry parameters and annual biosolids loading rate. Furthermore, wet-spring water chemistry parameters were not correlated to biosolids loading rate of the previous year either. Our finding therefore indicates the movement of biosolids nutrients and trace metals into surface water would not depend on biosolids loading rate if proper soil conservation measures take place.

CONCLUSIONS

Nitrate and ammonium in surface water increased with the application of biosolids for land reclamation, but the elevations observed at this site did not cause an impairment of water resources. The application of biosolids increased total P in surface water, but such effect occurs mainly after a long-term use of biosolids at a high rate, and the level of total P is still comparable to that from agricultural fields in the region. Cadmium concentration in surface water is below the MDL even after the 31 yr of application that produced loadings that exceed the cumulative loading limit in Part 503. Copper and mercury remained unaffected for nearly the entire period of application. Following the promulgation of 40 CFR part 503, the concentrations of all three metals in the surface waters fell below the MDL for nearly all samplings. Therefore, even with a high annual loading of nutrients and trace elements (735 kg N, 530 kg P, 4.5 kg Cd, 30.7 kg Cu, and 0.11 kg Hg ha^{-1} yr^{-1}; based on the area of application fields), 31 yr of biosolids application, managed with adequate runoff and soil erosion control, caused only a minor impact in terms of NO_3^-, NH_4^+, and total P, and little or no impact in terms of Cd, Cu, and Hg on surface water chemistry. At this site, over the 31-yr biosolids application period, cumulative applications of nearly 900 Mg ha^{-1} in both liquid and dewatered form were effectively managed using a simple low-tech system of earthen berms and runoff retention basins.

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