



Estimation of the Nutrient Value of Agricultural Slurries by Measurement of Physical and Chemical Properties

I. M. Scotford¹; T. R. Cumby¹; R. P. White¹; O. T. Carton²; F. Lorenz³; U. Hatterman³; G. Provolo⁴

¹Silsoe Research Institute, Wrest Park, Silsoe, Bedford, MK45 4HS, UK; ²Teagasc, Johnstown Castle Research Centre, Wexford, Ireland; ³LUFA, Jaegerstrasse 23-27, D-26121, Oldenburg, Germany; ⁴Universita Degli Studi di Milano, Istituto Di Ingegneria Agraria, Via Celoria 2, 20133 Milano, Italy

(Received 19 January 1998; accepted in revised form 12 June 1998)

A prototype nutrient sensing system was used to investigate relationships between the nutrient status of agricultural slurries and a range of physical and chemical properties. These properties were all measured using devices suitable for possible installation in full-scale slurry handling systems. The prototype system was tested on a total of 160 slurries, comprising approximately 20 cattle and 20 pig slurries from each of four European countries. Linear relationships were identified between ammoniacal nitrogen concentration and the electrical conductivity of the slurries and between total phosphorus and the density of the slurries. Generally, regressions for total potassium were weaker than those identified for either ammoniacal nitrogen or total phosphorus. The results show that a practical nutrient sensing system is feasible for farm use. For example, such a system could be used on a slurry tanker to estimate the nutrient status of the whole tanker contents, thus eliminating the sampling errors associated with sub-sampling from a large store. © 1998 Silsoe Research Institute

1. Introduction

Agricultural slurries contain useful amounts of the plant nutrients nitrogen (N), phosphorus (P) and potassium (K).¹ However, the amounts of these nutrients available in a particular slurry are not easy to quantify without laboratory facilities. Thus, when agricultural slurries are applied to land, their fertilizer potential is often unknown. Hence, the spreading procedure becomes one of waste disposal rather than one of nutrient utilization, therefore increasing the risks of air, water and soil pollution.

In order to encourage farmers to make better use of slurry, and to reduce pollution risks, convenient methods and means are necessary to quantify the nutrients and to

spread them efficiently and accurately in accordance with codes of good agricultural practice.²⁻⁴ Some machines are available that spread accurately on a volumetric basis, but these tend to be large and sophisticated and thus best suited to large farms or agricultural contractors. However, this technology is of limited use unless the nutrient status of the slurry can be determined easily and rapidly.

There are various methods available of reliable nutrient estimation on farms. For ammoniacal nitrogen, there are the Agros⁵ meter or Quantofix⁶ meters which use the hypochlorite-oxidation method and for total phosphorus there is the hydrometer.⁷ However, these methods rely on taking sub-samples of stored slurry. Without complete mixing of the store contents, the results are unlikely to represent the overall nutrient status. This is because random sampling from a large volume of settled slurry is unlikely to represent accurately the relative amounts of settled and unsettled material. Ideally, methods are required which can be used to measure the nutrient value of slurry either during transport or spreading. In principle, these methods could be used on a slurry tanker to determine the nutrient status of the whole contents of the tanker, thus avoiding sampling errors. Such applications require robust nutrient estimation methods with specific features including an electrical output signal and suitability for installation in a practical slurry handling system. For example, measurement of electrical conductivity (EC) meets these requirements and has been used previously⁸⁻¹⁰ to estimate the ammoniacal nitrogen content of slurries.

The range of properties which might provide useful practical estimates of plant nutrient concentrations in slurries has been reviewed previously.¹⁰ These properties were incorporated in a prototype nutrient sensing system¹⁰ and this paper details how this device was used in four European countries to measure a range of physical and chemical properties of agricultural slurries and to

find relationships between them and the nutrient concentrations in the slurries. The best fitting regression equations were identified for estimating plant nutrients from the data gathered in each country. The nutrient sensing system included a selection of sensors with the required features for incorporation into a farm slurry spreading system. In consequence, the results that emerged from this investigation enabled the selection of appropriate sensors for a subsequent tanker-mounted prototype nutrient sensing system.

2. Materials and methods

2.1. Prototype nutrient sensing system

Full details of the prototype nutrient sensing system, its calibration and operation are provided elsewhere.^{10,11} The main features were as follows: (a) a commercially available submersible sonde containing sensors for redox potential, pH, temperature, electrical conductivity with automatic temperature compensation (EC) and ammonium ions (AI); (b) a sample reservoir of approximately 60 l capacity containing the sonde and a submersible grinder pump; (c) a loop of pipe with an internal diameter of 30 mm fed by the pump and returning the flow to the sample reservoir; (d) instruments installed in the loop of pipe included an in-line twin-tube vibrating density meter, an ultrasonic TS meter (TS_u), a Doppler flowmeter and a differential pressure transducer to determine the pressure loss along a 21 m section of the pipe; (e) a manual sampling valve to enable collection of slurry samples from the loop of pipe for subsequent laboratory analysis and a manual in-line valve for varying slurry flow rates so that differential pressure could be determined at various flow rates; and (f) a personal computer (PC) to collect the data from the individual sensors.

2.2. Slurry sample collection, data collection and slurry analysis

The nutrient sensing system was used in the United Kingdom, Ireland, Germany and Italy. Approximately, 20 cattle and 20 pig slurries were tested in each country (Table 1). During the initial series of experiments in the United Kingdom, it was found that the ultrasonic TS meter (TS_u) did not work satisfactorily and this was subsequently removed from the system. In addition, it was noted that the redox sensor was set up incorrectly, thus no data on redox potential were obtained for the United Kingdom slurries; this was corrected before use in the other countries. In each of the countries, 50 l slurry samples were collected from a wide range of differing

Table 1
Number of slurry samples collected in each European country

Slurry type	Number of samples			
	United Kingdom	Ireland	Germany	Italy
Cattle	20	27	17	20
Pig	18	17	17	20
Total	38	44	34	40

farming systems. Various storage periods could be tolerated between acquisition of the samples and their analysis because laboratory and nutrient sensing system procedures were undertaken concurrently. Therefore, any change in slurry properties affected both sets of results equally. Each of the samples was placed into the slurry reservoir and the circulation pump was operated for several minutes to ensure complete mixing. Data collection was then initiated using the PC; 15 sets of readings were taken before the liquid flow was progressively decreased by closing the in-line valve. The flow was decreased in steps of approximately 0.14 l/s from 1.6 l/s to a minimum of 0.14 l/s before the valve was fully reopened. Several readings were taken at each flow rate so that a total of approximately 50 sets of readings were obtained for each sample. A 1 l sub-sample of slurry was then collected for laboratory analysis of total solids (TS), total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (AN), total phosphorus (P) and total potassium (K). The methods used for the laboratory analysis in each of the countries are detailed in Table 2. These methods were typical of those used in the respective countries to provide analytical service to commercial farmers. Comparison and harmonization of these methods was not the objective of this study, and therefore it was necessary to assume that the various laboratory procedures could produce differing analytical results between the countries involved. Therefore, the data were interpreted on a country-by-country basis to provide nutrient estimation procedures related to the established local procedures.

3. Results

3.1. Diversity of collected slurries

The slurries investigated in this study (Tables 3 and 4) were collected from many different farming systems in four European countries, although they were not intended to be a representative sample of all slurries in those countries. The TS and TKN measurements were

Table 2
Laboratory analysis methods used

Measured variable	Laboratory method used			
	United Kingdom	Ireland	Germany	Italy
Total solids (TS), %	Oven drying at 105°C for 16 h	Oven drying at 100°C until constant weight	Oven drying at 105°C for 16 h	Oven drying at 105°C until constant weight
Kjeldahl nitrogen (TKN), mg/l	Digestion followed by steam distillation			
Ammoniacal nitrogen (AN), mg/l	Steam distillation		Ammonia sensitive electrode	Steam distillation
Total phosphorus (P), mg/l	ICP (inductively coupled plasma spectrophotometry)	Digestion followed by autoanalyser	Digestion followed by colorimetry	Digestion followed by spectrophotometry
Total potassium (K), mg/l	Digestion followed by atomic absorption spectrophotometry		Digestion followed by flame photometry	

used solely as indicators of slurry concentration; the wide ranges of these values, 0.27–9.81% and 181–8340 mg/l, respectively, illustrated that a comprehensive selection of slurries was used. Values of these properties were not used for the subsequent data analysis.

Comparing the AN, P, and K concentrations identified in this study with the typical nutrient contents¹² of cattle slurries (AN = 1300 mg/l, P = 600 mg/l, K = 2800 mg/l) and pig slurries (AN = 3000 mg/l, P = 1500 mg/l, K = 2700 mg/l) shows that the slurries collected ranged both above and below these typical figures.

3.2. Data analysis

The amount of data from each experiment was reduced by calculating an average value from the 50 readings obtained, during a typical test run, for each measured property except flow and differential pressure. Instead, these values were used to derive $\ln(k)$, a term associated with the rheological properties of the slurry defined by the following relationship:

$$\ln(k) = \ln(\tau) - n \ln(\dot{\gamma}) \quad (1)$$

where τ is the shear stress, Pa; $\dot{\gamma}$ the shear rate, s^{-1} ; and k and n are parameters for each slurry.

The procedures to determine $\ln(k)$ and n for each slurry sample are detailed elsewhere.^{10,13}

To facilitate statistical analysis the data were split into four groups, each group representing one country. In

each case, the average values determined from the individual sensors and the derived values of $\ln(k)$ were compared with AN, P and K concentrations derived from the laboratory analyses. It was suspected that these concentrations might, in some instances, be related to more than one of the measured properties. Therefore, the following generalized equation was used in linear regressions analyses:

$$Y = wC_i + xC_j + z \quad (2)$$

where Y = AN, P or K, mg/l; w , x , z are regression coefficients and C_i , C_j are the measured properties.

Single and multiple properties regressions were fitted using the Genstat program¹⁴ (the coefficient x was assigned a value of zero for the purposes of single property regression). Alternative regression models were considered representing cattle and pig slurries either as two independent populations, or as one combined population. The most appropriate were selected using a "forward selection procedure".¹⁵ The statistical analysis was designed to provide predictive models for subsequent use, without excessive complexity. The details of the statistical procedures are described in the Appendix 1.

The single regressions were completed first and the resulting relationships between concentrations of the key nutrients (AN, P and K) and each of the measured properties were compared to find those which provided the best fit to the data, i.e. those which gave high values of

Table 3

Comparison of the minimum, maximum and mean for total solids, Kjeldahl nitrogen, ammoniacal nitrogen, total phosphorus and total potassium for cattle slurries in each of the participating countries

<i>Property measured by laboratory analysis</i>		<i>United Kingdom</i>	<i>Ireland</i>	<i>Germany</i>	<i>Italy</i>
Total solids (TS), %	Minimum	0.27	1.60	1.30	0.60
	Maximum	8.34	7.10	5.04	4.15
	Mean	3.58	3.02	3.61	2.54
Kjeldahl nitrogen (TKN), mg/l	Minimum	181	700	685	500
	Maximum	5050	3970	4700	2200
	Mean	1890	1610	2280	1260
Ammoniacal nitrogen (AN), mg/l	Minimum	94	390	363	20
	Maximum	2120	2150	4000	1120
	Mean	767	915	1410	435
Total Phosphorus (P), mg/l	Minimum	28	100	114	40
	Maximum	515	730	624	910
	Mean	310	271	329	237
Total potassium (K), mg/l	Minimum	135	650	719	70
	Maximum	2020	5550	5810	4780
	Mean	753	2290	2430	1150

percentage variance accounted for (pva). Subsequently, the multiple regressions technique was applied using a subset of the measured properties. The combinations of properties included in this subset were selected by inspection of the results of the single regressions. Upon completion of the linear regressions, the resulting residual deviations of the data were examined for systematic effects; none was found and this indicated that there was no clear justification for considering more complex models.

The best-fit single and multiple regressions were used to evaluate forecast standard errors (fse) to indicate the likely accuracy with which nutrients could be estimated in future slurry samples. Since these fse values were dependent upon the values of the properties measured by the individual sensors, the procedure was undertaken at the 10 and 90% quantile values of the measured properties. This procedure was completely separate for cattle and pig slurries. In situations where multiple regressions provided the best fit, the procedure was completed for each combination of the 10 and 90% quantiles of each measured property.

The best-fit single property regressions are presented in *Figs 1–14* and the regression coefficients of the best-fit multiple property regressions are presented in Tables 5, 6 and 7 for AN, P and K, respectively.

3.3. Ammoniacal nitrogen

In the United Kingdom, Ireland and Germany, the best single property regressions for AN were with electrical conductivity (EC) (*Figs 1–3*), with pva values of 84.1, 80.6 and 91.9%, respectively. In Italy, the regressions of AN with all of the measured properties produced pva values of less than 50%. For example, the regression of AN with EC gave a pva value of 39.1% (*Fig. 4*). The best regression identified for Italian AN was with $\ln(k)$, which had a pva value of 45.5% (*Fig. 5*) although the weakly negative slope of the regression line for cattle slurries suggests that the AN concentration in only the pig slurries could be reliably estimated in this way.

In the United Kingdom and Italy the best-fit multiple property regressions for AN included EC and $\ln(k)$ (pva values of 85.1 and 50.1, respectively). In Ireland and Germany, the best-fit multiple property regressions for AN included EC and density (pva values of 83.4 and 92.5%, respectively) (Table 5). The data from the United Kingdom, Ireland and Germany showed that the multiple property regressions for AN which included EC were consistently superior to all others. In contrast, this strong relationship between AN and EC was less apparent from the Italian data; the pva values from

Table 4

Comparison of the minimum, maximum and mean for total solids, Kjeldahl nitrogen, ammoniacal nitrogen, total phosphorus and total potassium for pig slurries in each of the participating countries

Property measured by laboratory analysis		United Kingdom	Ireland	Germany	Italy
Total solids (TS), %	Minimum	0.50	0.53	1.80	0.79
	Maximum	7.16	6.90	6.50	9.81
	Mean	3.32	2.52	4.53	3.15
Kjeldahl nitrogen (TKN), mg/l	Minimum	824	550	2200	700
	Maximum	8340	5200	6900	7100
	Mean	4240	2700	4870	3410
Ammoniacal nitrogen (AN), mg/l	Minimum	616	629	1450	200
	Maximum	5600	3950	5100	3510
	Mean	2690	2140	3620	1400
Total Phosphorus (P), mg/l	Minimum	38	50	262	80
	Maximum	2330	1800	1750	1770
	Mean	694	626	1162	642
Total potassium (K), mg/l	Minimum	328	450	1266	290
	Maximum	1520	3200	4400	5690
	Mean	988	1850	2990	1720

all of the multiple regressions were between 20 and 50.1%.

The statistical analysis showed that the best-fit relationships for the data from the United Kingdom and Germany were provided by single property regressions between AN and EC, leading to fse values ranging from ± 548 to ± 571 mg/l and from ± 442 to ± 457 mg/l, respectively. In Ireland and Italy, multiple property regressions were better. In the former, AN was related to EC and density (fse values ranging from ± 375 to ± 407 mg/l) and in the latter AN related to EC and $\ln(k)$ (fse values ranging from ± 710 to ± 801 mg/l).

3.4. Total phosphorus

The total phosphorus in most cattle and pig slurries is largely insoluble, and it was therefore expected that P would relate to properties reflecting the total solids content of the slurries, i.e. density and $\ln(k)$. The single property regressions in Ireland, Germany and Italy showed that this was the case; regressions of P with density (Figs 6–8) produced pva values of 64.8, 83.6 and 76.1%, respectively. The second best regression in each of

these countries was with $\ln(k)$ with respective pva values of 22.3, 75.8 and 59.0%. In all cases, the statistical analysis indicated that separate regression equations were required for pig slurries and cattle slurries. In the United Kingdom, the equivalent regressions were not as good; all had pva values of less than 50%. For example, the regression of P with density had a pva value of 35.8% (Fig. 9). The best regression for United Kingdom P was with the pH with a pva value of 45.6% (Fig. 10). Again, separate regression equations were required for pig slurries and cattle slurries.

For all four countries, the best-fit multiple property regressions for P included density and either pH in the United Kingdom and Italy or $\ln(k)$ in Ireland and Germany with respective pva values of 67.0, 82.0, 69.7 and 89.9% (Table 6). Overall, the general observation was that those multiple property regressions which included density had higher pva values than those which did not.

Although the single property regressions showed that the P concentrations of the slurries tested were related to density, the best results were achieved in all four countries using multiple property regressions of P with density and pH leading to fse values ranging from ± 308 to ± 322 mg/l (United Kingdom) and from ± 192 to

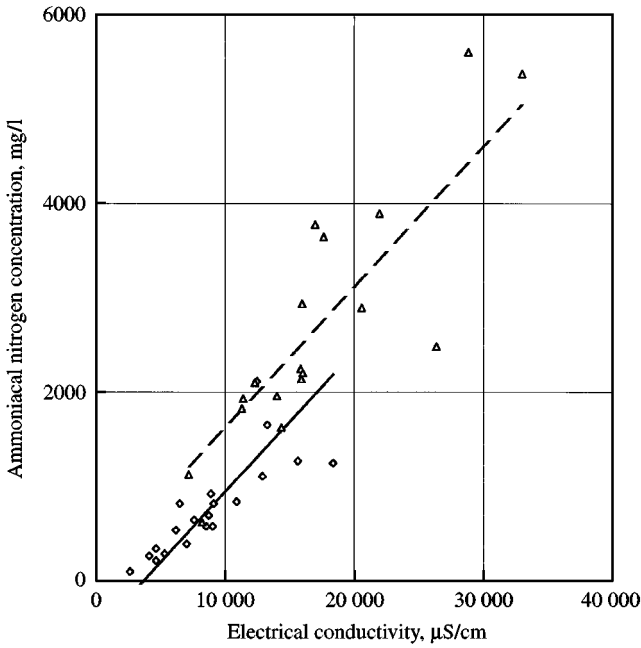


Fig. 1. Relationship between ammoniacal nitrogen (AN) concentration and electrical conductivity (EC) for UK slurries \diamond , cattle slurry; \triangle , pig slurry; —, $AN_{cattle} = 0.149 EC - 552$ (fitted); ----, $AN_{pig} = 0.149 EC + 131$ (fitted); percentage variance accounted for 84.1%, $p < 0.01$

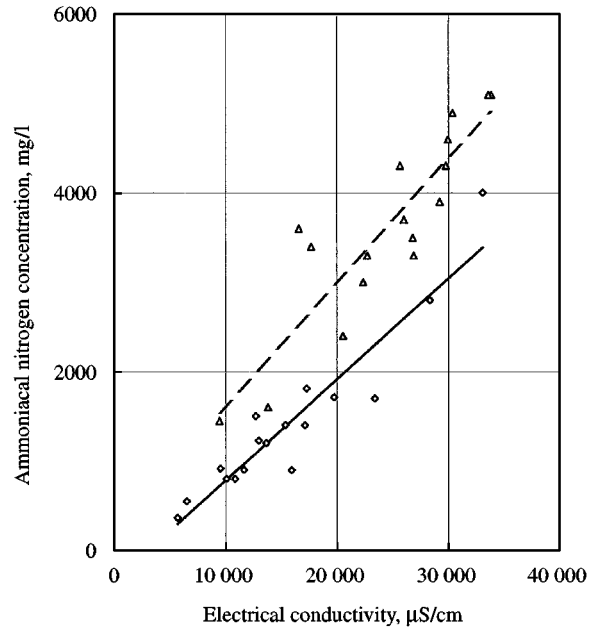


Fig. 3. Relationship between ammoniacal nitrogen (AN) concentration and electrical conductivity (EC) for German slurries \diamond , cattle slurry; \triangle , pig slurry; —, $AN_{cattle} = 0.113 EC - 348$ (fitted); ----, $AN_{pig} = 0.139 EC + 217$ (fitted); percentage variance accounted for 91.9%, $p < 0.01$

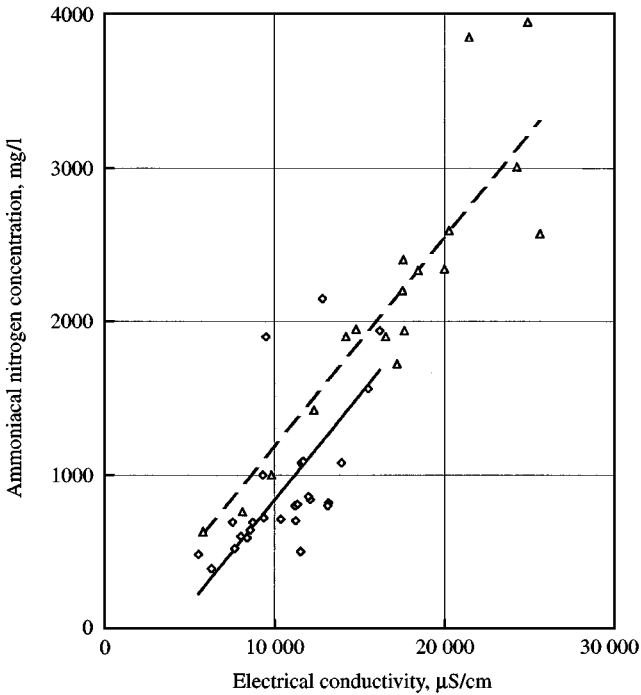


Fig. 2. Relationship between ammoniacal nitrogen (AN) concentration and electrical conductivity (EC) for Irish slurries \diamond , cattle slurry; \triangle , pig slurry; —, $AN_{cattle} = 0.136 EC - 523$ (fitted); ----, $AN_{pig} = 0.136 EC - 174$ (fitted); percentage variance accounted for 80.6%, $p < 0.01$

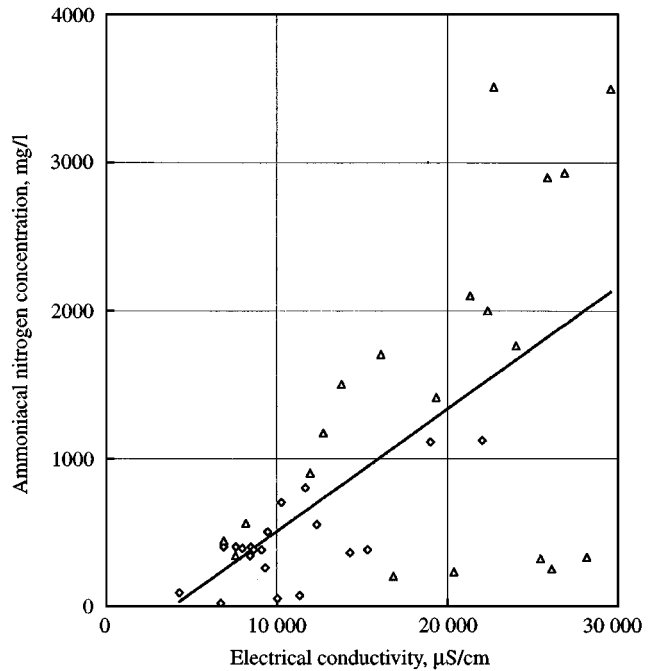


Fig. 4. Relationship between ammoniacal nitrogen (AN) concentration and electrical conductivity (EC) for Italian slurries \diamond , cattle slurry; \triangle , pig slurry; —, $AN_{cattle \text{ and } pig} = 0.083 EC - 327$ (fitted); percentage variance accounted for 39.1%, $p < 0.01$

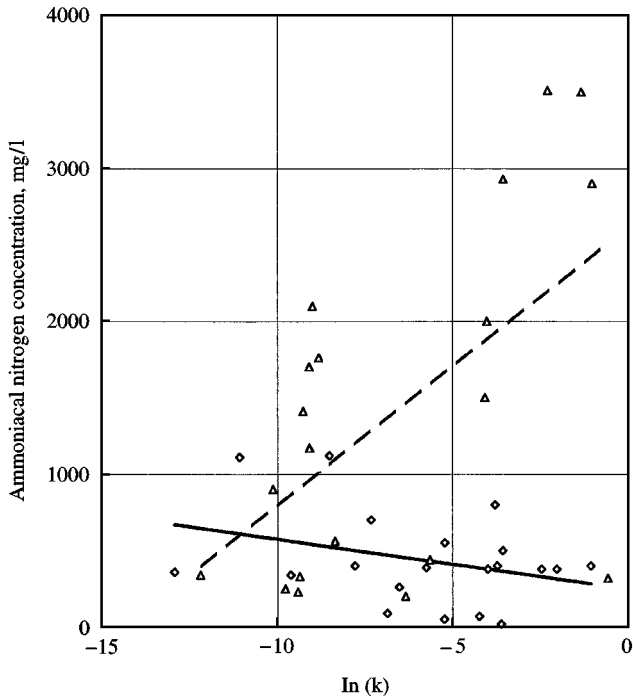


Fig. 5. Relationship between ammoniacal nitrogen (AN) concentration and $\ln(k)$ for Italian slurries \diamond , cattle slurry; \triangle , pig slurry; —, $AN_{\text{cattle}} = -32.5(k) + 248$ (fitted); ----, $AN_{\text{pig}} = 182.2 \ln(k) + 2619$ (fitted); percentage variance accounted for 45.5%, $p < 0.01$

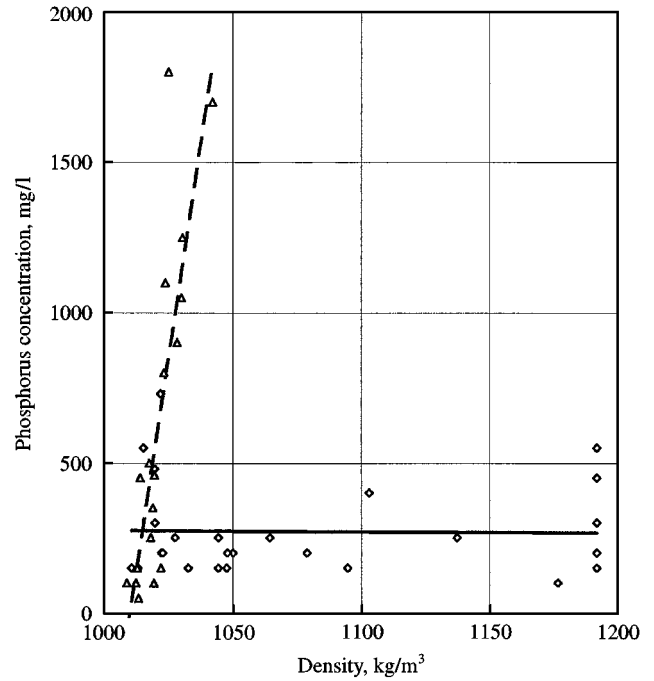


Fig. 6. Relationship between total phosphorus (P) concentration and density (ρ) for Irish slurries \diamond , cattle slurry; \triangle , pig slurry; —, $P_{\text{cattle}} = -0.041\rho + 315$ (fitted); ----, $P_{\text{pig}} = 56.86\rho - 57426$ (fitted); percentage variance accounted for 64.8%, $p < 0.01$

± 203 mg/l (Italy); or with density and $\ln(k)$ leading to fse values ranging from ± 234 to ± 293 mg/l (Ireland) and from ± 185 to ± 268 mg/l (Germany).

3.5. Total potassium

The single property regressions between K and the measured properties in the four countries were generally weak and not as good as either the AN or P regressions. In Ireland and Germany, the best regressions for K were with EC (Figs 11 and 12), with pva values of 19.2 and 80.0%, respectively. In the United Kingdom, surprisingly, the best regression for K was with ammonium ions (AI) (Fig. 13); the pva value of the regression was 50.2%. In Italy, the best regression for K was with density (Fig. 14) with a pva value of 42.4%.

Similarly, the multiple property regressions were generally not as good for K as those for either AN or P (Table 7). The German data provided an exception to this; the regression of K on EC and density produced a pva value of 84.8%. The best fit multiple property regressions for K in Ireland and Italy were also with EC and density with respective pva values of 27.9 and 56.4%. In the United Kingdom, the best-fit multiple property

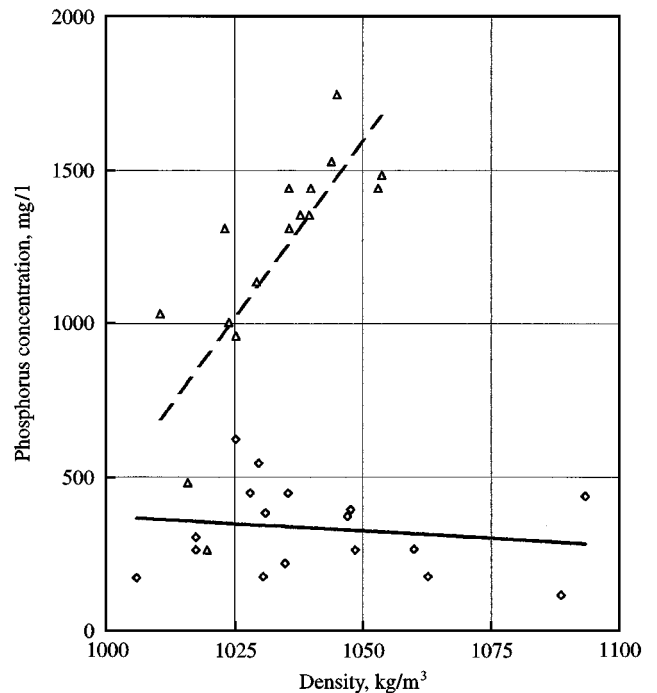


Fig. 7. Relationship between total phosphorus (P) concentration and density (ρ) for German slurries \diamond , cattle slurry; \triangle , pig slurry; —, $P_{\text{cattle}} = -0.96\rho + 1331$ (fitted); ----, $P_{\text{pig}} = 23.06\rho - 22618$ (fitted); percentage variance accounted for 83.6%, $p < 0.01$

Table 5
Best fit multiple property regressions coefficients (and associated standard errors) for ammoniacal nitrogen

<i>slurry type</i>	<i>Regression coefficients</i>			<i>Measured properties</i>		
	<i>w</i>	<i>x</i>	<i>z</i>	<i>C_i</i>	<i>C_j</i>	<i>pva (p)</i>
United Kingdom cattle	0.154 (0.018)	- 38.7 (38.0)	- 749 (247)	Electrical conductivity	ln(<i>k</i>)	85.1 (<i>p</i> < 0.01)
United Kingdom Pigs	0.154 (0.018)	- 38.7 (38.0)	- 98 (383)	Electrical conductivity	density	83.4 (<i>p</i> < 0.01)
Irish cattle	0.129 (0.014)	- 0.83 (1.03)	452 (1105)	Electrical conductivity	density	92.5 (<i>p</i> < 0.01)
Irish pigs	0.129 (0.014)	33.1 (11.0)	- 33866 (11170)	Electrical conductivity	ln(<i>k</i>)	50.1 (<i>p</i> < 0.01)
German cattle	0.1133 (0.014)	- 0.60 (4.05)	275 (4225)	Electrical conductivity	density	92.5 (<i>p</i> < 0.01)
German pigs	0.1362 (0.0159)	- 0.60 (4.05)	947 (4068)	Electrical conductivity	ln(<i>k</i>)	50.1 (<i>p</i> < 0.01)
Italian cattle	0.0426 (0.020)	- 10.5 (51.1)	- 79 (361)	Electrical conductivity	ln(<i>k</i>)	50.1 (<i>p</i> < 0.01)
Italian pigs	0.0426 (0.020)	143.6 (47.2)	1539 (613)	Electrical conductivity	ln(<i>k</i>)	50.1 (<i>p</i> < 0.01)

pva = percentage variance accounted for; *p* = level of significance.

regression was with the sensor-derived properties AI and pH yielding a pva value of 49.0%.

The K concentrations in the slurries were generally related to EC and density. In Germany and Italy, the best results were achieved using multiple property regressions of K with EC and density (fse values ranging from ± 499 to ± 547 mg/l and from ± 811 to ± 868 mg/l, respectively). In Ireland, the best fit was K with EC alone (fse values ranging from ± 1033 to ± 1084 mg/l). It should be noted that even though the pva for the best-fit multiple property regression for the Irish K was 27.9% compared with 19.2% for the single property regression, the single property regression was superior since addition of the density term was not statistically significant. The best fit in the United Kingdom for K was a single property regression with AI (fse values ranging from ± 297 to ± 306 mg/l).

4. Discussion

As noted in Section 1, the purpose of this investigation was to identify appropriate sensors for use in a prototype

tanker-mounted nutrient-sensing system. Single property regressions revealed general relationships between each of the nutrients examined (AN, P and K) and the measured properties in all four countries. For AN, in three of the countries, the best regression was found to be with EC. It could therefore be argued, for simplicity, that EC should also be used in the fourth country (Italy) despite not achieving the best fit on this particular set of data. Similarly, for P, density gave the best single property regression, except in the United Kingdom. Thus, it could also be argued that density should be used in the United Kingdom despite this not being the best regression identified with this data set. For K, there was no particular property that was best in all countries.

Multiple property regressions highlighted general patterns across the countries. In the case of AN, the best regressions were with EC and density in Ireland and Germany, and with EC and ln(*k*) in the United Kingdom and Italy. However, since both density and ln(*k*) are associated with the TS of the slurry, it could be argued that either could be used with EC to form a standard multiple property regression applicable in all four countries. For P, the best regressions were with density and

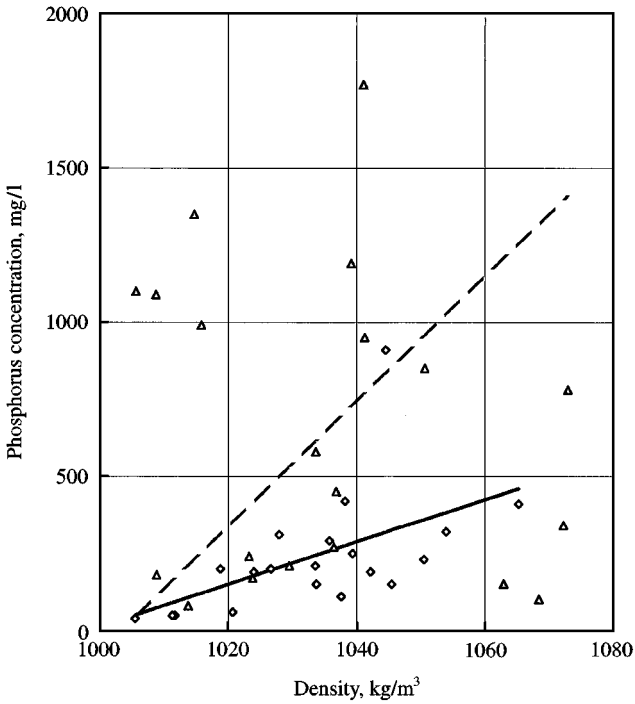


Fig. 8. Relationship between total phosphorus (P) concentration and density (ρ) for Italian slurries \diamond , cattle slurry; Δ , pig slurry; —, $P_{\text{cattle}} = 6.85\rho - 6837$ (fitted); ---, $P_{\text{pig}} = 20.25\rho - 20317$ (fitted); percentage variance accounted for 76.1%, $p < 0.01$

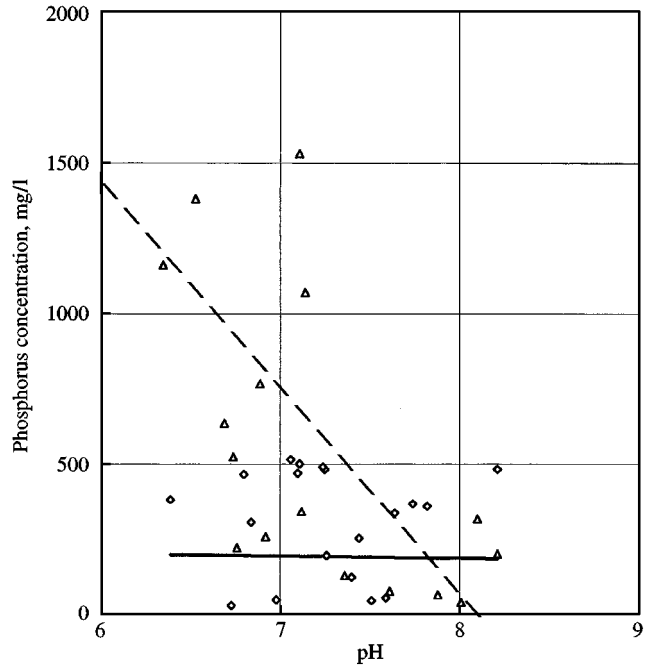


Fig. 10. Relationship between total phosphorus (P) concentration and pH for UK slurries \diamond , cattle slurry; Δ , pig slurry; —, $P_{\text{cattle}} = -8\text{pH} + 248$ (fitted); ---, $P_{\text{pig}} = -688\text{pH} + 5571$ (fitted); percentage variance accounted for 45.6%, $p < 0.01$

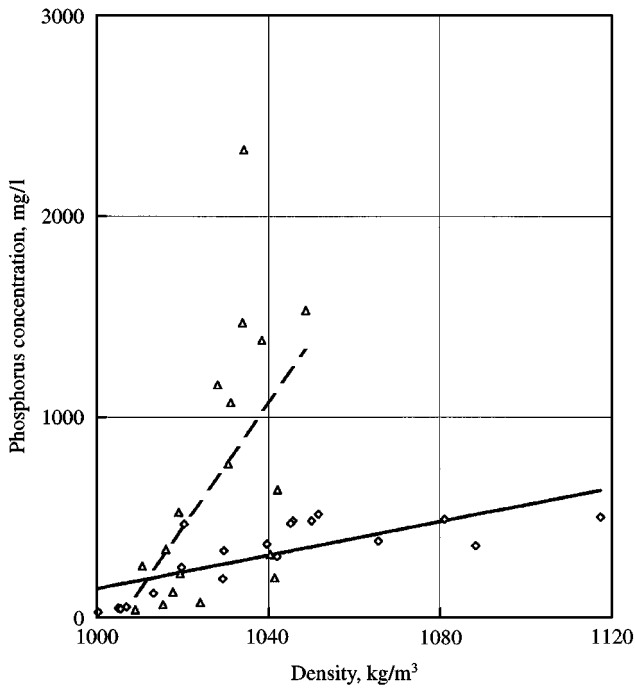


Fig. 9. Relationship between total phosphorus (P) concentration and density (ρ) for UK slurries \diamond , cattle slurry; Δ , pig slurry; —, $P_{\text{cattle}} = 4.18\rho - 4037$ (fitted); ---, $P_{\text{pig}} = 31.16\rho - 31337$ (fitted); percentage variance accounted for 35.8%, $p < 0.01$

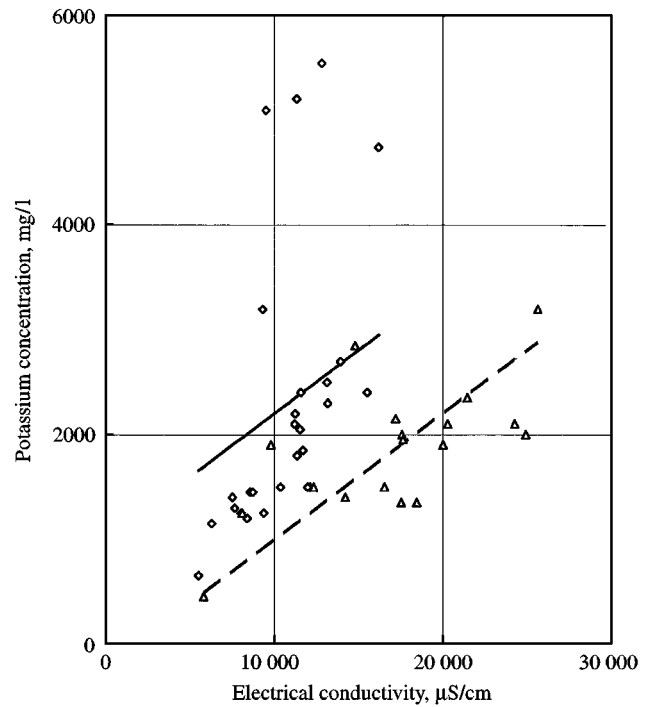


Fig. 11. Relationship between total potassium (K) concentration and electrical conductivity (EC) for Irish slurries \diamond , cattle slurry; Δ , pig slurry; —, $K_{\text{cattle}} = 0.121\text{EC} + 992$ (fitted); ---, $K_{\text{pig}} = 0.121\text{EC} - 215$ (fitted); percentage variance accounted for 19.2%, $p < 0.01$

Table 6
Best fit multiple property regressions coefficients (and associated standard errors) for phosphorus

<i>slurry type</i>	<i>Regression coefficients</i>			<i>Measured properties</i>		<i>pva (p)</i>
	<i>w</i>	<i>x</i>	<i>z</i>	<i>C_i</i>	<i>C_j</i>	
United Kingdom cattle	4.18 (2.11)	5.0 (153)	-4076 (2454)	density	pH	67.0 (<i>p</i> < 0.01)
United Kingdom Pigs	26.09 (5.82)	-619 (105)	-21734 (6136)			
Irish cattle	-0.311 (0.645)	15.1 (11.2)	627 (704)	density	ln(<i>k</i>)	69.7 (<i>p</i> < 0.01)
Irish pigs	74.25 (9.33)	-57.0 (21.7)	-75554 (9627)			
German cattle	-1.42 (1.94)	-46.2 (21.0)	1819 (2025)	density	ln(<i>k</i>)	89.8 (<i>p</i> < 0.01)
German pigs	29.22 (5.83)	-46.2 (21.0)	-29097 (6079)			
Italian cattle	4.62 (2.77)	-242.8 (67.5)	-2741 (3011)	density	pH	82.0 (<i>p</i> < 0.01)
Italian pigs	21.06 (1.93)	-242.8 (67.5)	-19386 (1997)			

pva = percentage variance accounted for; *p* = level of significance.

pH in the United Kingdom and Italy, whereas in Ireland and Germany they were with density and ln(*k*). In this case, the pva values associated with the regressions involving ln(*k*) were slightly better than those using pH. Hence, in view of the known associations between P and TS, and between TS and ln(*k*), the rheological property might be a better choice to achieve a standard approach for estimation in all countries. The best multiple property regressions for K were with EC and density in three of the countries; the United Kingdom was an exception: K related to AI and pH. In this case, a standard estimation could be used for all four countries based on the regression of K with EC and density.

Overall, therefore the results showed that the best regressions involved single properties in some cases and multiple properties proved to be better for others. In a few situations, a single regression was found to provide the best fit to both cattle and pig slurries, whereas separate regressions were needed in most cases. Table 8 lists the properties that should ideally be included in an in-line nutrient-sensing system. In the case of multiple property regressions, and in the interests of saving costs, careful consideration must be given to the degree of

improvement achieved by measuring two properties instead of one. For example, the improvements in pva achieved for AN estimation by using multiple property regression over single property regression for Irish and Italian slurries were only 2.8 and 4.6%, respectively. Thus, this would not justify the extra expense and complication of measuring the additional property. However, the comparable improvements achieved for P estimation by using multiple property regression over single property regressions for United Kingdom and German slurries were 21.4 and 6.2%, respectively, and thus measuring the extra property could be beneficial under these circumstances. For K estimation, the general relationships were weaker than for either AN or P; however, it is clear to see that the predicted values of K were strongly influenced by the electrical conductivities of the slurries.

The regression coefficients established were based on a wide range of slurries collected in each of the four countries. Previous evidence¹⁰ has shown that the prototype nutrient-sensing system is able to provide a good estimation of the dilution of a particular slurry. Thus, since the variability of nutrients in a particular slurry are mainly due to its dilution with water, it could be

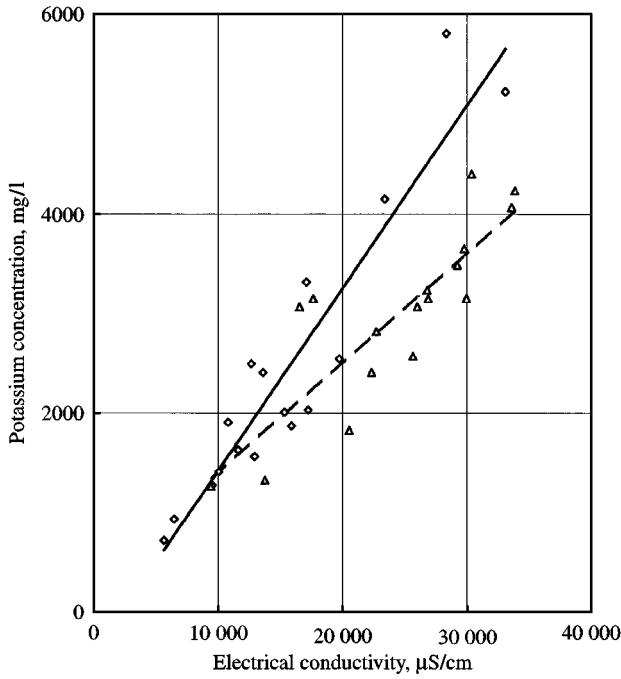


Fig. 12. Relationship between total potassium (K) concentration and electrical conductivity (EC) for German slurries \diamond , cattle slurry; Δ , pig slurry; —, $K_{\text{cattle}} = 0.184 \text{ EC} - 442$ (fitted); ---, $K_{\text{pig}} = 0.110 \text{ EC} + 306$ (fitted); percentage variance accounted for 80.0%, $p < 0.01$

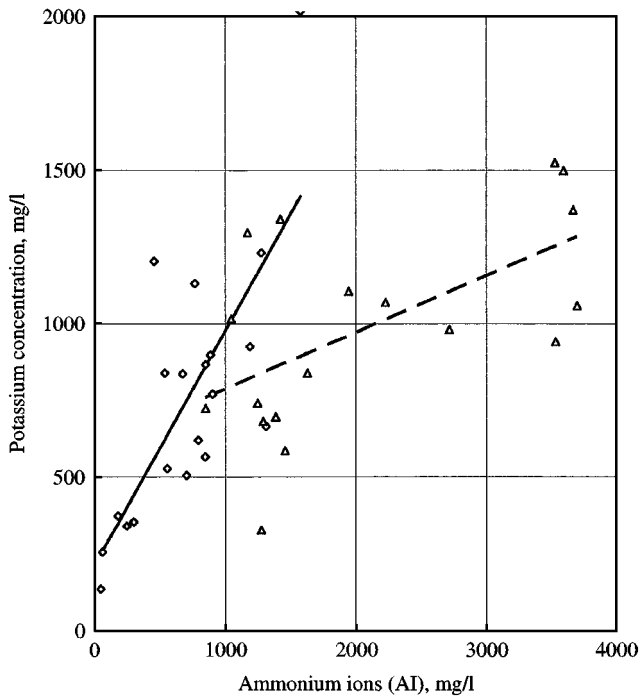


Fig. 13. Relationship between total potassium (K) concentration and ammonium ions (AI) for UK slurries \diamond , cattle slurry; Δ , pig slurry; —, $K_{\text{cattle}} = 0.763 \text{ AI} + 212$ (fitted); ---, $K_{\text{pig}} = 0.184 \text{ AI} + 603$ (fitted); percentage variance accounted for 50.2%, $p < 0.01$

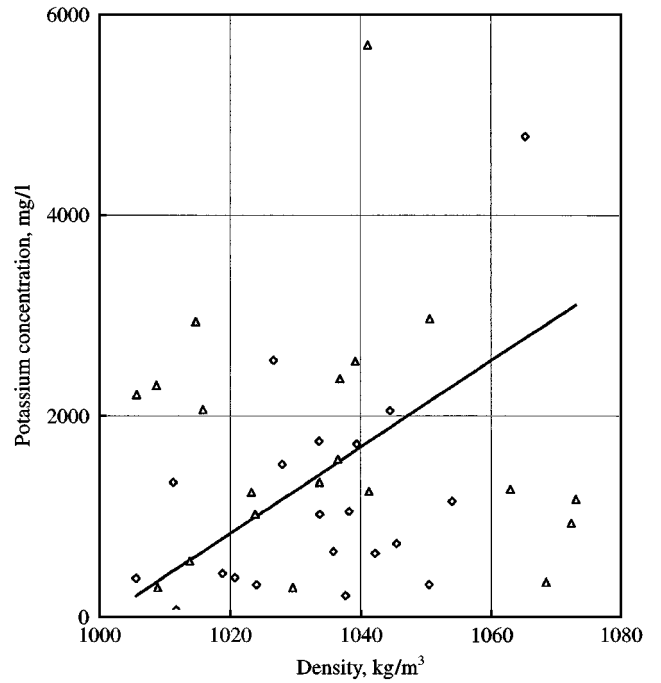


Fig. 14. Relationship between total potassium (K) concentration and density (ρ) for Italian slurries \diamond , cattle slurry; Δ , pig slurry; —, $K_{\text{cattle and pig}} = 42.97\rho - 43000$ (fitted) percentage variance accounted for 42.4%, $p < 0.01$

postulated that re-calibrating the nutrient-sensing system on a smaller range of slurries or even on an individual farm or store basis would improve the accuracy of the system. Clearly, nutrient estimation techniques incorporated on the tanker would enable the contents of a store to be analysed load by load during normal spreading operations, thus eliminating the errors associated with sub-sampling from a large store. This study has shown that it is feasible to develop a nutrient-sensing system that could be used on a slurry tanker to fulfil this role.

5. Conclusions

1. Data from the United Kingdom, Ireland and Germany indicated strong single property relationships between ammoniacal nitrogen and electrical conductivity with percentage variance accounted for (pva) values of 84.1, 80.6 and 91.9%, respectively. Data from Italy also indicated a single property, but weaker, relationship between the two (pva value of 39.1%).
2. Multiple property regressions for the prediction of ammoniacal nitrogen concentrations which combined electrical conductivity with density or with the rheological parameter $\ln(k)$, produced significantly

Table 7
Best fit multiple property regressions coefficients (and associated standard errors) for potassium

<i>slurry type</i>	<i>Regression coefficients</i>			<i>Measured properties</i>		<i>pva (p)</i>
	<i>w</i>	<i>x</i>	<i>z</i>	<i>C_i</i>	<i>C_j</i>	
United Kingdom cattle	0.746 (0.159)	36.0 (89.2)	- 37 (629)	Ammonium ions	pH	49.0 (<i>p</i> < 0.01)
United Kingdom Pigs	0.188 (0.067)	36.0 (89.2)	338 (674)			
Irish cattle	0.300 (0.075)	- 4.61 (2.78)	4080 (2862)	Electrical	density	27.9 (<i>p</i> < 0.01)
Irish pigs	0.0754 (0.0416)	- 4.61 (2.78)	5272 (2916)	Conductivity		
German cattle	0.184 (0.016)	9.25 (4.59)	- 10052 (4784)	Electrical	density	84.8 (<i>p</i> < 0.01)
German pigs	0.094 (0.018)	9.25 (4.59)	- 8795 (4606)	conductivity		
Italian cattle	0.066 (0.018)	34.93 (7.21)	- 35.683 (7380)	Electrical	density	56.4 (<i>p</i> < 0.01)
Italian pigs	0.066 (0.018)	34.93 (7.21)	- 35683 (7380)	conductivity		

pva = percentage variance accounted for; *p* = level of significance.

improved pva values of 83.4 and 50.1%, respectively, in Ireland and Italy. Corresponding improvements in the United Kingdom and Germany were not significant.

3. Data from Ireland, Germany and Italy indicated strong single property relationships between phosphorus and density (pva values of 64.8, 83.6 and 76.1%, respectively). Data from United Kingdom also

indicated a single property, but weaker relationship between the two (pva value of 35.8%).

4. Multiple property regressions produced significant increases in pva values for phosphorus predictions in all four countries. Density and pH was the best combination in the United Kingdom and Italy (pva values of 67.0 and 82.0%, respectively). Density and the rheological parameter $\ln(k)$ was the best combination

Table 8
Measured slurry properties which provided best fit relationships for ammoniacal nitrogen (AN), total phosphorus (P) and total potassium (K) in each of the four countries

<i>Country</i>	<i>Ammoniacal nitrogen (AN), mg</i>	<i>Total phosphorus (P), mg</i>	<i>Total potassium (K), mg</i>
United Kingdom	Electrical conductivity	Density and pH	Ammonium ions
Ireland	Electrical conductivity and density	Density and $\ln(k)$	Electrical conductivity
Germany	Electrical conductivity	Density and (k)	Electrical conductivity and density
Italy	Electrical conductivity and $\ln k$	Density and pH	Electrical conductivity and density

Note: $\ln(k)$ was derived from the measurement of slurry flow and the corresponding pressure gradient in a pipe.

- in Ireland and Germany (pva values of 69.7 and 89.8%, respectively).
5. In the United Kingdom, Ireland and Italy, the regressions for potassium were weaker than those for either ammoniacal nitrogen or phosphorus, with any of the measured properties. The best-fit relationships had pva values of 50.2, 19.2 and 42.4%, respectively. Germany was the exception to this, a multiple property regression with electrical conductivity and density led to a pva value of 84.8%.
 6. Forecast standard errors for nutrient estimation ranged from ± 375 to ± 801 mg/l for ammoniacal nitrogen; from ± 185 to ± 322 mg/l for phosphorus and from ± 297 to ± 1084 mg/l for potassium.
 7. The information determined in this investigation provides strong evidence that an in-line nutrient-sensing system could be designed and built for use on a slurry tanker, thus enabling nutrient estimation on a tanker by tanker basis, and reducing sampling errors.
 8. A prototype in-line nutrient-sensing system should include sensors for electrical conductivity (for ammoniacal nitrogen determination); density, $\ln(k)$ (based on measurement of slurry flow and corresponding pressure gradient in a pipe) and pH (for total phosphate determination); and electrical conductivity, density and ammonium ions (for total potassium determination).

Appendix 1: Statistical procedures used for selection of appropriate regression equations

The first stage of the analysis was concerned with establishing the most effective single property regressions, i.e. regressions of each of the measured nutrient concentrations (AN, P and K) with each one of the measured properties. The second stage extended the analysis to include two measured properties using a multiple regression technique.

Single property regression

The data were analysed as four separate groups: each group included data from only one of the four countries included in the experiments. For each group of data, the regression analysis considered the following cases representing increasing numbers of parameters: (a) single regression line, i.e. same slope and intercept for both cattle and pig slurries; (b) parallel regression lines for each slurry type, i.e. same slope but separate intercepts; and (c) separate regression lines, i.e. separate slopes and separate intercepts. The main principles of this process are outlined below.

- (i) Each group of data, comprising two slurry types (i.e. cattle and pig) was used to evaluate the coefficients w and z defined in Eqn (2) for each of the three regression cases. This procedure was applied separately for each of the 3 key slurry nutrients (AN, P and K), based on each of the measured properties.
- (ii) Each regression case produced an equation or equations which represented the variation in values of nutrient concentration as a linear function of a measured property. The sums of squares (SS) of the deviations of these values from the mean of the measured values of each nutrient concentration were evaluated for the regression equations representing each of the regression cases. These were represented in a cumulative form to show the amount by which each additional inclusion of another parameter to the regression contributed to the total sum of squares of the deviations of the measured values of nutrient concentration about their mean value. In addition, the sum of squares of the deviations of the measured values of nutrient concentration from the regression equations corresponding to regression case (c) were also calculated. In the context of this analysis, this was termed the residual sum of squares (RSS). The calculation of these sums of squares provided the first step towards completion of a summary analysis of the variance table, as illustrated in Table A1.

The second column of Table A1 lists the number of degrees of freedom (df) associated with each regression parameter and with the residual. The ratio of the SS values to the corresponding degrees of freedom enabled calculation of mean square deviation (MS) values, as shown in column four of Table A1.

- (iii) In general, and as expected, the analysis of variance showed that inclusion of more parameters reduced the SS values. However, the selection of the appropriate regression case was not simple based on choosing the regression case which resulted in the smallest SS value. Instead, the alternative regression cases were compared by evaluating the ratios of their MS values to the residual MS value, (i.e. variance ratios, as shown in column five of Table A1). The significance of these ratios was then determined using standard tables of the variance ratio (F) statistic (column six, Table A1).
- (iv) In those cases where the F_{pr} value corresponding to regression case (c) was less than 5%, the latter was selected as the most appropriate regression model. If this condition was not satisfied, then the regression case (b) was selected if $F_{pr(b)}$ was less

Table A1
Example analysis of variance table illustrating methods of selection of appropriate regression equation

<i>Parameter</i>	<i>Number of degrees of freedom (df)</i>	<i>Sum of squares of deviations (SS)</i>	<i>Mean square deviation (MS)</i>	<i>Variance ratio (F)</i>	<i>Probability (Fpr)</i>
Electrical conductivity, representing regression case (a)	1	<i>A</i>	<i>A/1</i>	$(A/1)/(D/(n-4))$	(Fpr) _(a)
Type of slurry, i.e. cattle or pig, representing regression case (b)	1	<i>B</i>	<i>B/1</i>	$(B/1)/(D/(n-4))$	(Fpr) _(b)
Type of slurry and electrical conductivity, representing regression case (c)	1	<i>C</i>	<i>C/1</i>	$(C/1)/(D/(n-4))$	(Fpr) _(a)
Residual, i.e. variation in measured values of nutrient concentration not accounted for by regression case (c)	<i>n - 4</i>	<i>D</i>	<i>D/(n - 4)</i>	—	—
Total	<i>n - 1</i>	<i>A + B + C + D</i>	—	—	—

than 5%. If this second condition was not satisfied, then regression case (a) was chosen.

- (v) Finally, a value was calculated for the percentage variance accounted for (pva) corresponding to the selected regression. Since the analysis considered the type of slurry (i.e. cattle or pig) as a variable, a single value of pva was determined for each country's data, appropriate to each of the key nutrients.

Multiple property regression

This procedure was similar to that followed for the single property regressions, although the analysis considered the three regression cases independently in connection with each of two measured properties. Thus, a total of nine combinations of regression cases were included in each analysis of variance.

Acknowledgements

This work was funded by the European Commission in the context of the "Sustainable Waste Application Management Project" (SWAMP). The authors gratefully acknowledge the help of their colleagues in Silsoe Research Institute, United Kingdom; Teagasc, Ireland; LUFA, Germany; UDSM, Italy; Algosystems SA, Greece; SAC, Scotland; IMAG, The Netherlands and JTI, Sweden, in the execution of this work.

Our thanks also go to many farmers in United Kingdom, Ireland, Germany and Italy for their cooperation, and for supplying the slurry samples that allowed this study to be completed.

References

- Ministry of Agriculture Fisheries and Food** Fertilizer Recommendations for Agricultural and Horticultural Crops. Reference Book 209, London: MAFF Publications, 1993
- Ministry of Agriculture, Fisheries and Food** Code of Good Agricultural Practice for the Protection of Air. Publication PB0618, London: MAFF, 1992
- Ministry of Agriculture, Fisheries and Food** Code of Good Agricultural Practice for the Protection of Water. Publication PB0507, London: MAFF, 1991
- Ministry of Agriculture, Fisheries and Food** Code of Good Agricultural Practice for the Protection of Soil. Publication PB0617, London: MAFF, 1993
- Kellerup V** Agros nitrogen meter for estimation of ammonium nitrogen in slurry and liquid manure. In: Efficient Land Use of Sludge and Manure (Dam Kofoed A; Williams J H; L'Hermite P eds), pp. 216–223 Barking: Elsevier Applied Science Publishers, 1985
- Smith K A; Nicholson R J; Williams J R; Chamber B J** A review of rapid methods for assessing the nutrient content of organic manures. ADAS Report to MAFF Environmental Protection Division, Project Number WA 0605, 1993
- Tunney H; Bertrand M** Rapid field tests for estimating dry matter and fertilizer value of animal slurries. In: Land and Water Use (Dodd V A; Grace P M eds), pp. 363–370, Rotterdam: Balkema, 1989
- Stevens R J; O'Bric C; Carton O T** Estimating nutrient content of animal slurries using electrical conductivity. *Journal of Agricultural Science, Cambridge*, 1995, **125**, 233–238
- Westerman P W; Safley L M; Barker J C** Lagoon liquid nutrient variation over four years for lagoons with recycle systems. In: Agricultural and Food Processing Waste, Proceedings of the 6th International Symposium on Agricultural and Food Processing Wastes, Chicago, 17–18 December 1990, 41–49
- Scotford I M; Cumby T R; Richards P A; Han L** Development of a prototype nutrient sensing system for livestock slurries. *Journal of Agricultural Engineering Research*, 1998, **69**, 217–228

- ¹¹ **Scotford I M; Cumby T R; Richards P A; Han L** Sustainable waste application management project. *In-situ* nutrient sensor using guide. Contract Report CR/707/96/8313, Silsoe Research Institute, 1996
- ¹² **Ministry of Agriculture Fisheries and Food** Fertiliser Recommendations for Agricultural and Horticultural Crops. Reference Book 209, London: MAFF Publication, 1993
- ¹³ **Hester W** Aspects of the aerobic processing of agricultural waste slurries. PhD thesis, Magdalene College, University of Cambridge, 1987
- ¹⁴ **Genstat 5 Committe** Genstat 5 Release 3 Reference Manual. Oxford: Clarendon Press, 1993.
- ¹⁵ **Snedecor G W; Cochran W G** Statistical Methods, 6th edn. Iowa: Iowa State University Press, 1967