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## Measuring the impacts of land use on water quality influenced by non-point sources

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**The objective of this study is to (a) test the proposition that the variance of water quality from undefined sources is a function of land use within the watershed, and (b) examine the premise that the impact of land use near the stream is more important than that far away from the stream in affecting the water quality from non-point sources. Results obtained using this approach support both these hypotheses. Moreover, these tests suggest the importance of considering the means by which chemical elements are delivered to the streams. Nitrate-nitrogen and phosphorus can probably be intercepted by different means because of their varying delivery systems. Nitrate-nitrogen can be intercepted by removal of fast-growing floodplain crops and phosphorus by sediment barriers at sites outside the floodplain. Further evidences suggest that reservoir trap-efficiency is considerably important in improving the downstream water quality as the former entraps clay nanominerals (with adsorbed particulates of phosphorus) that are found to be responsible for the fate and transport of phosphorus. The methodology of analysis of stream loads is ordinary least square regression analysis. Stream loads of nitrate-nitrogen and total phosphorus have been studied as a function of land use.**

**Keywords:** Land use, non-point source, nitrate-nitrogen, phosphorus, water quality.

THE primary objective of a non-point source (NPS) pollution control watershed project is to protect or restore the designated use of a water resource by reducing pollutant delivery to it. Because NPS of pollution is usually widespread, intermittent and undefined, mitigating a water quality problem, or potential problem, caused by such pollution is often difficult. The task is further complicated when sufficient time and funding are not available to implement all the recommended best management practices (BMPs). For this reason, a land treatment or watershed management strategy should be developed to guide the selection and implementation of BMPs. While

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strategies can vary widely depending on hydrologic, socio-logic and agronomic factors, a key component of the most effective strategies is identification and appropriate treatment of NPS areas contributing disproportionately to the water quality problem. Concentrating land treatment efforts on these critical areas, or sources, helps ensure that available resources are appropriated as efficiently as possible<sup>1-3</sup>.

The purpose of this study is to verify the assumptions involving the role of land management in maintaining the water quality in the watershed of a stream<sup>4</sup>. A river basin in Eastern Illinois, USA was selected for this study as a suitable exemplar because earlier studies<sup>2</sup> had demonstrated that majority of chemical constituent loadings came here from undefined NPS. These loadings derived from the land uses in the watershed consequently led to the thinking that if land-use patterns could be modified, the stream water quality could probably be controlled. It is, however, pertinent to mention here that there is no report on the presence of toxic metals in the soil worthy of investigation. The contents of metals like Cu, Zn, etc. are similar to their usual natural concentration in the soil<sup>5,6</sup>. The necessary database required for such a project was easily available for the Illinois river basin, USA, which further facilitated the decision-making<sup>4</sup>. This information is useful to inform all stakeholders and guide the development of response strategies for managing risk. The hydrologic budget of the stream is known to be well influenced by the area, immediately adjacent to the stream<sup>7,8</sup>. It was reported earlier<sup>9,10</sup> that land uses adjacent to streams had more impact on water quality than those farther away from the streams. The hydrologic budget of streams is known to be considerably influenced by the area immediately adjacent to the stream<sup>8,11</sup>. Thus, to improve the quality of stream water, controlling land uses close to the stream is a preferred decision in a land management strategy. In terms of the Indian river basins, our freshwater resources are dwindling<sup>12</sup>. This is because of an incorrect management strategy (sectoral or state-wise management of a single river basin as depicted by the present status of the River Ganges) and ill-planned use of land adjacent to the streams. All Rural Clean Water Programme (RCWP) projects are, therefore, required to identify and treat critical areas. However, project critical area criteria vary widely from simply all land within a set distance from a water resource, to a complex set of factors applied to individual farms. This study shows that, unless highly contaminated by some other upstream sources, controlling land uses close to streams is the proper land management strategy imperative for the modification or restoration of the stream water quality.

Since clay nanominerals play an important role in explaining the functions of land use, it is imperative that the definition of nanominerals be elucidated. Nanominerals<sup>13-16</sup> are as small as roughly 1 nm and as large as several tens of nanometres in at least one dimension. In

fact, nanominerals only exist in the nano-size range. The iron oxyhydroxide, ferrihydrite, is a typical example.

In this study, a chemical constituent is considered delivered when it becomes part of the stream flow. Its 'delivery system' refers to the means by which it is moved from its point of entry to the watershed up to the final outfall into the stream. The delivery system of a chemical constituent controls its impact on the water quality. Its delivery pathway depends on its solubility in water, tendency to get adsorbed to soil particles and stability of the chemical form in which the chemical constituent exists. Regardless of where a chemical constituent enters a watershed, if it has low water solubility, large particle size, better adsorption capability to soil particles, and/or chemical instability, then there is little possibility of its delivery in that form to the stream. Alternatively, if it has high water solubility, colloidal or nanoparticle size, and/or chemical instability, there is much higher probability of its delivery into the stream. Nitrate-nitrogen and phosphorus are very different in their water solubility and adsorptive capability to soil particles. Phosphorus gets adsorbed to soil particles readily, whereas nitrate-nitrogen is highly soluble. These two chemical constituents could thus be predicted to have different delivery systems. Phosphorus moves largely over land surface with eroded soil and nitrate-nitrogen moves largely in dissolved form in shallow groundwater. Since most of the shallow groundwater is presumed to be delivered to the stream at some later time, nitrate-nitrogen has a higher probability of being delivered, independent of its point of entry to the watershed, if it does not volatilize or is not taken up by plants at some point in its journey.

Eroded soils from upland areas have, on the other hand, a high probability of being intercepted by roadside ditches, native vegetation, hedge rows and fence rows. The probability of sediment delivery to the stream is observed to be inversely related to the distance from the stream. This is also true for phosphorus since it gets adsorbed to soil particles. Toxic metal contaminants, worthy of attention, in the form of adsorbed particles onto nano iron oxidic minerals in the watershed and in the surrounding stream water are not observed. This characteristic is rendered by the absence of (a) volcanic dust, (b) acid mine drainage or mine tailings or metallurgical effluents traversing the watershed and (c) any mine or metallurgical plant in the surroundings. Because of the absence of mining or metallurgical industries in the vicinity, atmospheric deposition of metallic elements is also insignificant. Moreover, the NPS water must not have traversed a metalliferous terrain on its journey to the stream – the absence of uploads of metal contaminants in water is indicative of this fate. It is thus pertinent to mention here that there is no report on the presence of toxic metals worthy of study in the soil. The contents of metals like Cu, Zn, etc. are similar to their usual natural concentration in the soil. The water quality impact due to entry

of phosphorus into a watershed is strongly dependent on location.

Sixteen water quality monitoring stations were selected to subdivide the Illinois river basin into 16 water quality sub-basins comprising the basin's upper 6000 sq. km. The subdivisions are based on hydrogeological parameters as determined jointly by the USGS and the Illinois State authorities. The results are found to be highly meaningful for Eastern Illinois.

Median constituent stream load values for nitrate-nitrogen and total phosphorus (the dependent variables) were used in the statistical analysis instead of mean values. By doing so, the few extreme errors in the record had impact on the statistics. Each median value was based on between 50 and 75 water samples collected on monthly basis and analysed by the Illinois State Agency over a six-year period, as part of its ambient water quality monitoring network. The monitoring network was determined jointly by the USGS and the Illinois State authorities. The stream loads were calculated by multiplying the median concentration (in mg/l) at each station by its contributing drainage area (in sq. km) and by a constant that relates flow to area and adjusts the instantaneous rate to metric tonnes per year<sup>17</sup>. This analysis did not attempt to predict the true annual load but rather a load characteristic of the median river condition, both in terms of flow

and concentration load. USGS maps describing the limits of the 100-year floodplain for the basin were used to delimit the study area (Figure 1). Land-cover data derived from LANDSAT TM multi-spectral imagery were used to infer the land use. Computer classification<sup>18</sup> was used to estimate the number of hectares in each water quality sub-basin under different land uses such as row crop agriculture, field crops, pasture and other agricultural land, and urban lands. For these land use data, with the upstream contribution measured at the water quality station immediately upstream of the sub-basin, a 'Dummy' variable for the adjacent lake Decatur and a 'Dummy' variable for the lake waste treatment facility were considered as the independent variables<sup>17</sup>. In an early analysis, the waste treatment variable fell quite short of statistical significance and was eliminated in the final analysis. Distance of flow between the measuring stations was also incorporated in early analysis, but it also had no statistical significance and was subsequently eliminated. Data for nitrate-nitrogen and total phosphorus only were analysed in the present case, and are presented in Tables 1 and 2. The presumption was that they would show significantly different results, reflecting different delivery systems. The final four equations to be analysed by ordinary least square (OLS) regression for each constituent are

$$L = f(\text{IN, Row, Field, Pasture, Forest}) + \mu, \quad (1)$$

$$L = f(\text{IN, Row, Field, Pasture, Forest, Urban}) + \mu, \quad (2)$$

$$L = f(\text{IN, Row, Field, Pasture, Forest, Dummy}) + \mu, \quad (3)$$

$$L = f(\text{IN, Row, Field, Pasture, Forest, Urban, Dummy}) + \mu, \quad (4)$$

where  $L$  is the median stream loading for nitrate-nitrogen or total phosphorus (in metric tonnes/yr), IN is the median upstream loading (in metric tonnes/yr), Row is the sub-basin floodplain in row crop agriculture (in ha), Field is the sub-basin floodplain in pasture or other unspecified agricultural use (in ha), Pasture is the sub-basin floodplain in pastures or other unspecified agricultural use (in ha), Forest is the predominantly wooded floodplain (in ha), Urban is the urban land use throughout the sub-basin (in ha), Dummy is the presence or absence of lake in the sub-basin and  $\mu$  is the random error term.

Spatial autocorrelation of error terms in a regression model can be a significant problem and the methods for dealing with it have been shown to be entirely adequate. One of the two most common methods of handling spatial autocorrelation<sup>19,20</sup> is the weight matrix approach in which the process generating the errors is modelled. The resulting correlation structure is then derived from the hypothesized process<sup>21</sup>. Once the structure of the correlation has been estimated, this information can be incorporated

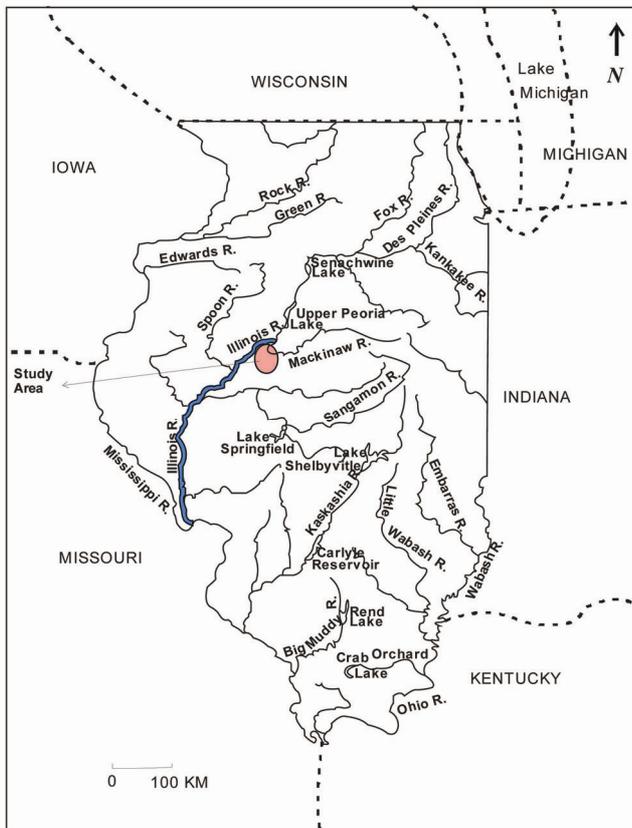


Figure 1. Study area.

**Table 1.** Total phosphorus<sup>a,b</sup>

Const	In	Row	Field	Pasture	Forest	Urban	Dummy	R <sup>2</sup>	H	Equation
14.62	0.882	-0.010	-0.420	0.393	0.089			0.973 (c)	-1.579	(1)
23.46	0.131 (b)	0.010	0.489	0.203 (b)	0.116					
15.30	0.928	0.002	-0.534	0.297	-0.030	0.027		0.975 (c)	-0.532	(2)
22.66	0.131 (c)	0.012	0.479	0.208 (a)	0.121	0.022				
-4.54	0.981	-0.037	0.381	0.114	-0.163		-159.83	0.979 (c)	-3.129	(3)
22.97	0.127 (c)	0.010 (b)	0.589	0.230	0.109 (a)		82.12 (b)			
-8.90	1.077	-0.010	0.440	-0.104	-0.096	0.040	-204.49	0.987 (c)	-1.886	(4)
18.14	0.106 (c)	0.010	0.469	0.200	0.089	0.015 (b)	66.88 (c)			

<sup>a</sup>Standard errors displayed beneath coefficients; (a) Coefficient significantly different from zero at 0.1; (b) Coefficient significantly different from zero at 0.05; (c) Coefficient significantly different from zero at 0.01. <sup>b</sup>Coefficients are metric tonnes per hectare per year, except for 'Const' and 'Dummy', whose dimensions are metric tonnes per year and 'In' which is dimensionless.

**Table 2.** Nitrate-nitrogen<sup>a,b</sup>

Const	In	Row	Field	Pasture	Forest	Urban	Dummy	R <sup>2</sup>	H	Equation
429.93	0.782	0.049	-7.957	3.477	1.475			0.993 (c)	-1.507	(1)
125.26 (c)	0.058 (c)	0.047	1.915 (c)	0.867 (c)	0.507 (c)					
486.71	0.813	0.146	-9.457	2.807	2.110	0.237		0.996 (c)	-0.739	(2)
96.21 (c)	0.046 (c)	0.049 (c)	1.564 (c)	0.707 (c)	0.450 (c)	0.084 (c)				
442.10	0.802	0.022	-6.430	2.918	1.374		-354.01	0.992 (c)	-1.935	(3)
145.40 (c)	0.064 (c)	0.062	2.844 (c)	1.164 (b)	0.536 (b)		477.97			
393.81	0.853	0.144	-6.926	1.693	2.024	0.274	-640.37	0.997 (c)	-2.257	(4)
95.42 (c)	0.044 (c)	0.047 (c)	1.853 (b)	0.828	0.393	0.074 (c)	320.42 (b)			

<sup>a</sup>Standard errors displayed beneath coefficients. (a) Coefficient significantly different from zero at 0.1; (b) Coefficient significantly different from zero at 0.05; (c) Coefficient significantly different from zero at 0.01. <sup>b</sup>Coefficients are metric tonnes per hectare per year, except for 'Const' and 'Dummy' whose dimensions are metric tonnes per year, and 'In' which is dimensionless.

into any predictions, thereby improving their accuracy<sup>21</sup>. Just as with time-series autocorrelation, maximum likelihood (ML) techniques are commonly used to estimate the autocorrelation parameters and the regression coefficients. The second method models the correlation structure itself, rather than the underlying process<sup>22</sup>. The second approach is to model the covariance matrix of the error terms directly. Correction for temporal autocorrelation is conceptually more straightforward. A common practice for time-series models is to add the lagged dependent as a treatment variable<sup>2</sup>. For the present analysis, the spatial equivalent to this procedure was to use the upstream loading as a predictor of downstream loading. This allows the use of the 'Durbin H statistic', which is a combination of the Durbin-Watson statistic for autocorrelation and the variance of the coefficient on the lagged dependent variable<sup>23-25</sup>. Such a combination yields a normally distributed statistics and provides an adequate test for autocorrelation in the presence of lagged dependent variable. Like the Durbin-Watson, this statistic is most appropriate for large sample tests (i.e. for  $n > 30$ ). Although nothing is known about its small sample properties, it does not present an alternative to the straight Durbin-Watson statistic; it is presented along with the OLS regression results. A Durbin H of greater than 1.64 leads to the rejection of the hypothesis of zero autocorrelation.

Regression coefficients, standard errors and related statistics derived from the OLS regression analysis are presented in Tables 1 and 2. Results for total phosphorus and nitrate-nitrogen are discussed below.

Since the regression analysis presented here deals directly with only floodplain land use and urban land use outside the floodplain, the effects of other land-use factors in the watershed, primarily agriculture outside the floodplain, are represented in an average sense by the regression constant. Here the constant varies in sign and is never significantly different from zero. It implies that agricultural land use outside the floodplain has minimal effect on phosphorus levels in surface waters. This is at least true in the North American continent. It also shows that upland agricultural erosion with its phosphorus is largely debarred from being delivered to the active floodplain.

The coefficient of 'IN' represents the average fraction of the upstream load persisting to the downstream measuring station. It means that phosphorus once delivered is relatively persistent in flowing streams because of its mode of occurrence in the form of adsorbed particulates in nanoferrhydrite, present in the clayey soil. Ferrhydrite is an effective adsorbent for inorganic phosphate in the soils. In fact, ferrhydrite acts as a large sink of phosphate. And ferrhydrites in nature<sup>26</sup> exist as a nanominerals. Uptake of phosphate by ferrhydrite to water systems is dependent on pH and the Fe(II) : PO<sub>4</sub> ratio. Manceau

and Charlet<sup>27</sup> suggested that the phosphate adsorbs onto ferrihydrite by forming binuclear bridging complexes that bond with two singly coordinated OH groups. Incidentally, phosphate adsorption onto ferrihydrite inhibits the transformation of ferrihydrite to other iron oxy-hydroxides. This means that when iron oxides like hematite and oxy-hydroxides like goethite, akaganeite, lepidocrocite and ferrihydrite are absent in water from a NPS in agricultural fields, but ferrihydrites are significant by their presence, the probability of phosphate in the said water is high. At that point the whole agricultural plan should be re-examined.

The coefficient of 'Forest', on the other hand, indicates that the forested land consistently reduces the phosphorus loadings, even though the effect appears to be relatively small. Generally, it is observed that the majority of phosphorus is adsorbed to nanoferrhydrites. If the sediment barriers in the floodplain forest do a relatively inefficient job of trapping the clay nanominerals, as opposed to larger silt and sand particles, phosphorus would tend to persist in the flowing stream in a non-reduced mode. But it is not the case. Interestingly, however, the lake 'Dummy' variable presents a significant finding for control of in-stream phosphorus levels. It is clear that this reservoir has a considerable trap efficiency, thereby reducing the in-stream total phosphorus.

The two different scenarios illustrated above lead us to argue that the differential behaviour of clay nanominerals containing adsorbed particulates of phosphorus could be a function of their sizes. It is known that for any particular composition, each mineral expresses a set of specific physical and chemical properties. Nanominerals and mineral nanoparticles satisfy these criteria, except that even with a fixed composition, they express a range of physical and chemical properties depending on their size and shape. For example, it has been confirmed<sup>25</sup> that 12 nm particles of magnetite are roughly 200 times more efficient in removing As(III) and As(V) from water than 20 and 300 nm magnetite particles. Nanomagneites have also varying magnetic properties which change with size. Moreover, the adsorption complex associated with the smaller nanoparticles is much more stable than with the larger particles.

Depending on the nanomaterials and their size range, reactive surface area and surface free energy of the particle may change, atomic structure variations may occur and modification of electronic structure may take place. In the present theme, depending on the size of the nanoparticle, its surface area and reactive surface will vary and accordingly, its uptake of phosphorus as adsorbed particulates will tend to change. Thus the behaviour of nanoferrhydrite (containing adsorbed phosphorus particulates) of varying sizes may certainly alter at different environs. Hence phosphorus uptake will be influenced by these factors. It will be reflected in different surroundings by its presence in varying proportions.

Some nanominerals have been enmeshed in the sediment barriers of the forested land, while some have been entrapped in the reservoir. The reduced phosphorus value in the flowing streams is probably on account of a specific size fraction of nanominerals which escaped entrapment.

The coefficients of 'Urban' in eqs (2) and (4) are both positive and in eq. (4), it is significant. Urban run-off may be a NPS contributor to phosphorus loadings.

It is interesting to note that in the present study area, aluminosilicates allophane and imogolite are present as a minor component of the soil. They are basically nanominerals, occurring here as mineral nanoparticles. These nanoparticles are reactive towards a variety of molecules and ions, making them potentially useful for many environmental applications. Besides inorganic (mineral) nanoparticles, soils also contain organic nanoparticles, notably humic substances. A discussion on nanoparticles of humic substances lies beyond the scope of this communication. The reactivity of allophane and imogolite towards extraneous ions and molecules depends on four surface properties – surface area, porosity, surface charge and functional groups. In case of allophane and imogolite, important chemical reactions in the soil environment such as adsorption, precipitation, catalytic transformation and redox reactions occur on their surface where chemical bonds are incomplete, the free energy from which provides a driving force to speed up interactions with extraneous ions and molecules. These two nanominerals also adsorb cations in the following order of decreasing affinity<sup>28</sup>:  $Pb > Cu > Zn > Co = Cd > Mg = Ca$ . Since the toxic metals in the specific area are non-eligible for any discussion, the question of adsorption of cations onto allophane and imogolite is avoided. However, it is relevant to mention that phosphorus (phosphate) can be adsorbed by allophane-rich soils at pH 6.8. The strong ability of allophanic soils to adsorb phosphorus often leads to the deficiency of this nutrient in crops. On the other hand, nanoferrhydrites are not known to take up phosphorus to a significant extent to cause phosphorus deficiency to the crops. In this area, the sediments are not derived from volcanic ash hence the activity of both allophane and imogolite is weak and has not thus affected the extent of adsorption of phosphorus onto ferrihydrites.

The strongly positive and highly significant regression constants indicate that factors outside the floodplain and urban areas are contributing nitrate-nitrogen to the stream in significant amounts. Shallow groundwater delivery of nitrate-nitrogen may also be relevant. The 'IN' coefficient suggests that nitrate-nitrogen has a tendency to persist, but is assimilated strongly from station to station. Algal and other in-stream plant growth could be a substantial 'sink' for dissolved nitrate-nitrogen. The strongly negative regression coefficients for field cropland are surprising. The reason may be that most of this land is in hay and undergoes several cuttings in a year. Since the

main (food) value of hay is a rich source of nitrogen-based protein for livestock, it follows that the crop's nitrogen uptake is rapid. Most of such crops are fast-growing with dense fibrous root systems. As the above-ground growth is harvested and removed from the system, it is possible that floodplain crops of hay could be withdrawing a significant amount of nitrate-nitrogen from shallow groundwater. The major per acre contributor for nitrate-nitrogen is pasture land. Livestock concentrations are well known to contribute substantial levels of nitrogenous wastes. If the plant community in the pasture has a considerable representation of legumes, grazing could prolong such plants in a rapid-growth state, ultimately resulting in a significant positive contribution as livestock waste. The high 'Forest' contribution could also be explained as livestock and wildlife nitrogenous waste, because the forested floodplain regions that were grazed in the study area could not be distinguished from those that were ungrazed using LANDSAT interpretation. One land management possibility inferred from the foregoing discussion would be to graze livestock in floodplain pastures separated from the stream by fields of hay. Such an arrangement should both mitigate the effects of the livestock waste and promote the growth of hay crop.

Urban land contributes positively to in-stream nitrate-nitrogen concentrations, as expected. The 'Dummy' variable for the lake indicates that impoundments have a major impact on downstream nitrate-nitrogen concentrations.

Two conclusions can be drawn from this work. First, stream water quality is a function of land use within the watershed. Secondly, there is a general support for the hypothesis that land areas closer to a stream have greater impact on water quality than those further away from the stream, for phosphorus and other sediment-related contaminants. It, therefore, follows that those land uses with a tendency to contribute large amounts of contamination to the watershed are to be best located as far away from the drainage channels as possible. On the contrary, those with a tendency to intercept contaminant constituents should be located as close as possible. The fate and transport of nanoparticles in suspension (in water) are determined by the controlling parameters of the physical ambience of fluid (in this case, flowing water). Buoyancy suspends the nanoparticles in water. Relatively weak forces, resulting from transient shifts in electron density, cause the nanoparticles of ferrihydrite to be attracted to one another and to other environmental constituents. As the size of the agglomerates increases, due to the force of attraction, buoyancy is reduced and the force of gravity causes the particles to settle out of suspension. Since these nanoparticles under discussion have similar electrostatic surface charges, the repulsive force will counter the attraction resulting from van der Waals forces and keep the particles in suspension. Since this probably is the case, most of the phosphorus should be transported by

water. A combination of accurate water quality data, land-cover pattern and understanding of the physical and chemical properties and delivery systems of contaminants, inclusive of their mineralogy and state of occurrence, wherever applicable, may help guide attempts to control non-point contributions to water quality.

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## Cloud point extraction and spectrophotometry in the determination of As(III) using amaranth in water samples of rivers located in industrial and non-industrial areas

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**Cloud-point extraction (CPE) method was employed for the extraction of trace quantities of arsenic(III) (As(III)) from various water samples using spectrophotometry. For this mixed micelle-mediated extraction, amaranth, Triton X-114, cetyl trimethylammonium bromide (CTAB) and NaCl were applied as chelating, sensitizing agent, extraction and co-extraction agents respectively. The various effective parameters on CPE, including pH, type of surfactants and electrolytes, concentration of chelating agent, surfactant, sensitizing agent (CTAB), electrolyte, temperature and duration were investigated. Additionally, analytical performance was estimated (limit of detection, recovery, sensibility and relative standard deviation (RSD) and linear range). A linear calibration curve in the range**

**30–1500  $\mu\text{g l}^{-1}$  of amaranth was acquired. Under the optimized conditions, the limit of detection (LOD) was 2.8  $\mu\text{g l}^{-1}$  and RSD for 300 and 600  $\mu\text{g l}^{-1}$  was 2.23 and 1.73 respectively ( $n = 10$ ). LOD was found to be 2.8  $\mu\text{g l}^{-1}$ . The regression equation acquired by the least square method is  $A = 2.05 \times 10^{-3} C_{\text{As}} + 1.21 \times 10^{-2}$  for 30–1500  $\mu\text{g l}^{-1}$  of As(III) with a correlation coefficient of 0.997 ( $n = 12$ ), where  $A$  is the absorbance and  $C_{\text{As}}$  is the concentration of As(III) ( $\mu\text{g l}^{-1}$ ). The results indicate that the As(III) quantity in water samples of the rivers located in industrial areas is considerably higher than that in the non-industrial areas.**

**Keywords:** Amaranth, arsenic, cloud point extraction, spectrophotometry.

ARSENIC (As) is ranked first among the hazardous elements and has serious effects on plants, animals and human health<sup>1</sup>. As contamination is a matter of concern world over, especially in India and Bangladesh<sup>2</sup>. Millions of people worldwide are exposed to As in their drinking water and ingested As is an established cause of bladder, lung and skin cancer. In addition to cancer, As in water has also been associated with cardiovascular disease, skin lesions, diabetes, reproductive disorders, cognitive defects in children and other health effects<sup>3</sup>. Data indicate that As is cytotoxic and genotoxic to human lung primary cells. Reactive oxygen species (ROS) generation associated with As exposure is known to play a fundamental role in the induction of adverse health effects and diseases (cancer, diabetes, hypertension, cardiovascular and neurological diseases)<sup>4</sup>. Generally, the inorganic species of As are more toxic than the organic forms; the toxicity of As(III) is 60 times greater than As(V)<sup>5</sup>. In view of these, several researchers have devised various methods measuring of As<sup>6–13</sup>.

In analytical chemistry, azo dyes play an important role as organic complexing reagents. These dyes are considered as tridentate ligands and form chelates with metal ions through oxygen atom of the ortho-hydroxyl group, nitrogen atom from pyridine, and one of nitrogen atoms of the azo group, giving two five-membered chelate rings. The complexes are stable with rather limited solubility in aqueous solution but much greater solubility in organic system. Because of their non-selectivity, azo dyes have been widely applied in different areas of analytical chemistry such as spectrophotometry, solid phase extraction (SPE), electrochemistry, liquid–liquid extraction and CPE<sup>14</sup>.

In the last decade, there has been increasing interest in the use of aqueous micellar solution in the field of separation science<sup>15</sup>. The cloud point extraction (CPE) technique has also been applied as a procedure for determination and removal of dyes and pigments as well as analysing metals<sup>16,17</sup>. This simple technique enables us to refrain from hazardous organic solvents and allows us to reach a much higher concentration of analyte than in the case of

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