Controlled Release Fertilizers

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CRF’s - “High Agronomic Use Efficiency while minimizing Environmental Impact, in one single application”

Conventional fertilization goes with high N (and other) losses to GW (NO$_3$) and to air (NH$_3$, N$_2$O, NO$_x$)

➤ Great efforts to develop approaches, techniques and Fertilizers to minimize damage and sustain agriculture (soil, water, production potential)

➤ Increasing awareness to fertilizer impact on Environment
**Pathways of Loss**

**Plant Uptake - N-P-K and Me**

**Microbial Reactions**

**Pathways of Loss**

- **SYNCRONIZATION** - Plant Demand vs. Nutrients Supply

- **SUPPLY**: Preferred & Bio-Available Nutrient Compositions
  - ammonium/nitrate;
  - $\text{NH}_4^+$ / P
  - $\text{NH}_4^+$ or K / Microelements
**Improve Application Methods or Modify Fertilizers**

- **Positioning:** Banding, nesting, Super Granules (high NH$_4$ conc. To reduce nitrification)
- **Bio-Inhibitor** Amendments (NI’s)
- **Controlled Release Fertilizers**
- **Targeted Delivery** Fertigation, Precision Agriculture

**CRF vs. SRF**

<table>
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<tr>
<th>SRF</th>
<th>UF, MEU, SCU, PSCU?</th>
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<tr>
<td>CRF</td>
<td>Polymer coated</td>
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One single application provides prolonged supply of nutrients

**Matches (better) plant demand...**

- (level, proportions, timing)
- The closer the synchrony
- higher NUE and lower LOSSES
CRF vs. SRF

- **Release** less sensitive to:
  - Soil/medium type, moisture, pH, microbial activity

- **Minimizes:**
  - Losses to environment,
  - Application cost,
  - Stress on plants,

- **Ensures:**
  - Better growth & yields,
  - High quality food/product

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YET - CRF COST is A LIMIT
Release from a Single Coated Urea Granule: Diffusion vs Failure

Release Affected by:
- Permeability
- Radius $r$
- Coating thickness $l$
- Slightly affected by water content, pH, medium type

Diffusion
- Linear release
- Decay

Failure
- Lag

Immediate release
- Dissolution
- Rupture

Gradual release
- Diffusion / convection

Water vapor

Coatings: Alkyd Type, Polyurethane like, Poly-Olefin (modified), Latex, Sulfur Coated

Release Affected by: Permeability $\rightarrow T$, Solubility $?!$

Radius $r$, Coating thickness $l$

Slightly affected by water content, pH, medium type
Model of Urea (or single fertilizer) Release

Shaviv et al, 2003a,b, Envir. Sci & Tech,

\[ g(r, l, t) = \frac{3P_c}{rl\rho_s} C_{sat}(t - t') t' \leq t \leq t^* \]

\[ g(r, l, t) = 1 - \exp\left(\frac{3P_c}{rl}(t - t^*)\right) \]
Energy of Activation for Release helps in Modeling Temperature effect

\[ R_{linear} \sim C_{sat} \times P_S = C_{sat} \times \exp\left(-\frac{E_A}{RT}\right) \times P_S \times \exp\left(-\frac{E_A}{RT}\right) \]

\[ R_{linear} \sim C_{sat} \times P_S \times \exp\left[-\left(\frac{E_A + E_A}{RT}\right)\right] \]

\[ \log R_{linear} \quad vs \quad \frac{1}{RT} \quad \Rightarrow \quad E_A = E_A + E_A \]

or, the concept of Cumulative Rate of N release (Gandeza et al., 1991)

\[ CRN = a + b \times (CT) + c \times (CT)^2 \]
Important Release Features

- **Pattern:**
  - Fickian (parabolic), linear, sigmoidal, bi-modal

- **Duration:**
  - Time of release of content (75%, 80%)?
  - at given temperature, \(21^\circ C\) or \(25^\circ C\)?

- **Burst** (initial release < few %)

- **Tailing - Lockoff** (non utilised nutrient)

![Cumulative Urea Release Diagram](image)

- **Alkyd type**
- **PSCU**
- **Polyolefin**
- **Polyurethane**
Release Prediction Important for Better Synchronizing Plant Demand with Nutrient Supply

Note – Sigmoidal Pattern

Practically – release from large population => high variation – $P_h, P_s, I, r, \Rightarrow \text{Statistics}$
Temperature Effect
Various CRFs

~ 1.5 – 2.0 increase
for 10°C

~ 1.5 – 2.0 fold increase for each 10°C

~ ? ~ Q10 factor
Effect of soil/medium properties (or water status?)

Release at 30°C

- Release only slightly affected by soil type and soil pH

Effect of drying-wetting cycles (=irrigation)

- Important: Drying-wetting cycles do not damage the coating
- The release is slowed down when the soil is dry –
  (this prevents salt accumulation and root scorching)
Release from a compound CRF

more complicated

• Different Solubilities of \( \text{NO}_3 \), \( \text{NH}_4 \), P, K

• Limited amount of WATER for dissolution

• Moisture content Changes:
  
  Free Water,
  
  Saturated Soil
  
  Unsaturated Soil

• Temperature Changes

Different Release Patterns/
Rate

Typical For All single Ferts.,
basis CRFs
NO₃ ~ NH₄ > K > P

Characteristic Coated CRF – limited water amount in granule

• Characterization
• Testing
• Performance Evaluation
Failure 1
Determine Release Mechanism - "Failure" or "Diffusion" by testing individual granules

- Obtain curve for release in water at 25°C; evaluate: % initial release, lag period, release period of 80%, release rate during "linear release" (% per day)
- Determine release in water at 3 to 4 additional temperatures between ca. 10 to 50°C; calculate "Effective Ea"
- Determine release in at least, one typical growth medium, at least, at 25°C; correlate between release characteristics in water and growth medium
Experiments in Different Planting Systems

- **Pots, low volume**
- **Containers (detached media), 30 Liter**
- **Lysimeters, 130 liter** (to mimic field conditions, ACAP)
- **Real soil experiments, complicated/difficult when Mass Balance & Environmental Impact needed**
**Ryegrass Experiment – to test the effect of**

**Urea Release Pattern on Growth and Leaching**

4 cuttings (each 4-5 weeks)  
Leaching  before each cutting  
CRFs –

**Three N levels**  0.8, 1.2, 1.6 gN/pot  
**Special CRU** 932; CRU 948; CRU 1049 with different **SIGMOIDAL N release patterns and Durations**  
**PSCU** – Polymer sulphur Coated Urea - with “burst” and “lockoff”

**Compared to urea application**  1/3 at start (solid)  1/3 after 1st harvest (liquid);  1/3 after 2nd harvest.

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**WATER RELEASE 30 C**

![Graph showing water release over time for different samples at 30°C](image)
Synchronizing Urea Supply with plant demand resulted in maximal DM yield and Minimal N losses, No Damage to Plants.
Container Experiments:

Red Volcanic Tuff, 0-8 mm (porous)
CEC 15 meq/100g, Qsat 50%
(Amorphous Clay, Volcanic Glass, Primary Min., Iron Min.)

Perlite, 2-3mm (porous)
low CEC, Qsat 65%

Basil - 4 Harvestes (30 days)
3-5 fertigations/days
continuous leaching + collection
monitoring: fertigation, leachate, assay: plants => nutrient uptake

Experimental setup, Tuff, 1999.

<table>
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<td>A- Fertigation: First 1/3 irrigation only, 2/3 with 100% of reference. Total applied 65% of reference</td>
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<tr>
<td>B- 20% fertigation and 45% as banded CRF.</td>
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<tr>
<td>C- Fertigation with 65% of reference level, no leaching period. Total applied- 65% of reference</td>
</tr>
<tr>
<td>D- Fertigation according to commercial recommendations, Reference treatment. Total applied- 100% (reference)</td>
</tr>
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</table>

Reference Treatment: 70 ppm N after planting, raising to 120 after 2 weeks.

1. Fertilizer used for fertigation: 6-3-6 +6ME (Deshen Gat), ammonium/nitrate – 60:40
2. Applied controlled release fertilizer (CRF) “Multicote” (Haifa Chemicals), with a “tailor made” composition of : 16.5-8.5-16.5
Lysimeters (substitute experiment in “real” soil)
Cumulative yield in lysimeter-grown basil plants

- **Yield (dry weight g/lysimeter)**
  - Treatment-A (100% reference)
  - Treatment-B (80% reference)
  - Treatment-C (N coat 80)
  - Treatment-D (Multigrow-80)

- **Time from planting (weeks)**: 3.5, 8, 12

- **Yield Values**
  - Treatment-A: 135, 127, 109
  - Treatment-B: 78, 74, 50
  - Treatment-C: 57.67, 50, 50
  - Treatment-D: 20.67, 50, 50
  - Treatment-A (N coat 80): 18.67, 50, 50
  - Treatment-D (Multigrow-80): 3.5, 8
Cumulative leaching of nitrogen in drainage of basil lysimeters

- Treatment A (100 reference)
- Treatment B (80 reference)
- Treatment C (Ncoat-80)
- Treatment D (Multigrow-80)

Cumulative - P uptake g / lysimeter

- Treatment A (100 reference)
- Treatment B (80 reference)
- Treatment C (Ncoat-80)
- Treatment D (Multigrow-80)
Important Features Summary

• Release Pattern, (shape, lag, lock off)
  • Release Duration
  • Differential Release N-P-K
• Temperature effect on Release
• Medium/Env. Cond. effect on Release

Additional points for consideration ……

• Microelements release (?)
• Ammonium/Nitrate Ratio
• Urea in the CRF (?)
• Degrability (erodibility)/Bio-degrability of coating
When are “real” advantages of the CRF vs. “More Conventional” alternative expected?

Depends on factors such:

- **Culturing Conditions**: field (row, whole bulk, orchard), greenhouse (soil or detached media), potting media (small, large)
- **Medium or soil type**: Light? Heavy? CEC? OM?
- **Leaching**: (irrigation system, rain-fed),
- **Nutrient loss mechanisms**
- **Balanced/Imbalanced** nutrient supply (availability problems)
- **Environmental aspects**
- **pH**, **Ec**, **Eh** constrains
- **Special needs**: e.g. ionic species combinations of ammonium-nitrate, ammonium-P,

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**Future Needs, or Improvements**

- Improved **utilization** of advanced technologies, development of new concepts for preparing more cost-effective CRFs
- Better **Quantification** of the agronomic and economic advantages
- Better **assessment** of expected benefits to the environment
- Development/Standardization of **tests** for characterizing the release performance of SRF/CRFs to improve
  - user's decision-making process,
  - industrial quality control,
  - assist legislation efforts.
- Utilization of mechanistic-mathematical **models for predicting** release of nutrients under laboratory and field conditions, and as a design tool for technologists
• **Knowledge Integration to result in:**
  - Better Use Instructions,
  - Proper definitions of products
  - Improved/Relevant Performance Information

• **Users should be exposed** to this knowledge to help them choose SRF/CRFs professionally and on quantitative basis

• **Agronomists, Environmentalists** should be **exposed** to this knowledge to help them in better advising from both Agronomic (&economic) and Environmnetal points of view

Thanks
Specific Points in Case of Questions

Urea hydrolysis increases soil pH and losses of Ammonia

\[(\text{NH}_2)_2\text{CO} + \text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{HCO}_3^-\]

\[(\text{NH}_4)\text{CO}_3 \Leftrightarrow \text{NH}_3 + \text{H}_2\text{CO}_3\]

**High pH and Ammonia** reduce activity of Nitrobacter and hence cause accumulation of “toxic” Nitrite during nitrification.

**Nitrification - FIRST STEP - inhibited by:**
- specific inhibitors
  
  \[2\text{NH}_4^+ + 3 \text{O}_2 \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4 \text{H}^+\]
  (Nitrosomonas, Nitrosospira)

  \[2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-\]
  (Nitrobacter) (high pH, NH₃)
Application of local high urea concentrations (e.g., basal placement) may cause:

1. Increased pH (due to formation of ammonium carbonate)
2. Increased ammonia levels due to the decomposition of the ammonium carbonate and high pH. In calcareous soils the effect is dramatically enhanced!!
3. In containers, with restricted volume – the local concentration of applied urea may be high (if not carefully applied) and may stimulate processes like in 1 and 2.
4. High pH and ammonia may damage roots and also affect the fast oxidation of nitrite into nitrate and cause accumulation of Toxic levels of Nitrite

Any system providing metered supply or controlled supply of urea has a great potential to reduce the above effects.

Too high (local) levels of applied urea may turn soon into Ammonium after urea the hydrolysis (~half a day).

Exposing plants to high loads of ammonium and particularly in containers (detached media) with restricted volume and neutral to slightly acidic pH, may induce further acidification due to nitrification or ammonium uptake by plants.

Metered or Controlled Supply of the ammoniacal source (including urea) is not expected to cause dramatic acidification, particularly when a balanced supply of urea/ammonium and nitrate is given.
Potting media

Accumulating Fe with leaching time

Accumulating Zn with leaching time

LEVEL 1 Fe in drainage (Melisa exp)

LEVEL 2 Zn in drainage

DSN 482 ME/0
DSN 496 W/0 ME
OSMOCOT

Accumulation

Accumulation