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THE USE OF STREAM SEDIMENTS TO INFER WATER QUALITY ON A STREAM IN NORTHWESTERN OHIO[1]

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Abstract. A primary sewage treatment plant discharges its effluents into Butler Ditch, Oak Openings, Lucas County, Ohio. A marsh habitat near the discharge outlet, high turbidity, sludge covering the stream bed and pungent odor gave reason to believe that the effluent from the sewage treatment plant contaminated the ditch. Water and stream sediment samples were collected from 24 sample locations over a 2 mile stretch downstream from the discharge outlet of the sewage treatment plant and analyzed for chemical composition. At the time of sample collection, the sewage treatment plant had discharged its effluents into the ditch for a period of 2 years. The water and the −80 mesh fraction of the sediment samples were analyzed for mineral content, the chemical components, alkalinity, hardness, total dissolved solids, specific conductance, pH, cation exhange capacity and mineralogy of the sediments. The tests showed that there was a cutoff point 450 ft downstream from the effluent outlet, where most of the element concentrations dropped abruptly, except sedimentary iron, which increased. Heavy vegetation retarded the flow of water, resulting in a more anaerobic environment upstream. Precipitation of many ions increased downstream probably as a result of increased oxygenation of the water. The use of sediment chemistry proved advantageous to infer the long term quality of the stream water.

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In the summer of 1974, water and stream sediment samples from Butler Ditch in Oak Openings, northwestern Ohio, were collected and analyzed for a number of chemical elements and compounds. The purpose of this study was to determine the impact of the effluent from a sewage treatment plant on the ditch that receives its inflow mainly from effluent during the summer. Both water and stream sediment chemistry were analyzed because the water chemistry only assesses the effluent impact at time of sampling, while the stream sediment geochemistry gives a cumulative assessment of the pollution. If samples can be collected only once, and speed is important, this seems to be a good method to study stream pollution.

Water was analyzed by the usual techniques, while stream sediments were subjected to cold hydrochloric acid extraction. Fortescue *et al* (1971) first used this technique in studies of landscape geochemistry. Exploration geochemists use similar techniques because in their studies a fast and inexpensive approach is necessary and adequate. Alther (1975) used stream sediments successfully to determine the impact from the runoff of a pigyard on the stream environment.

LOCATION AND DESCRIPTION OF OAK OPENINGS

Oak Openings town, an unincorporated area, is located approximately 14 miles west of Toledo, Ohio, in Lucas County, Spencer Township. Oak Openings is a narrow sand belt extending from Detroit, Michigan to Maumee, Ohio and is 5 to 10 miles wide near the community with the crest of the belt roughly bisecting the area. Low hummocky dunes stabilized by vegetation characterize the land surface. All ditches in the area are man made and receive mostly ground water. Precipitation readily infiltrates into the sandy soil. Many of the ditches, including Butler Ditch, are ephemeral and experience high winter and spring floods.

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The soils in this area are slightly acidic to neutral and sediments dissected by the ditch are mainly iron stained quartz sand with about 1% silt and clay. The soil profile is poorly developed but the sand is texturally mature and well rounded.

The ground water is derived mainly from the silurian-devonian aquifer, largely a dolomitic bedrock. The shallow water table fluctuates 2 to 4 ft seasonally, is in the average 6 to 20 ft deep, and follows the surface topography (Knukle 1971). The sewage treatment plant contributes daily some 40,000 gal of domestic sewage effluent to Butler Ditch (Rabel, personnel comm. 1974), which constitutes the major inflow during the dry season since the water table is then usually below the bed of the ditch. Precipitation recharge does not dilute the effluent significantly during the dry season.

Butler Ditch originates near Oak Terrace Road to the east of the community. The sewage treatment plant is located at the head of this stream. The ditch flows through Spencer and Springfield townships into Wolf Creek, eventually draining into the Maumee River.

The water in the upper section of the ditch was dark, muddy and had the familiar rotten egg smell due to hydrogen sulfide. A 1 in thick layer of black sludge covered the stream bed. The color and odor of the water improved with increasing distance away from the sewage plant outlet. The upper portion of the ditch was lined with marsh vegetation such as cattails, cannon cleaners, and reeds, and the water was covered with blue-green algae. This type of vegetation was not present before the plant started discharging its effluent into this ditch. Meadows and small woods line the rest of the ditch.

METHODS AND PROCEDURES

Field sampling was conducted on 12 June 1974 when water and sediment samples were collected over a 2 mile stretch of the ditch downstream from the sewage treatment plant. The distance between sample locations increased from the effluent outlet in a logarythmic fashion downstream over the 2 mile stretch. Accurate spacing was not always possible because of inaccessability to the sites. The entire distance through to the last station was 11800 ft. An untreated sample was collected in a manhole near the sewage plant, representing precipitation recharge that moved laterally through the soil. A sample from the treated effluent was also collected at the outlet of the settling tank inside the plant. All samples were collected and analyzed in the usual manner by wet chemical methods and with a Perkin Elmer 403 Atomic Absorption Spectrophotometer. Stream sediments were collected by means of a stainless steel shoffle next to the water samples. They were stored in plastic cups and immediately taken to the laboratory and ovendried at 110 °C for 24 hr. An −80 mesh fraction was then mechanically separated for trace element analysis, because it provides a good compromise between obtaining sufficient sample and provides a good contrast between background and anomalies (Bradshaw *et al* 1972). Sediment sample was weighed out (1 g) and placed into acid-rinsed Nalgene bottles and digested with 20% cold hydrochloric acid for 32 hr (Fortescue *et al* 1971, Gawron 1973). To assure good mixing of sediment and acid and maximum extraction, the samples were placed on an automatic roller and agitated for this time period. The samples were then left standing for 8 hrs, and the extract was passed through a 0.45μ millipore filter and analyzed by flame atomic absorption.

RESULTS AND DISCUSSION

Averages were computed for the upper 450 ft and lower portion of the ditch (See table 1). On first inspection, these data revealed that there was an abrupt decrease in concentration of iron and a slight decrease of several other elements on or near 400 ft to 600 ft below the sewage treatment plant outlet (that is why this point was chosen to divide the stream into two segments). Background data from earlier studies in streams nearby and in a groundwater well not far from the plant are presented in table 2. Comparison of background data from Drennan Ditch (Valkenburg 1972) with the data from lower Butler Ditch (more diluted with runoff and groundwater) shows close agreement for K, N, total dissolved solids and pH. Marked differences exist between most of the other variables, particularly zinc and chlorides, which were much higher in those ditches, possibly due to water contacting sphalerite deposits. This may be in part because the samples were collected in March. The groundwater data from well G17 show no similarity at all except alkalinity. Concentration of many variables in the water from the manhole were much lower than in the ditch, as would be expected since this is rain water. Only sul-

TABLE 1

Chemical data from water, effluent and sediment samples.

Chemical Parameter	Manhole* Water	Effluent	Butler Ditch† Water Upper 400 ft	Butler Ditch† Water Lower Portion	Butler Ditch† Sed Upper 400 ft	Butler Ditch† Sed Lower Portion
Ca (ppm)	23.8	59.5	86.0± 6.7	77.6 ± 2.8	10091 ±3908	5801 ±3121
Mg (ppm)	8.3	31.0	27.3± 4.1	23.9 ± 2.1	143 ± 72	139 ± 126
Mn (ppm)	0.05	0.1	0.2± 0.37	0.2 ± 0.1	1.4± 0.9	1.6± 1.1
Fe (ppm)	10.0	55.0	53.4± 3.7*	29.7 ± 0.5	1390 ± 736	1744 ± 696
Zn (ppm)	0.2	0.2	0.2± 0.34**	0.2 ± 0.1	742 ± 721**	364 ± 299
Ni (ppm)	0.0	0.6	0.3± 0.3	0.3 ± 0.2	6.5± 2.5	6.2± 2.1
Cu (ppm)	0.0	0.1	0.0± 0.0	0.0 ± 0.0	2.2± 0.8	2.1± 0.5
Na (ppm)	9.0	45.5	23.1± 4.1	24.8 ± 2.2	72.0± 22	63.0± 24
K (ppm)	1.2	14.3	3.5± 0.57	3.3 ± 0.2	76.0± 16	63.0± 10.4
Sulfates (ppm)	18.3	9.5	9.5± 2.7	7.8 ± 2		
Nitrates (ppm)	0.2	1.5	2.8± 2.3	3.1 ± 1.9		
Chlorides (ppm)	1.0	52.0	36.0± 2.9	32.3 ± 4		
T. Phosphates (ppm)	0.2	13.0	1.0± 0.46	0.7 ± 0.5		
Alkalinity (mg l)	83.0	152.0	118.0± 2.8	113.0 ± 4		
Tot. Diss. Solids (mg l)	97.0	422.0	298.0±28	319.0 ±25		
Hardness (mg l)	112.0	375.0	419.0±37	346.0 ±13		
Spec. Cond. (µmhos/cm)	186.0	580.0	352.0±20	351.0 ±18		
pH	7.4	7.4	7.6± 0.1	7.6 ± 0.1	7.6 ± 0.2	7.0± 0.1
Loss on Ignition (450 C., 4 Hours)	—	—	—	—	3.47± 0.6	3.0± 0.9

†data reported as mean±SD.
*345 Feet.
**455 Feet.
***675 Feet from Effluent.

fates turned out to be much higher, which could be a result of sulfuric acid present in the rain water. The concentrations in the effluent were generally somewhat higher than in both portions of the ditch, which is most likely attributable to dilution by surface runoff and some limited ground water infiltration into the ditch (there was a stormy day before sample collection). Calcium, manganese, nitrates and the hardness of the water was higher in the water than the effluent, suggesting secondary sources. Noteworthy is that the concentration of iron and magnesium was almost the same in the effluent and the upper ditch, but that the concentration of sodium, potassium, chlorides, phosphates and total dissolved solids was much higher in the effluent. Noteworthy also is that the concentration of calcium and zinc was much higher in the upstream sediments, while that of iron was much higher downstream.

TABLE 2

Data from Valkenburg's study (1972).

Chemical Parameter	S7*	S6*	G17**
Ca (ppm)	51.3	59.3	35.7
Mg (ppm)	10.2	10.5	4.8
Na (ppm)	15.9	15.9	3.3
K (ppm)	3.1	2.0	0.5
Fe (ppm)	20.0	15.0	696.0
Zn (ppm)	12.0	12.0	322.0
Nitrates (ppm)	6.8	3.7	0.0
Sulfates (ppm)	55.7	43.2	25.6
Chlorides (ppm)	19.9	22.7	1.7
Alkalinity (mgl)	155.0	192.8	112.6
Hardness (mg l)	180.0	202.0	116.0
Spec. Conductance (µmhos/cm)	452.0	479.0	219.0
Total Diss. Solids (ppm)	273.0	230.0	136.0
pH	7.5	7.9	8.4

*S7 and S6 are surface water samples from Butler Ditch and Drennan Ditch, respectively, in Spencer and Springfield Townships, OH.
**G17 is a ground water well near Butler Ditch.

It should be mentioned at the onset of this discussion that two very important parameters, in terms of interpretation, namely the dissolved oxygen content and the biological oxygen demand, were not measured due to a different design of the original project. I attempted to interpret the distribution of the chemical variables, particularly the abrupt break in concentration at 450 ft, based on the available data and by seeking to correlate the distribution of variables in water and sediment.

An immediate indicator of a biochemically stressed environment was the hydrogen sulfide smell that prevailed near the effluent outlet. This type of smell suggests anaerobic conditions, as is well known. Data provided by the Lucas County Sanitary Engineers showed a dissolved oxygen content of 3.7 in the effluent, which is very low. Since the stream water was dark and muddy, little photosynthesis was likely taking place, thus the DO would be expected to be very low. Since the sludge that covered the stream bed was mainly organic, slightly acidic and relatively reducing conditions were expected to prevail at the sediment (sludge ?) water interface, which would then result in the production of hydrogen sulfide, decay of organic matter and release of elements and compounds adsorbed by clays and organic matter. At about 450 ft from the discharge outlet, where the concentration break occurred, the vegetation was found to be particularly heavy, resulting in a buildup of sludge and a backup of the already slowly moving water, thus rendering almost stagnant conditions. Below this site the water started to move swifter, become clearer, and less sludge was deposited on the stream bed, and the rotten egg smell disappeared. Table 1 reveals that, in general, the standard deviations are lower downstream than upstream, also suggesting a more stable environment. From these observations, it is clear that the stressed environment upstream is the reason why the concentration of many of these variables changes so abruptly.

TABLE 3

Significant correlation coefficient between related variables.

a) Water	
Iron versus Hardness	0.82
Mg versus Ca	0.74
Sulfates versus Ca	0.56
b) Water versus Sediments	
Ca versus CA	0.59
Zn versus Zn	0.59
c) Sediments	
Mn versus Fe	0.7
Fe versus Mg	0.53
Cu versus Ni	−0.58 (Min. sign. at 0.05 is 0.44)

In order to determine the relationship between the chemical variables, the correlation coefficient between all variables was calculated. The significant relationships were determined and are shown in table 3. These results allow the following statements about the conditions in this ditch:

1. Iron is the main contributor to the hardness of the water;
2. calcium and sulfates seem to precipitate as gypsum;
3. iron and manganese, not surprisingly, coexist as oxides and hydroxides in the sediments;
4. some of the calcium, magnesium and iron seem to have been derived from the same source, namely dissolved by groundwater from the dolomitic bedrock;
5. even though a junkyard downstream from the outlet contaminates the ditch with zinc, some seems to have been contributed by groundwater (via effluent, which is originally groundwater) as also shown in the data from well G17;
6. some nickel may enter the stream from the junkyard.

Most of these relationships are what one would except in a normal stream environment.

Since many of these variables showed a distinctly higher concentration upstream than downstream (sedimentary iron was the reverse), a trimmed t-test was performed on all data, comparing, in most cases, the population above and below 450 ft. The trimmed t-test is derived from the students t-test but does not require a normal distribution and can thus be employed instead of a nonparametric test (Yuen 1971). Its application to this type of problem has already been demonstrated (Alther 1979). The significant data are presented in table 4. The obvious reason for higher distributions upstream are the stagnant, stressed environ-

TABLE 4

Trimmed -t statistics for sediment and water data for Butler Ditch, Oak Openings, Ohio.

Element	Trimmed Mean (ppm)		Degrees of Freedom
	Upper Mean	Lower Mean	
Fe (Water)**	53.00	29.67	6.13
Hardness**	416.40	347.14	7.59
Ca (Water)*	85.70	78.56	9.52
Mg (Sediments)*	132.67	62.33	8.95
Fe (Sediments)*	1095.00	1497.78	12.75
Zn (Sediments)*	602.00	280.00	11.11
Mg (Water)*	27.25	23.58	9.91
Ln Ca (Sediments)**	9.18	8.36	12.3

*Significant.
**Highly Significant.

ment. Iron seems to be the most important variable in terms of interpreting the data. Upstream it seems to stay mainly in solution, which is reflected by the lower accumulation of iron in the sediments, while downstream it is lower not only because of dilution, but also because it precipitates more freely. There are several mechanisms by which this happens. Anaerobic bacteria, which are undoubtedly present in the sludge upstream, reduce and release iron hydroxides, forming free soluble iron (Hall 1972). Furthermore, ferrous iron tends to be associated with a high content of organic matter (Stumm and Morgan 1970), which was also present upstream. Ferrous iron does not precipitate freely, which would account for the difference found in water and sediment upstream and downstream. Since the DO obviously increases downstream as the velocity of the stream increases, the dissolved iron is then oxidized and precipitates more freely, which is substantiated by the data. The data for manganese in table 1 show that it follows the same trend in water and sediments as iron, as expected. However, perhaps due to the low concentration, the relationships are statistically not significant. The reason that zinc is significantly higher in the sediments upstream than downstream may be related to the behavior of iron. Watanabe *et al*(1965) reported that the uptake of zinc by plants sharply decreases in the presence of iron, which would result in increased precipitation. Some or most of this zinc may be derived from ground water.

Lastly, an explanation seems to be required for the higher concentration of calcium and magnesium upstream than downstream. Both calcium and magnesium are derived mainly from the dolomitic bedrock. Calcium, however, has another source. The effluent flows through concrete tilings before it enters the ditch and these tilings contain considerable amounts of calcium. Since the effluent is often backed up into the tilings and since sulfates react with the cement in the pores of the concrete and adsorb calcium, some of the additional calcium may be derived in this manner, assuming a lower pH within the tilings. Furthermore, CO_2 also reacts with the cement, resulting in $CaCO_3$ and $MgCO_3$, which will then precipitate upstream (Isaak 1966). The source of the CO_2 could be the available decaying organic matter. This second source would then explain why there is more calcium and magnesium in the water and sediment upstream than downstream, despite the fact that its concentration is only slightly less than that of sodium, sodium did not show this trend.

The stream sediment data clearly showed a build up of several contaminants, particularly iron and calcium. While the variability of the data is high, this is probably a result of not enough sampling (replication was not done) and variations in stream flow due to vegetative obstructions.

It is apparent that the sewage effluent is the main reason why this stressed environment developed upstream, although not necessarily because treatment was inadequate. If the gradient of the ditch was somewhat higher, I believe flow stoppage and particulate buildup would not occur, implying that engineering and construction of the ditch carrying away the effluent is as important as the treatment of the raw sewage itself in terms of environmental safety and control. Furthermore, the use of stream sediments to determine long term contamination of a stream ought to be considered as a standard procedure to insure complete understanding of the events, particularly since prevailing water conditions such such as redox and pH can be discerned with the use of these data.

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Correction: It was inadvertantly omitted from the OHIO JOURNAL OF SCIENCE July 1981 Necrology that Ronald L. Stuckey researched and wrote the Robert Benson Gordon obituary. Dr. Stuckey and Dr. E. D. Rudolph coauthored the obituary of Andrew Denny Rodgers III that also appeared in the July 1981 OJS.